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SERDP Annual Report - 1998
Project Number CP 1105

MEMBRANE-MEDIATED EXTRACTION AND BIOTREATMENT OF VOCs

PERFORMING ORGANIZATION:

U.S. ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
AIR POLLUTION PREVENTION AND CONTROL DIVISION
RESEARCH TRIANGLE PARK, NC

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Project Background

This project is in response to the Statement of Need for FY98 SERDP, Compliance New Start Number 2 (CPSON2), entitled, "VOC Control Technology for Aircraft Painting and Depainting Facilities." Painting and coating operations present a number of environmental problems and economic challenges. Volatile organic compounds (VOCs) and other hazardous air pollutants (HAPs) are present in all currently used coatings. The toxic compounds include metals, metal oxides and VOCs. Many of these compounds are either direct or indirect health threats; VOCs are ozone precursors and may be designated as toxic, and many metals and metallic oxides are identified on toxic compound lists. Driven by the Clean Air Act Amendments of 1990, VOCs and HAPs in coatings are being reduced, thereby reducing emissions of ozone precursors and toxic compounds from painting operations. However, additional controls are mandated in specific instances, such as aircraft booths. The National Emissions Standard for Hazardous Air Pollutants (NESHAP) specific to aircraft painting will force the 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.

Control technology cost is primarily dependent on contaminated air flow rates. Paint spray booth exhausts are high volume streams because OSHA requires a minimum velocity of 100 feet per minute (fpm) through all booth section areas. Conventional booth design approaches include no provision for adjusting flowrate, relying instead on using a high flowrate with clean filters that will remain above the 100 fpm minimum after the filters are dirtied. If controls are required for VOC destruction, the necessary equipment must be sized for the maximum exhaust flowrate. As a result, typical booths emit large volumes of air contaminated with low concentrations of VOCs and HAPs. Many current technologies treat the VOCs within the entire gas volume directly, leading to large volume incineration, absorption, or biofiltration systems. These technologies are extremely expensive, both in terms of capital and operating expenses. Also, they often generate hazardous byproduct streams which must be further treated. The proposed system will both minimize the treated volume and concentrate the VOCs within that treated volume to further reduce the size and cost of the control equipment. These advantages make this VOC treatment option viable over a broad range of spray booth sizes.

The proposed VOC control system can reduce a significant portion of toxic materials emissions from DoD installations. Recent data taken from "Air Force Times" in the area of aircraft service indicate that 5 of the top 10 air discharges that triggered Toxic Release Inventory reporting thresholds from 131 DoD installations were typical paint constituents. Significant reduction of these emissions in a cost effective manner is important to DoD's adherence to the 1995 Aerospace NESHAP for Aerospace Manufacturing and Rework Facilities and existing requirements for VOC emissions in ozone non-attainment areas.

Technical Objectives

The overall objective is to validate and further develop a cost-effective VOC control system for painting facilities that meets the requirements of the Aerospace NESHAP, an 81 percent reduction in VOCs from non-compliant coatings. This will be accomplished using the partitioned recirculation flow reduction technique and a novel VOC concentrating and biological treatment process. The objective of this project in Phase I is to demonstrate that membrane-supported extraction, coupled with membrane-supported biotreatment, is a technically feasible VOC treatment process for DoD painting emissions. In Phase II, the objective is to establish the technical and economical efficacy of this process to treat actual aircraft painting emissions, using the paint booth facilities at Tyndall AFB as our pilot test site. Phase II will include cost analyses for various facility size ranges and the dissemination of information about the technology to appropriate DoD sites and organizations.

The initial cost estimates of the technology have been based on preliminary lab-scale performance. In support of project technical objectives and economic feasibility, it is necessary to answer the following critical questions:

1. Under conditions of 85-95 percent reduction of VOC emissions, what are the mass transfer rates of VOCs present in DoD painting and depainting operations (e.g. MEK, MIBK, xylenes, toluenes)
    a) from air to organic solvent via membrane?
    b) from organic solvent to aqueous phase via membrane?
2. Can a membrane supported biofilm be stably maintained?
3. What are the degradation rates of the above cited VOCs?
4. Using commercially available membrane units for design purposes, what is the projected cost of treatment in:
    a) $/cfm of air treated?
    b) $/unit of VOC removal?

