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Mass Transfer and Benzene Removal from Air Using Latex Rubber Tubing and a Hollow-Fiber Membrane Module

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Abstract

A dense-phase latex rubber tube and a polyporous propylene hollow-fiber membrane module (HFMM) were investigated for control of benzene-contaminated gas streams. The abiotic mass flux observed through the latex tube was 3.9–13 mg/(min·m^2) for 150 ppm of benzene at various gas and liquid flow rates, while a 100-fold lower mass flux was observed in the HFMM. After seeding with an aromatic-degrading culture enriched from activated sludge, the observed removal was 80% of 150 ppm, corresponding to a mass flux of 45 mg/(min·m^2). The observed mass flux through the HFMM during biofiltration also rose, to 0.4 mg/(min·m^2). Because the HFMM had a 50-fold higher surface area than the latex tube, the observed benzene removal was 99.8%. Compared to conventional biofilters, the two reactors had modest elimination capacities, 2.5–18 g/(m^3·h) in the latex tube membrane bioreactor and 4.8–58 g/(m^3·h) in the HFMM. Although the HFMM had a higher elimination capacity, the gas-phase pressure drop was much greater.

Index Entries: Biofiltration; biofilter; benzene; membrane; latex; hollow-fiber membrane module; biokinetic.

Introduction

Volatile organic compounds (VOCs) are commonly emitted air pollutants throughout the United States. The National Air Quality and Emissions Trends Report for 1996 reported that VOC emissions totaled 18 million tons *(1)*. Current VOC treatment processes are primarily physicochemical and employ mechanisms such as absorption, adsorption, and thermal oxidation.

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Biofiltration of VOCs offers both low cost and the potential for complete contaminant destruction by biodegradation *(2–4)*. Biofiltration involves passing VOC-contaminated gas through a biologically active reactor, typically consisting of bacteria growing in a biofilm attached to solid media. The solid media may be an inert material such as plastic (fixed-bed biofilter) or natural material such as earth, leaves, compost, or peat. The VOC transfers from the gas phase to the liquid phase and is then degraded by the bacteria in the biofilm. The contaminant is usually the only carbon source for the bacteria. Common problems associated with such conventional biofilters include large pressure drops across the filter, large size requirements to achieve efficient removal, and a need for constant monitoring of moisture content *(5)*.

Membrane biofiltration is a way to achieve biologic removal of VOCs without some of the disadvantages of fixed-bed biofilters. In membrane biofiltration, the air and the liquid phase remain separated by a membrane. Flat, dimpled, hollow tubular, or bundled hollow tubular membranes (hollow-fiber membrane module [HFMM]) may be used as the basic membrane configuration. The membranes may be semipermeable hydrophobic or microporous. Semipermeable hydrophobic membranes are made from dense-phase materials such as silicone rubber that have a high permeability for aromatic compounds. Microporous membranes contain pores, typically 0.2 μm and less in diameter, that allow VOCs to transfer through the air-filled pores in the membrane. The VOCs transfer from the gas phase through the membrane and into the liquid phase, where bacteria grow as a biofilm on the outer surface of the membrane. The liquid contains nutrients and bacteria in suspension that are capable of degrading any VOC that penetrates the biofilm. Because of the separation of the air and liquid side, the membrane bioreactor configuration offers several potential advantages over conventional biofilter systems including low or no pressure drop across the reactor, ease of nutrient and moisture control, no clogging or channeling, and the potential to treat high contaminant loads.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) and other volatile compounds are known to be degraded by bacteria, and both conventional and membrane biofilters have been developed and put into use for their removal. Conventional biofilters have been found to be very successful for odor and VOC removal *(4,6,7)*. In general, BTEX removal is in the range of 10–100 g/(m^3·h) using conventional biofilters *(4)*. Membrane biofiltration of air *(8–14)* and liquids *(15–17)* has been reported. Additionally, one group modeled and used successfully a membrane biofilter for the removal of toluene, a chemical structurally similar to benzene *(18)*. Based on these studies, benzene removal from contaminated gas streams might be accomplished effectively and inexpensively by using membrane bioreactors.

The study reported here applied both dense-phase and polyporous membrane bioreactors to remove benzene from a contaminated gas stream. The objectives of this research were threefold: to isolate a bacterial consortium capable of degrading aromatic compounds as their sole carbon source and characterize the bacterial kinetics of that consortium, to characterize abiotic mass transfer and the effect of varying gas flow rates and liquid flow rates in two specific membrane systems, and to operate two specific membrane bioreactors and determine the benzene removal efficiencies.