    The design is to be based on modules capable of controlling streams from 20,000 to 300,000 ft^3/min of exhaust treated at typical VOC concentrations found in DoD operations.
5. What is the impact of particle and particle-bound contaminants such as isocyanates on membrane performance? How does this impact filtration requirements?

Answers to the above questions are the subject of this project, and are necessary for process scale-up and design, and process economics determination. Preliminary targets for mass transfer rates for VOCs from air and VOC degradation rates are 10^{-5} mol/ m^2 s and 3 x 10^{-10} mg/cell-hr, respectively.

Technical Approach

During the first year of this project, critical issues related to realistic conditions (mixed cultures, VOC mixtures in the air stream) are to be investigated at the bench- and pilot-scale. Bench-scale evaluations will occur at North Carolina State University (NCSU) and EPA/APPCD and installation and evaluation of a 2000 ft^3/min pilot-scale system will occur in the EPA/NRMRL/APPCD laboratories at the Environmental Research Center in Research Triangle Park. The system will be installed in the Pollution Prevention and Coatings Laboratory (PPCL) and will be evaluated using actual aircraft coatings such as Mil-Spec 83286 or 85285. The PPCL is equipped with a small spray booth. The booth exhaust will be directed into the pilot system. Other means of delivering the organics to the Membrane BioTreatment (MBT) system will be investigated to optimize the efficiency of data collection. The goal of Phase I (FY1998 funding) testing is to provide sufficient data to support a go, no-go decision and to characterize and optimize the process flow rates and membrane module sizes for the Tyndall pilot-scale testing. The following experimental tasks have occurred or will occur during the proposed project:

1. *Evaluation of hollow fiber material of construction.* The results reported previously have been for microporous polypropylene fibers. To avoid entrainment of the stripping fluid ***in*** the exhaust gas stream, a 1-2 PSI overpressure must be applied to the gas phase. This forces the air/liquid interface inside the pores, stabilizing the interface. Operationally, a non-porous material would require no gas-phase overpressure, reducing blower or compressor requirements.

Materials and procedures that will be employed in the work have been chosen. Celgard® X-30 hollow fibers, which are microporous polypropylene fibers with approximately 40% porosity, have been used. The membrane architecture evaluated for air separation is the Hoechst-Celanese Liqui-Cel® design, using either uncoated Celgard®, silicone rubber coated Celgard®, or Celgard® coated with an amorphous co-polymer of tetrafluoroethylene (TFE) and perfluoro-dimethyl dioxole (PDD). Laboratory scale Liqui-Cel® units (1.4 m^2 membrane surface area) have been used in all air separation experiments. Uncoated Celgard® fibers in a Liqui-Cel contactor were used for biomembrane reactor experiments. Specific experiments conducted are outlined below.

Prior to beginning mass transfer experiments with any coated fiber membrane module, the absorptive capacity of the coated fibers was investigated. Flow of VOC laden air was initiated through the membrane units at a VOC concentration set at 150 parts per million (ppm) on a mole/mole basis with a syringe infusion pump. Inlet and outlet air stream samples were collected and analyzed by GC/FID

immediately after they are withdrawn from the sample port. This procedure was continued until there was no change detected in the outlet air concentration. A mass balance around the membrane unit allowed determination of the amount of VOC absorbed by the fibers.

Initial evaluation of membrane module mass transfer coefficients was conducted by examining the removal of each individual VOC from an air stream. Experiments were performed to determine the effect of air flow 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. Air flow rates between 1 and 5 ft^3/min (28 and 140 L/min), and octanol stripping fluid flow rates between 0.1 and 1.0 L/min were studied. Contact times for both streams were calculated based upon the geometry of the membrane unit. Samples of inlet air, outlet air, and the stripping fluid reservoir were taken at regular time intervals and analyzed to allow calculation of the overall mass transfer coefficient via an appropriate design equation for the membrane contactor. With air run through the system in a single pass and stripping fluid being circulated in a closed loop, a mass balance can be made around the system. Air samples are collected and analyzed by gas chromatography using a flame ionization detector (GC/FID) immediately after they are withdrawn from the sample port. Stripping fluid samples were placed into 1.5 mL polypropylene microcentrifuge tubes and stored headspace free in a -20 °C freezer until analysis by UV-Vis spectrophotometry or high performance liquid chromatography (HPLC) with an ultra-violet (UV) or refractive index (RI) detector.

2. *Evaluate the mass transfer rates of VOC mixtures* Following the completion of experiments with single compounds, an evaluation of the preferred membrane module performance with mixtures of compounds was performed. The preferred module was selected on the basis of high mass transfer rates for individual species and a small gas phase pressure drop through the module. Experimental methods and analysis are identical to those described above. Compounds were serially added to the experimental matrix and represented equally on a volume basis. By adding equal volumes of each compound, any effect of an individual compound on mass transfer was readily apparent. Once all of the representative VOCs have been tested in equal volume mixtures, their relative proportions will be adjusted to reflect the speciation present in surface coating exhaust streams, and the experiments repeated.

Although candidate stripping fluids, such as octanol, canola oil, mineral oil and silicon oil, are deemed technically feasible and cost effective, octanol was chosen for these experiments because, as a pure compound, analysis of VOC concentrations would be more straightforward than using the other fluids, which contain mixtures of compounds. For military use, the ultimate goal is to select the stripping fluid that provides the best performance within reasonable cost considerations and to establish a mathematical relationship between stripping-fluid flow, contact time, and VOC removal efficiency. This will facilitate the design of a full-scale separation/ concentration system.

The efficacy of hollow-fiber membrane-mediated gas-liquid extraction to remove MEK, MIBK, toluene and xylenes at low concentrations (<100 ppm total) from air streams must be established. Air flowing at a rate of 1 - 10 ft^3/min, carrying each of the named components individually and in combination, was passed through a hollow-fiber contactor with a nominal membrane surface area of 1.4 m^2. Initial quantification of mass-transfer coefficients using octanol as the stripping fluid was accomplished.

3. *Evaluate biotreatment module performance.* A series of experiments was performed to determine the stripping efficiency of the bench-scale biotreatment module with and without biofilms present. Octanol stripping fluid generated by membrane separation experiments was used as feedstock for the biotreatment module studies. The overall mass transfer coefficient for the uncoated Celgard® hollow fiber unit was determined. The issue is to correctly account for both the additional mass transfer resistance added by the biofilm as well as the enhancement to transfer afforded by simultaneous degradation of the VOC contaminants (MEK, MIBK, toluene, xylenes). It is critical to quantify the degradation rates and the biofilm cell density within the biodegradation unit.

Initial evaluation of membrane module mass transfer rates was conducted by examining the removal of individual VOCs from an octanol stream. These experiments were conducted in the same way as those performed for air separation membrane modules. Experiments were performed in the absence of a biofilm, and in the presence of a live biofilm. Experiments were and are being performed to determine

the effect of stripping fluid flow rate, aqueous (or biomedium) flow rate, stripping fluid VOC concentration, and aqueous (or biomedium) VOC concentration on overall mass transfer rates. Stripping fluid reservoir concentrations were set in the range of 5,000 to 50,000 ppm on a mole per mole basis. Stripping fluid and aqueous (or biomedium) flow rates were set between 0.1 and 2.0 L/min. Contact times for both streams were calculated based upon the geometry of the membrane unit. Liquid samples were placed into 1.5 mL polypropylene microcentrifuge tubes (cells are removed from biomedium samples upon collection by centrifugation) and stored headspace free in a -20 °C freezer until analysis by HPLC with a UV or RI detector or GC/FID. Design equations for mass transfer in the biomembrane module will be developed, and results obtained from sample analysis will be used to calculate overall mass transfer coefficients for VOCs in this module.

4. *Evaluate the mass transfer rates at bench scale of VOCs generated using MilSpec-C- 83286 or -85285 topcoats.* The efficacy of hollow-fiber membrane-mediated gas-liquid extraction to remove compounds from air streams will be quantified for typical concentrations found in aircraft booths. Exhaust from the small paint spray booth in the Coatings Laboratory will be routed to the bench-scale separation/concentration (S/C) unit, using octanol to remove the VOCs from the air stream.