Materials and Methods

Bacterial Inoculum

Bacterial cultures were initially grown within a room temperature, aerated, continuous stirred tank reactor (CSTR), with a 2-L filtration flask resting on a stir plate and equipped with a constant liquid feed. The CSTR was seeded with return activated sludge obtained from the Rolla, MO, Southeast wastewater treatment plant; operated with a 6-d hydraulic retention time, and supplied with a nutrient solution adapted from ATCC Culture Medium 1981 M-R2A: 800 mg/L of NH_4Cl, 250 mg/L of KH_2PO_4, 326 mg/L of Na_2HPO_4, 505 mg/L of KNO_3, 15 mg/L of $CaCl_2 \cdot H_2O$, 16.1 mg/L of $MgSO_4$, 7 mg/L of $FeSO_4 \cdot 7H_2O$, 5 mg/L of $MnCl_2$, 0.5 mg/L of H_3BO_3, 1.05 mg/L of $ZnSO_4$, 0.5 mg/L of $CoCl_2 \cdot 6H_2O$, 0.45 mg/L of $NiCl_2 \cdot 6H_2O$, 0.3 mg/L of $CuCl_2 \cdot 2H_2O$, 10 mg/L of $Na_2MoO_4 \cdot 2H_2O$. The resulting pH of the nutrient solution was 6.8. The carbon sources initially supplied to the CSTR included 500 mg/L of glucose, 15 mg/L of benzene, and 15 mg/L of toluene. The glucose was supplied for only 1 wk to promote biomass growth; after the glucose feed was ended, 15 mg/L of xylene (a mixture of *o*-, *m*-, and *p*-isomers) was added.

Biokinetic Parameters

Batch cultures were taken from the CSTR, grown with varying concentrations (50–100 mg/L) of benzene, toluene, and xylene. Biokinetic parameters were determined from these subcultures using multiple batch degradation assays. Aromatic compound degradation rates were determined as a function of substrate concentration in the liquid phase using an averaging of time course data. A pulse of benzene was added to a 50-mL subculture within a 250-mL bottle capped with a Mini-nert® valve, and the headspace concentration was monitored over time. Headspace concentrations were related to liquid concentrations by use of the dimensionless Henry's Law coefficient for benzene assuming instantaneous equilibrium (confirmed in abiotic samples). Subcultures were maintained at room temperature (~23°C) and agitated on a shaker table at 80 rpm. Aromatic compound and biomass concentrations were determined using gas chromatography (GC) and volatile suspended solids (VSS) analyses *(19)*, respectively. The resulting concentration vs time data were fit using numeric differentiation to find the utilization rate, which was divided by the VSS to give a specific utilization rate for each time datum. VSS was assumed constant over the course of these short batch assays. The resulting specific rate against concentration plot was fit to Monod-like kinetics using nonlinear least squares regression.

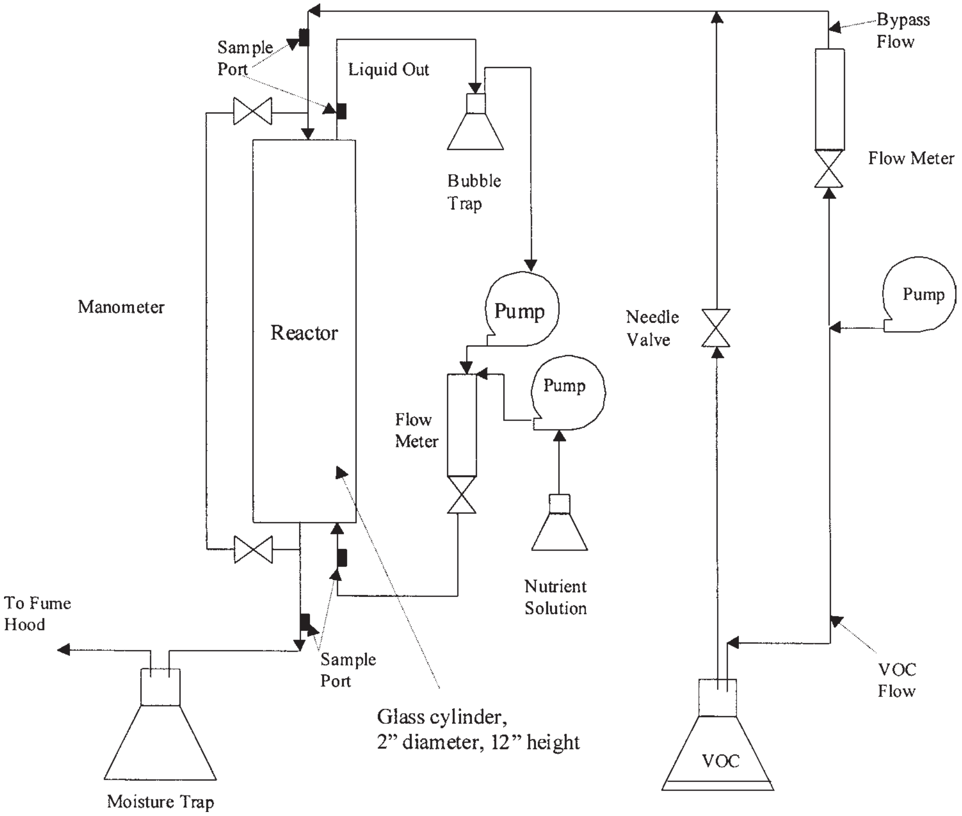

Fig. 1. Gas- and liquid-phase schematic.