5. *Design an air-handling manifold for 2,000 ft^3/min.* Preliminary plans for the pilot scale system include the use of various module designs currently under development by Celgard and Bend Research, Inc. Modules with a membrane surface area of 1453 ft^2 (135 m^2) or larger are planned. Design of a manifold to distribute exhaust gas to two units in parallel will allow the handling of 2,000 ft^3/min.

At the end of these steps, results will be reviewed and a go, no-go decision will be made on program continuation. Key criteria for continuation include rate of transport across the membrane and ability of the membrane to maintain performance with a dirty exhaust stream.

6. *Construct, install and evaluate the exhaust air handling manifold.* The previously-designed manifold will be attached to the small paint spray booth in the EPA Pollution Prevention Coatings Laboratory (PPCL). The flow distribution through the individual membrane modules will be measured to verify that equal flow partitioning has been achieved. A mixture of representative solvents will be sprayed into the booth and the manifold surfaces will be monitored for solvent condensation. If necessary, modifications to minimize condensation and achieve equal flow partitioning will be implemented.

7. *Install and evaluate an integrated 2,000 CFM MBT system at EPA's PPCL.* It is anticipated that after the system is installed and checked out, approximately 8 weeks of data collection will follow. These data will be used to evaluate the MBT system's removal and decomposition efficiency for specific paint VOCs. Sample analysis will be conducted using GC/MS and on-line GC/FID. A gas stream containing mixtures of MEK, MIBK, toluene and xylenes will be used to demonstrate that mass transfer and biodegradative performances are comparable to bench-scale levels. The exhaust from a small paint spray booth using MIL-C-83286 and -P-23377 or other Mil-Spec paints or simulated booth exhaust will be used to evaluate process effectiveness for aircraft painting emissions. The impact of particles on the performance of the module will be evaluated by spraying paint through a filter to determine the effect on flow rate, pressure drop, average capillary diameter, and module life in a realistic environment. Because some resin-forming components such as isocyanates are sub-micron in size and likely to pass through standard spray booth filters, their effect on the long-term effectiveness of the membrane must be evaluated.

8. *Prepare and submit an interim report for Phase I.* Upon completion of the data analysis from the pilot testing, a report will be submitted which summarizes the results and addresses the criteria developed to assess the value of continued development. This report will be used to make the go, no-go decision for Phase II.

Project Accomplishments

Materials and Methods

Calibration standards for GC and 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. The low and medium calibration standards bracketed the actual concentration of the effluent. The medium and high standards bracketed the influent concentrations.

GAS CHROMATOGRAPHIC ANALYSES

In all cases, the GC was operated as outlined in 40 CFR Part 60, Appendix A, Method 18 "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography". Compound identification was based on retention time comparisons with known standards.

Vapor phase samples were taken automatically from the membrane contactor apparatus by a multi-port 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 detectors are FIDs 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 detector temperature of 250 °C.

Aqueous samples taken from biomembrane units for analysis of VOC concentration were subject to pentane extraction (2:1, pentane:aqueous) for 2 minutes. 1-5 mL of the pentane phase 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 injector temperature of 200 °C, and a detector temperature of 250 °C, using a J&W Scientific capillary column (DB-624) and FID detector connected to an HP 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 a 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/H_20 flow. The detector was a UV/VIS spectrophotometer, operating in the range of 260-270 ηm. Aqueous phase samples from biomembrane experiments were analyzed in a similar fashion. Operation was isocratic with a 20/80 acidified methanol/H_20 flow. The detector was a UV/VIS spectrophotometer, operating in the range of 260-270 ηm.

HENRY'S LAW ANALYSES

A variable volume headspace technique was used to determine Henry's Law Constants for several VOCs in organic fluids. This method was described by Poddar et al. in 1996 (J. Chem. Eng. Data, 1996, 41, 1329-1332).

This technique involved two main procedures, preparation of stock solutions and loading of sample vials. Stock solutions were prepared by first chilling the solvents, solutes, stock solution containers, and container caps and septa to 4 °C in a walk-in refrigerator (cold room). Stock solution containers were 500 mL screw top flasks sealed with Teflon faced septa. Next, the solvent of interest was transferred to a stock solution container and the VOC solute of interest was added to achieve a dilute solution of known concentration (150 to 1000 mg/L). The density of the stock solution was assumed to be that of the solvent at the temperature of interest. The stock solution was well mixed, and placed in a cooler filled with 95% ethanol that had been stored at -70 °C in preparation for loading sample tubes. EPA vials with PTFE faced silicone rubber septa and screw top closures (volume previously determined by weighing the amount of water required to completely fill them at 25 °C) were placed in liquid N_2 to prepare them to be loaded with stock solution. After chilling in the N_2, the vials were placed on an analytical balance

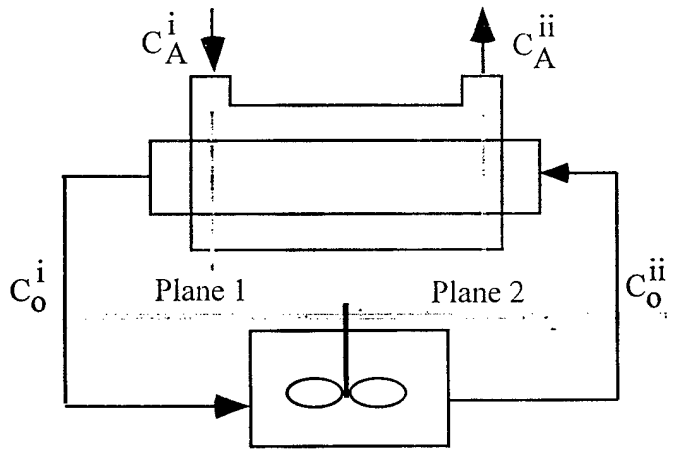
and tared. A volume of stock solution was transferred via a glass pipette from the stock solution container to the sample vial on the balance and the weight of stock solution recorded. Tubes were sealed with the screw top caps and Teflon faced septa. For each experiment, three sets of five tubes were loaded with volumes of stock solution to obtain gas/liquid volume ratios between 2 and 20. Each set of tubes was allowed to equilibrate at a different temperature, 23, 30, or 40 °C, for a minimum of 2 hours. 50 microliter samples of the headspace in the tubes were manually withdrawn in a gastight syringe and analyzed on an HP 5890A GC equipped with a capillary column (J&W Scientific DB-624) and FID detector. To determine Henry's Law constants, plots of 1/area count vs. gas volume/liquid volume were prepared for each set of tubes and least squares fits were made for the data. By dividing the resulting slopes by the resulting y-intercepts, Henry's Law constants were obtained.

BIOREACTOR STUDIES

Microorganisms used were originally isolated from a soil sample contaminated with motor fuel from a site in western North Carolina. This isolate was enriched on MEK, and a pure culture was established. Minitan™ tangential flow units (Millipore Corp.) were used in flat sheet bioreactor studies. These units have a membrane contact area of 7.6 cm^2 and a contact volume of 48 cm^3. Hollow fiber experiments were performed using a Liqui-Cel® 2.5" diameter x 8" long membrane contactor (obtained from Celgard LLC, formerly Hoechst-Celanese Corporation). This unit contains Celgard® X-30 microporous polypropylene membranes, with a mass transfer surface area of 1.4 m^2, a shell side volume of 195 cm^3, and a tube (fiber) side volume of 145 cm^3. The hollow fiber units were operated with the biofilm on the shell side. All experiments were performed at room temperature (25 °C) using L-salts minimal medium. L-salts medium was prepared as follows (all compositions are weight %): NH_4Cl 5%, 5mL/L; $CaCl_2$ 1.5%, 1mL/L; $FeSO_4$ 0.1%, 1mL/L; $MgSO_4$ 20%, 1mL/L; $NaNO_3$ 20%, 5mL/L; KCl 4%, 1mL/L; Na_2HPO_4 2.1%, NaH_2PO_4 0.9%; 10mL/L; MoO_3 0.1%, 1mL/L. A trace element solution contains: $CuSO_4 \cdot 5H_2O$ 0.00005%; H_3BO_3 0.1%; $MnSO_4 \cdot 5H_2O$ 0.1%; $ZnSO_4 \cdot 7H_2O$ 0.1%; and is added to L-salts at a ratio of 1mL/L. The only carbon source present was MEK.