Membrane Bioreactors

Two separate bioreactors were constructed; the first incorporated a 3/8×1/16 in. (0.95×0.16 cm) natural latex rubber tubing membrane (Fisher, Fair Lawn, NJ), and the second used a Spectrum Microgon polypropylene HFMM with 2600 fibers of 0.2-µm diameter, 0.2 mm nominal pore size in the walls, and a total of 0.5 m^2 of surface area. The reactors consisted of a 2-in. (5 cm) id and 12-in.(25 cm)-long glass Kimax process beaded pipe and two neoprene rubber stoppers cored to accommodate 1/8-in. (0.32 cm) stainless steel tubing carrying the gas phase and 1/4-in. (0.6 cm) Teflon® tubing containing the liquid phase. The membrane unit was contained within this reactor.

The gas phase schematic is shown in Fig. 1. Air supplied by an aquarium air pump was split with both flows passing through rotameters; a small amount of the air flowed through the headspace of a flask containing benzene. The split of air was controlled to deliver the concentration of benzene desired. After rejoining, the airstream passed into the bioreactor, through a moisture trap, and was vented. The air flow was downward, allowing any liquid passing into the gas phase to flow out of the system easily. Sampling ports for gas extraction and pressure measurement were

Table 1
Initial Operating Parameters of Bioreactor

Parameter	Latex tubing reactor	HFMM reactor
Gas flow rate (mL/min)	700	200
Recycle rate (mL/min)	10	6.5
Feed flow rate (mL/min)	0.2	0.2
Gas residence time (s)	1.4	4.3
Inlet gas concentration goal (ppm)	150	200
Operation time (d)	40	100

placed in-line. Sampling ports were brass tees with one side sealed with a Teflon/silicone rubber septum. Stainless steel tubing, brass Swagelok® fittings, neoprene rubber stoppers, and Teflon-lined silicone rubber septa were used for all VOC-containing gases to minimize any losses.

The liquid phase schematic is also shown in Fig. 1. Liquid flow through the reactor was from bottom to top, countercurrent to the gas flow. The choice of flow direction allowed any gas bubbles in the liquid to be purged up and out of the reactor. Two peristaltic pumps fed the nutrient solution and drove the recycle line. After observation of some gas in the liquid, a bubble-catching system was added to minimize disturbance of the biofilm. This bubble catcher was a glass Erlenmeyer flask with a submerged liquid inlet and outlet, and an opening vented to a fume hood sink to allow any excess liquid or any gas bubbles to be removed from the system. The liquid side had a total liquid volume of 800 mL. Flexible Tygon® tubing and Teflon-lined silicone rubber septa were used throughout the liquid-phase configuration.

Abiotic Mass Transfer

Mass transfer, pressure drop, and the effect of varying gas and liquid flow rates through the system were determined abiotically at steady state. Five abiotic trials were completed using the latex tubing membrane. Seven abiotic trials were accomplished using the HFMM. Gas inlet, gas outlet, and liquid outlet concentrations were monitored periodically to determine progress to an apparent steady state; parameters were measured after steady-state conditions were attained.

Biofiltration

After characterizing abiotic mass transfer in the reactor, the reactors were operated as biofilters. Aromatic-degrading bacteria from batch cultures were used to seed the reactors by injection through the liquid inlet sampling port. The flow rates used are given in Table 1. Gas and liquid inlet and outlet benzene concentrations were monitored to determine concentrations and removal efficiencies. Sextuplicate gas samples and triplicate liquid samples were taken from each respective sampling port and the results averaged. At the end of the experiments, biofilm thicknesses were both measured by direct ruler comparison and approximated by the method presented by Freitas dos Santos and Livingston *(15)* in which the membrane with biofilm is placed on a transparency projector, the projected image is measured, and the measurements are compared with a projected image of known dimension. By using the projection method, membrane and biofilm dimensions were approximated with a linear measurement error of ±0.03 mm.

Gaseous and Liquid Standard Preparation

All aromatic and gaseous standards were prepared with distilled, deionized water and certified A.C.S. grade benzene, and analytical reagent grade xylene and toluene. Benzene analyses by GC used external calibration standards. Gaseous standards were made by adding 52.5 μL of benzene to 50 mL of deionized water, contained within a 250-mL bottle capped with a Mini-nert valve, to make a liquid concentration standard of 500 mg/L after equilibrium with the headspace at 23°C *(20)*. Measured amounts of the 500 mg/L standard were then added to 250-mL bottles containing 50 mL of deionized water to give the desired equilibrium air concentrations in the headspace.

To make liquid standards, aliquots of the 500 mg/L standard were added to 250-mL bottles containing 50 mL of deionized water to give the desired liquid concentration. The bottles were then allowed to equilibrate on a shaker at 80 rpm for a minimum of 30 min.

Sample Collection and Analysis

Gaseous samples were collected through sampling ports using a 1-mL gastight sampling syringe and liquid samples using a 2.5-mL gastight sampling syringe. After collection, liquid samples were expelled into a 12-mL vial containing 20 μL of 5 N H_2SO_4 to acidify the sample. The vial was capped and then placed on an orbital shaker for a minimum of 10 min at 80 rpm, and the sample was allowed to reach equilibrium.

Headspace samples were analyzed in triplicate using a Hewlett Packard 5890 Series II Gas Chromatagraph with Flame Ionization Detector (FID). A J&W Scientific 30-m, 0.45-mm id, 2.5-μm film thickness DB-VRX capillary column was used during analysis. Nitrogen flow was 40 mL/min at an isothermal temperature of 90°C. Benzene standards were observed to elute at 0.7 min using this method. Gaseous headspace sample concentrations were related to liquid-phase concentrations by use of the dimensionless Henry's Law Constant.

Biofilm Staining

At the end of bioreactor operations, membranes were destructively sampled. Sample preparation was kindly done by the Phelps County Regional Medical Center Pathology Department, where 5-μm cross-sec-

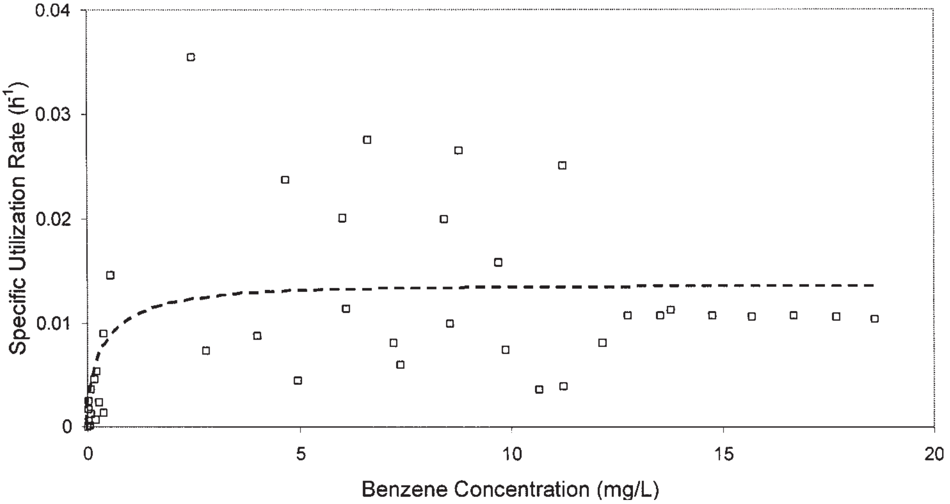

Fig. 2. Specific substrate utilization rate as function of benzene concentration in mixed bacterial consortium. Benzene concentration is the liquid phase. The line is the best fit of Monod-like parameters: $k = 0.013\ h^{-1}$; $K_s = 0.33$ mg/L.

tional samples of the membranes were obtained by gelling in plasma, fixing in paraffin, staining with hematoxylin and eosin, and slicing with a microtome. Cross-sectional samples were mounted on slides and viewed at ×4–40 magnification.

Results

Bacterial Consortium

Biokinetic parameters for the CSTR culture were calculated from 11 batch assays of 5.5 h or less in duration. Figure 2 shows the specific utilization rates plotted against the substrate concentration.

Monod-like biokinetic parameters were fitted to the data shown in Fig. 2 *(21)*. Nonlinear least squares regression produced a specific utilization rate, *k*, in the range of 0.01–0.02 h^{-1} and a half-saturation constant, K_S, in the range of 0.04–2 mg/L. Expressed as theoretical oxygen demand, the best fit, $k = 0.014\ h^{-1}$ and $K_S = 0.33$ mg/L, is a utilization rate of 1.0 d^{-1} and half-saturation constant of 1.2 mg/L. Compared to typical activated sludge values of 2–10 d^{-1} and 15–70 mg/L *(22)*, the culture in this research showed low activity. The culture's utilization rate was considerably lower than some previous reports of benzene utilization rates from 0.1 to 0.5 d^{-1} *(21,23)*.

Abiotic Mass Transfer

Mass flux (*J*) was calculated as the mass lost per time in the air phase from the inlet to the outlet, divided by the membrane outer surface area. The overall mass transfer coefficient was calculated from the log mean driving force between the gas- and liquid-phase concentrations. The flux