MASS TRANSFER ANALYSIS

In order to scale up the process, the overall mass transfer coefficient (K_o) for the contactor must be known. The following analysis relates K_o to operating variables {volumetric flow rates of air (Q_A) and octanol (Q_O), concentrations of VOC in air (C_A^i, C_A^{ii}) and octanol (C_O^i, C_O^{ii})}, physical properties {H, Henry's Law constants},and module configuration {air contact area of the module, Am}. Differential balances are performed at two different planes within the hollow fiber contactor, and in two separate phases, as indicated in the following figure.



Using differential balances at the air/octanol interface:

Air side: $Q_A C_A|_z - Q_A C_A|_{z+\Delta z} - K_o \pi D \Delta z (HC_A - C_o) = 0$, where D is the outer diameter of the fiber, and z is a length along the fiber. This balance, taken over a differential length, reduces to equation (1):

$$Q_A \frac{dHC_A}{dz} = -HK_o \pi D (HC_A - C_o) \tag{1}$$

A similar balance is taken on the octanol side. As in the air side development, this balance would reduce to equation (2):

$$Q_A \frac{dHC_A}{dz} = -HK_o \pi D (HC_A - C_O) \tag{2}$$

Subtracting equation 2 from equation 1 yields the following:

$$\frac{d(HC_A - C_o)}{dz} = -K_o \pi D (HC_A - C_o)\left(\frac{1}{Q_o} - \frac{H}{Q_A}\right)$$

Integrate this equation over the hollow fiber module from plane 1 to plane 2 and from length zero to L,

$$\int_1^2 \frac{d(HC_A - C_o)}{(HC_A - C_o)} = K_o \pi D \left(\frac{1}{Q_o} - \frac{H}{Q_A}\right) \int_0^L dZ$$, or

$$\ln\left[\frac{HC_A^{ii} - C_o^{ii}}{HC_a^{i} - C_o^{i}}\right] = K_o A_m \left(\frac{1}{Q_o} - \frac{H}{Q_A}\right) \tag{3}$$

Dividing equation (1) by equation (2) and integrating from plane 1 to plane 2 yields

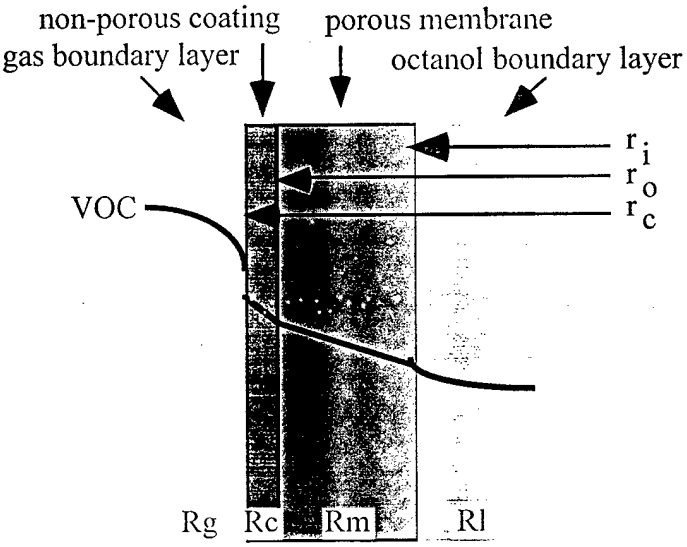
$$\left(C_A^{ii} - C_A^{i}\right) = \frac{Q_o}{Q_A}\left(C_o^{ii} - C_o^{i}\right) \tag{4}$$

The solution method for K_o is a simple one. First, perform overall mass balances of the VOC in the air stream and the octanol stream: $Q_A \Delta t\left(C_A^{i} - C_A^{ii}\right) = V_o\left(C_o^{ii}(t = t_2) - C_o^{i}(t = t_1)\right)$. Since the inlet air concentration C_A^{i} is constant and the outlet air concentration C_A^{ii} is essentially constant over short time periods D_t, this equation can be solved for the exit air concentration, C_A^{ii}. Equation 4 can be solved for the concentration of VOC in the octanol stream exiting the unit, C_o^{i}. Equation 3 can then be solved directly for K_O.

$$\frac{\ln\left[\frac{HC_A^{ii} - C_o^{ii}}{HC_a^{i} - C_o^{i}}\right]}{A_m\left(\frac{1}{Q_o} - \frac{H}{Q_A}\right)} = K_o \tag{5}$$

This equation was used in the calculations reported in the separation/concentration section.