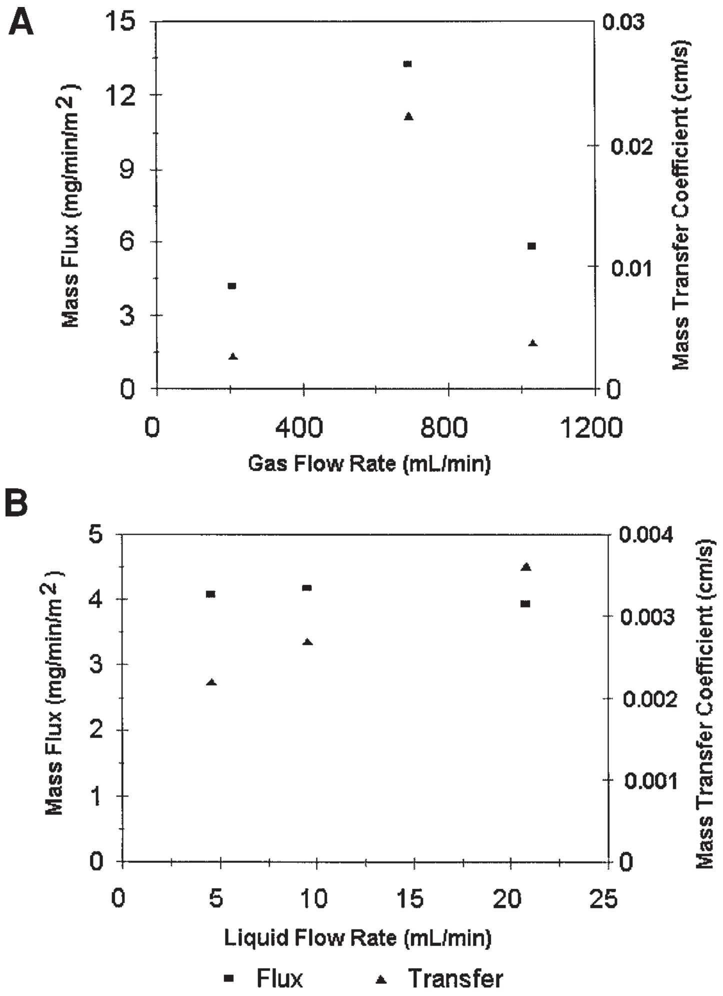

Fig. 3. Latex tubing reactor: abiotic gas **(A)** and liquid **(B)** flow rate effect. (■) Mass flux values; (▲) mass transfer coefficients.

from the air phase was used to determine the overall mass transfer coefficient using the equation

$$J = K_{ov} \Delta C_{lm}$$

in which ΔC_{lm} is the log-mean concentration difference and K_{ov} is the overall mass transfer coefficient. Mass closure was found by comparing total mass in and total mass out, while the mass removal was calculated from the fraction of outlet-to-inlet concentration in the air phase. The overall mass transfer resistance can be modeled as a sum of the gas, membrane, and liquid resistances:

$$1/K = 1/k_g + 1/k_m + H/k_1$$

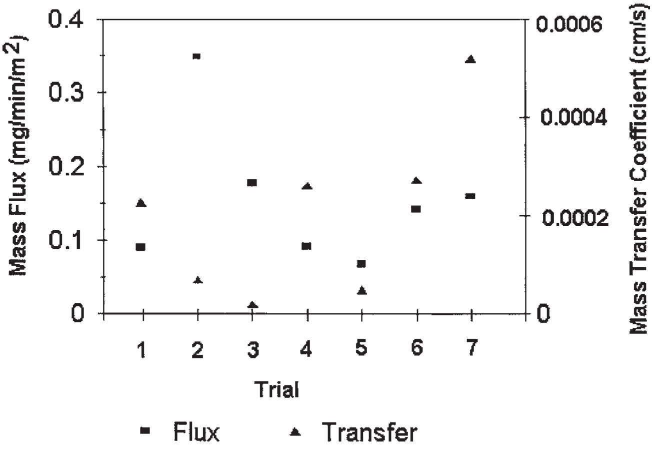

Fig. 4. HFMM reactor: abiotic mass flux and mass transfer coefficients. (■) Mass flux values; (▲) mass transfer coefficients. Benzene sorption rates may have varied significantly for each trial.

For the case of the polyporous HFMM, the gas-phase and membrane resistances are considered to be negligible *(9,24)* with the liquid-phase resistance dominating.

For the five abiotic trials with the latex tubing reactor, mass closure ranged from 84.8 to 95.9% while removal percentages ranged from 7.6 to 15.4%. Possible reasons for somewhat low mass closure may have been absorption of benzene into the membrane or the neoprene rubber stoppers. For the latex reactor, mass flux values ranged from 3.9 to 13 mg/(min·m^2), and mass transfer coefficients were below 3.0×10^{-2} cm/s.

Variation in gas flow with a fixed liquid flow rate (approx 10 mL/min) resulted in little effect on mass flux at the high and low flow rates measured, as shown in Fig. 3. The apparent maximum flux at 700 mL/min might be related to variations in gas residence times or the gas-phase resistance. Increasing the liquid flow rate increased the mass transfer coefficient; the mass transfer coefficient varied linearly with the liquid flow rate in the range evaluated ($R^2 > 0.99$). During these same experiments, pressure drop was determined. The 9.5 mm (3/8-in.) latex tubing had virtually no pressure drop when the air flow rate was <150 mL/min. The HFMM, with 2400 fibers of 0.25-mm diameter, had considerably greater pressure drops, up to 28 cm (11 in.) of water at 1 L/min air flow.

Figure 4 shows the mass transfer coefficients and mass flux of the HFMM reactor system. The highest mass flux did not correspond to the highest observed mass transfer coefficient but, rather, to one of the lowest mass transfer coefficients. The discrepancies in mass flux and closure suggests that sorption varied significantly from run to run. The lack of abiotic mass closure/removal for the HFMM reactor reached as high as 40%; the mass closure on the system was poor, and this missing mass can account for almost all the observed removal from the gas phase.

Table 2
Comparison of Abiotic Reactor Mass Parameters

Item	Latex tubing reactor	HFMM reactor
Maximum mass flux (mg/[min·m^2])	13	0.34
Total mass flow (mg/min)	0.08	0.1
Mass flux under same conditions (mg/[min·m^2])	4.1	0.07
Mass transfer coefficient (m/s)	2.2×10^{-2}	5.2×10^{-4}
Mass transfer coefficient under same conditions (m/s)	2.2×10^{-3}	5.0×10^{-5}

There was no significant effect on the mass flux and the mass transfer coefficient when the gas flow was varied in the range of 100–600 mL/min. Five abiotic trials using the HFMM at a constant gas flow rate and varying liquid flow rates showed that in a liquid flow range of 2 to 6 mL/min, there was little effect on the mass flux or the mass transfer coefficient. Most of the observed variance in mass transfer was probably related to sorption of benzene by polymers in the HFMM and/or error inherent to the use of GC-FID.

A comparison of abiotic data for both reactors is provided in Table 2. Mass flux in the latex tubing reactor was consistently much higher than in the HFMM reactor. Both reactors had similar rates of mass flow (0.08 vs 0.1 mg/min), but significantly different membrane area: the HFMM reactor had an inner surface area of 0.5 m^2 compared with 0.006 m^2 for the latex reactor. When both reactors were operated with a gas flow rate of 200 mL/min and a liquid flow rate of 4 mL/min, the latex tubing reactor achieved a higher mass flux, 4.1 mg/(min·m^2), compared with 0.07 mg/(min·m^2) for the HFMM reactor. All trials for the latex tubing reactor had greater mass transfer coefficients than the maximum observed mass transfer coefficient for the HFMM. Comparison of the reactors under similar operating conditions showed that the latex tubing reactor had a mass transfer coefficient two orders of magnitude greater than the HFMM reactor. Nonetheless, the 50-fold greater surface area of the HFMM reactor resulted in a similar mass removal.

Biofilter Operation in Latex Tubing Reactor

The latex tubing reactor was operated for 40 d with initial operating parameters as shown in Table 1. Initial attached growth occurred as clumps and was largely a function of the orientation of the membrane and the distance from the reactor liquid inlet. The majority of the biomass was initially near the inlet and on horizontal areas where it could settle. Freitas dos Santos and Livingston *(15)* observed a similar correlation to the amount of initial attached growth and the proximity of the liquid inlet for a membrane bioreactor.

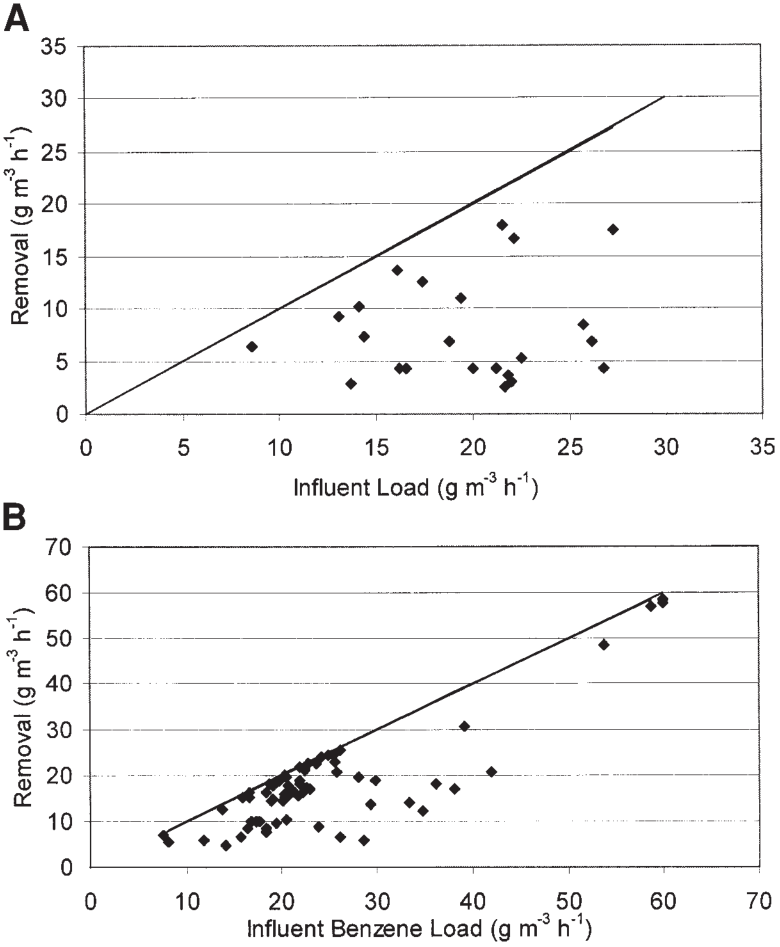

Fig. 5. Bioreactor average removal on a total reactor volume basis and variability for **(A)** latex tubing reactor, and **(B)** HFMM. Lines indicate 100% removal.