Interpretation of the mass transfer results for the coated membranes is based on a sum of resistance model for mass transfer in cylindrical coordinates. In the following schematic, r_i, r_o, and r_c represent the radial distances from the center of the fiber to the membrane inner and outer surfaces, and coating surface, respectively. Mass transfer resistances can arise from the gas (R_g) and liquid (R_l) boundary



layers, the membrane (R_m) and the non-porous coating layer on the membrane (R_c). These resistances act in series, so that one can write an equation for the total resistance in the following way:

$$R_o = \frac{1}{K_o} = R_g + R_c + R_m + R_l \qquad (6)$$

where $R_g = \frac{1}{k_g}$, $R_c = \frac{d_o}{H_c (d_c)_{lm} k_c}$, $R_m = \frac{d_o}{H_o (d_m)_{lm} k_m}$, and $R_l = \frac{d_o}{H_o d_i k_l}$, where $(d_m)_{lm}$ represents the log mean diameter of the membrane, and d_i, d_o, and d_c represent the inner, outer, and coating diameters, respectively. The mass transfer coefficients in the gas and liquid phases (k_g, k_l) are generally dependent upon local Reynolds number. The membrane pore mass transfer coefficient, k_m, can be related to the pore fraction (ε), pore tortuosity (τ), and the diffusion coefficient for the VOC in octanol ($D_{i,l}$) as follows:

$$k_m = D_{i,l}\, \varepsilon / \tau (r_o - r_i \qquad (7)$$

The coating mass transfer coefficient, k_c, is related to the permeability of the VOC through the coating (q_c):

$$k_c = q_c / (r_c - r_o \qquad (8)$$

Results

Henry's Law values

Three stripping fluids have been evaluated thus far; silicon oil, octanol, and canola oil. Octanol has been used extensively throughout this project, and is a standard for extraction studies. Silicon oil offers the promise that the microorganisms will not use it as a carbon source, and canola oil is much less expensive than octanol. The following results were obtained.

Henry's Law Values			
Solvent	Solute	Temperature (°C)	H ($x10^{-3}$)
Octanol	acetone	23	8.9
		30	**5.9**
		40	9.4
	MEK	25	1.4*
		30	3.3*
		41	55
	m-xylene	24	3.0*
		40	16*
Silicon oil	acetone	26	**42**
		30	26
		42	27
	MEK	23	21
		29	**8.2**
		39	28
	m-xylene	24	27
		29	4.6*
		41	68
Canola oil	MEK	25	4.6
	m-xylene	24	11

* Values are preliminary, subject to more rigorous testing. Values in **bold** are anomalous and subject to verification.

Separation/concentration

Gas separation experiments were performed using a Celgard X-30 polypropylene hollow fiber module (2.5" diameter x 8" long) with 1.4 m^2 membrane surface area. The shell side of these fibers was coated with an amorphous co-polymer of tetrafluoroethylene (TFE) and perfluoro-dimethyl-dioxole (PDD) at a thickness of approximately 0.1 micron. The shell side volume is approximately 195 cm^3 and the tube (fiber) side volume is 145 cm^3. The module was operated with air on the shell side, contacting in a single pass at two flow rates, 60 L/min and 28 L/min. Octanol flowed through the tube (fiber) side at either 120 cm^3/min or 350 cm^3/min, and is recirculated through a 2L mixing tank. The units were operated at room temperature (25 °C), and the octanol contained as little as 5 ppm VOC (m-xylene experiments) or as much as 1300 ppm (MEK experiments).