The removal of benzene by the latex tubing reactor is shown in Fig. 5A. Initial removal was essentially the same as the abiotic removal. However, benzene removal improved after d 20. Biofilm growth was observed to improve between d 20 and 30 while average removal increased from 25 to 70%. An apparent steady state was reached near d 40, with approx 80% removal of benzene and a mass flux of 45 mg/(min·m^2). This was an increase of 3.5-fold from the abiotic flux observed at the same operating conditions. Aqueous benzene concentrations at the liquid outlet continually decreased after d 20, indicating that growth in the system, most likely on the membrane, had increased and was responsible for increased benzene removal. No biofouling of the interior membrane was evident; the air-side pressure drop remained constant at 1.27 cm (0.5 in.) of water over the operational period. Although the target gas inlet concentration was 150 ppm, the observed inlet concentration was sometimes highly variable.

Biofilter Operation in HFMM Reactor

The HFMM reactor was operated for 100 d. Initial operating parameters are shown in Table 1, and benzene removal is shown in Fig. 5B. Benzene removal rose shortly after startup to a very high level, declined, and then rose once again. At d 16, the recycle rate was decreased to ensure direct comparison of abiotic and biotic reactor removal. Removal continued to grow, to an average of 75%. An increased pressure drop was observed at d 79, suggesting biofouling of the inside of the membranes. At the end of operation, the membrane was destructively sampled, fixed on slides, sliced by microtome, and stained. Microscopic analysis of the membranes' interior confirmed the presence of bacteria along the membranes' edges but did not, however, prove that bacterial growth had occurred inside the membranes owing to separation of the membrane slices from the fixative on the slide.

Growth on the outside of membranes was visible. The decrease in liquid benzene concentrations from 1 mg/L at startup to below detection (10 μg/L) by d 7 provided a positive indication of biodegradation associated with this growth. Attached growth was observed primarily at the gas inlet of the membrane. At the end of the experiment, approx 30 measurements of biofilm thickness were made along the HFMM, and an average biofilm thickness of 0.14 mm was found. Based on the measured average biofilm thickness, average length of cut fibers, and number of fibers, the biofilm volume was approximated. A biomass density of only 0.7 mg/L was calculated from VSS measurements and the approximated biomass volume, a very low value for biomass density *(25)*.

Biofilter Comparison

The latex tubing reactor achieved a maximum flux of 45 mg/(min·m^2) (mass flow of 0.27 mg/min) compared with 0.4 mg/(min·m^2) (mass flow of 0.12 mg/min) for the HFMM reactor. As a caveat, the reactors were not operated under identical conditions in terms of dimensionless parameters. The observed maximum flux through the HFMM reactor was under conditions resulting in the removal of virtually all the entering gas-phase benzene. A higher flux might have been achieved with further exploration of higher flow rates and higher concentrations. When compared to the abiotic performance under the same conditions, operating the latex tubing reactor as a biofilter gave a 3.5-fold increase in mass flux, and the HFMM increased mass flux by a factor of 6.

Discussion

Bacterial Consortium

Benzene is a commonly encountered contaminant and is usually found with chemically similar compounds—BTEX. Numerous studies have examined the degradation of BTEX by specific strains of bacteria and mixed cultures from subsurface soils, calculated the bacteria's biokinetic parameters, and determined benzene degradation rates *(21,23,26–28)*. Biokinetic parameters for BTEX degradation have been found to vary significantly among specific bacterial strains and consortiums. The low specific utilization rate (0.01 h^{-1}) and half-saturation constant (0.3 mg/L) reported here are not unanticipated based on this variability. The utilization rate may be lower because the CSTR cultures were initially grown with a combination of organics, perhaps contributing to the development of a suboptimum culture for the degradation of benzene. The low values might also be related to low oxygen conditions that may have developed within the batch cultures. More likely, because the bacteria were taken from the waste of the CSTR and then supplemented periodically, their metabolic state might have been lower than during the activated sludge process in which substrate is continually available. The scattering seen in Fig. 2 is a result of the experimental technique but is consistent with kinetic tests completed during other bioreactor studies by our research group (data not shown).

Mass Transfer

The limiting factor in operation of the biofilter is either biokinetic or mass transfer. Because benzene is somewhat structurally different from compounds studied by others, some differences in mass transfer parameters were anticipated. The latex tubing reactor achieved significantly higher mass flux, 13 mg of benzene/(min·m^2), than the observed flux of 0.26 mg of dichloroethylene (DCE)/(min·m^2) through a silicone rubber membrane *(10)*. A microporous membrane of the same manufacture and dimensions as the HFMM used in this study achieved a maximum mass flux of 1.3 mg of toluene/(min·m^2) and a mass transfer coefficient of 3.2×10^{-5} m/s at a liquid flow rate of 8.6 L/min *(29)*. By comparison, reactor no. 2, the HFMM, achieved a maximum mass flux of 0.34 mg of benzene/(min·m^2) and a mass transfer coefficient of 2.3×10^{-6} m/s at a flow rate of 2 mL/min. The fourfold decrease in mass flux is probably directly related to the lower liquid flow rate.

The mass transfer characteristics of the latex tubing reactor were nonetheless an order of magnitude higher than the maximums observed by Shumway *(29)*. In terms of the mass transfer rate, the higher surface area of the microporous membrane, 0.5 m^2, led to a similar mass flow rate, 0.1 mg/min, as observed with the latex tubing. When the mass flux and mass transfer coefficients were compared, the latex tubing reactor outperformed the HFMM on a per-area basis. The latex tubing reactor achieved a 40-fold increase in mass flux over the HFMM reactor. The latex rubber may have transferred more benzene because latex has a very high permeability for benzene. As a result of the high mass flux achieved by the latex tubing reactor, more benzene would be transferred using a latex tubing membrane than an HFMM with the same surface area. In addition, the latex tubing reactor is significantly more economical, with standard latex rubber tubing being relatively inexpensive compared to HFMMs. The cost differential involved certainly points toward highly permeable rubber tubing as a candidate for continued study in membrane bioreactors.

Bioreactor Operation

Although previous research studies using silicone rubber membranes *(10,16,17)* showed a decrease in mass flux with increasing biofilm thickness from diffusion limitations, the mass flux in the latex tubing reactor continued to improve as the biofilm thickness was visually observed to increase. Perhaps the reason for the increased flux was the low density of the biofilm. The biofilm appeared as a thick fuzz that may not have limited the diffusion of benzene. The less dense biofilm is consistent with other research using silicone rubber membranes *(30)*. At high Reynolds numbers, a denser, better adhering biofilm formed, compared with low Reynolds numbers, at which a less dense and partially covering biofilm formed. Long-term operation of the reactor in the present study might change the characteristics of the biofilm, resulting in a density change and diffusion limitation.

Using membranes similar to the HFMM, Shumway *(29)* achieved a mass flux during biofiltration of 1.9 mg of toluene/(min·m^2) at an inlet concentration of 550 ppm. The HFMM reactor achieved a mass flux that was slightly less than the previously reported values for microporous membranes. However, the HFMM was evaluated under limited operating conditions.

The latex rubber membrane was apparently much more efficient per unit area in benzene removal than the HFMM. However, the surface area of the HFMM was approx 0.5 m^2, compared with 0.006 m^2 for the latex tubing, and both were approximately the same total volume; consequently, the HFMM has the potential to remove more pollutant mass, and thus to have a higher elimination capacity. Additionally, the HFMM never achieved full coverage of a stable biofilm, thus making it difficult to determine the pollutant removal potential of this system.

Elimination capacities for biofilters as listed by Devinny et al. *(31)* ranged from 5 to 299 g of contaminant/(m^3·h); benzene removal in compost-based biofilters ranged from 8 to 23 g of benzene/(m^3·h) while BTEX removal by biofilters with a variety of packing materials ranged from 14 to 60 g/(m^3·h^1). A more recent report of a conventional peat biofilter removing a mixture of VOCs showed removal of 120 g of VOCs/(m^3·h) *(32)*, and a trickle-bed reactor gave benzene removal of 58 g/(m^3·h) *(33)*. When compared with other types of reactor systems, the latex tubing reactor and the HFMM had similar performance ranges, as shown in Fig. 4: 2.5–18 and 4.8–58 g/(m^3·h), respectively.

Conclusion

Based on the abiotic and biotic results, latex rubber tubing was significantly more efficient for benzene removal than a microporous HFMM on a flux (per-surface-area) basis. A latex rubber membrane would likely be a highly cost-effective treatment for the biofiltration of benzene. Although less removal per surface area was seen, the HFMM system gave a greater total removal (99.8 vs 82%), apparently owing to the high surface area–to–volume ratio.

One engineering concern for a membrane biofilter is the head loss for the airstream. The latex rubber membrane had a minimal pressure drop, whereas the microporous HFMM had a significant pressure drop, most likely caused by entrance and exit losses related to the membrane's configuration in the HFMM's inlet and outlet manifold.

Further investigation into membrane biofiltration of benzene using a latex rubber membrane is warranted. Because of the high mass flux per surface area, the use of thin-walled latex rubber membranes assembled as a module could offer a cost-effective treatment for benzene-contaminated air. Factors that might improve the mass flux across the membrane include smaller-thickness tubing for reduced membrane resistance; configuration within the reactor to achieve more surface area in the same volume, such as spiral configurations *(10)*; and use of the liquid recycle flow rate to produce a thinner and denser biofilm to increase flux *(30)*. Further, the benzene-degrading culture isolated from an activated sludge sample displayed a significantly lower utilization rate than observed in previous research, so inoculation with a culture with a higher utilization rate would probably increase the mass flux.

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