S/C Unit Mass Transfer Coefficients				
Compound transferred	Loading (ppm/s)	Air flow (L/min)	$Re_{octanol}$	K_O (x10^5 cm/s)
m-xylene	110	28 28	.12 .34	.85 .91
	260	28 28	.12 .34	.96 1.0
	360 1500	60 60	.12	1.3 1.6
MEK	675	28	.34	.68
	1900	28 28	.11 .34	2.0 2.0
	5500	30 60	.18	4.3 9.4

The loading rate reported is the air feed VOC concentration divided by the mean air residence time in the shell volume, and gives an indication of the relative amount of VOC flowing into the module on the shell side. Several interesting trends can be noted:

1. The octanol Reynolds number has little effect on K_O, suggesting that the fluid boundary layer offers insignificant resistance to mass transfer. This is in accordance with similar results found for liquid-liquid systems with regard to the fluid in which the VOC is most soluble. It may also be due to the fact that all octanol flows considered are in the laminar flow region.

2. The gas phase flow rate has a significant effect on the mass transfer coefficient. This is indicated by the 2-fold increase in K_o observed for MEK at a loading rate of 5500 ppm/s as the gas flow increases from 30 L/min to 60 L/min.

3. Increasing the loading rate causes an increase in K_o. It is known that the permeability of the coating (q_c), which in turn effects R_c through k_c, increases with VOC concentration. This result suggests, therefore, that the coating contributes significantly to the overall resistance to mass transfer.

Experiments were also performed with toluene and toluene/MEK mixtures in the gas stream. Analytical techniques for toluene analysis in the octanol phase are still under development, so overall mass transfer coefficients cannot be calculated. However, the following fluxes were observed, based on gas phase concentrations:

Air Separation Results				
Air Conc. (ppm)	Air Contact Time (s)	Reoctanol	Observed flux (mol/ m^2s)	Average removal (%)
1300 Toluene	0.40	0.25	1.6×10^{-6}	78
900 Toluene	0.19	0.25	1.6×10^{-6}	76
800 Toluene	0.11	0.25	1.6×10^{-6}	74

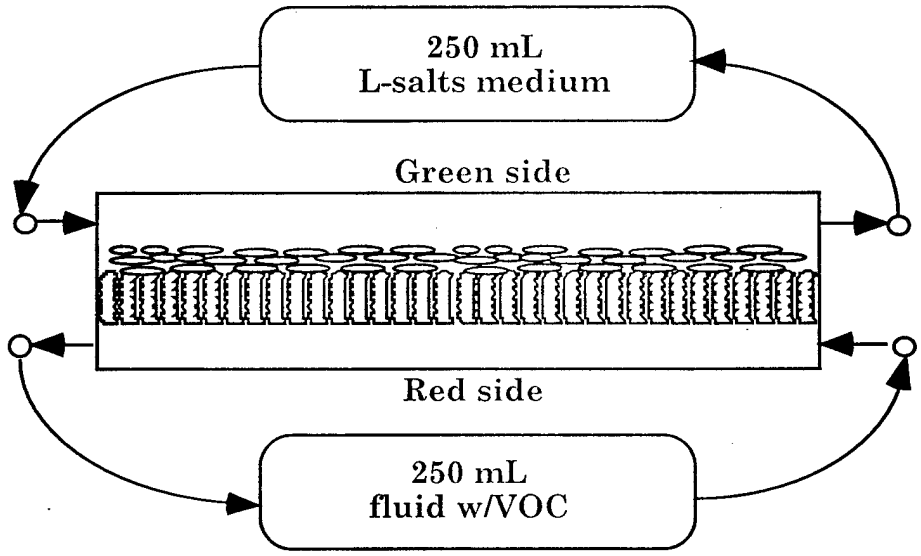
850 MEK, 650 Toluene	0.41	0.25	1.0×10^{-6} 8.0×10^{-7}	80 70
500 MEK 250 Toluene	0.19	0.15	1.0×10^{-6} 6.0×10^{-7}	80 60

Biomembrane reactor

Biofilm reactor studies have focused on two questions:

1. Does the biofilm enhance mass transfer of VOCs from the octanol stripping fluid to the aqueous phase?
2. Does the octanol have a significant effect on the VOC degradation rate?
3. Does the octanol degrade significantly over time?

With these questions in mind, experiments have been performed using flat sheet and hollow fiber contactors. The flat sheet bioreactor studies involved the use of tangential flow contactors. These contactors were initially seeded with a bacterial culture capable of degrading MEK and toluene on the "green" side of the membrane, and containing 250 ppm MEK in aqueous L-salts on the "red" side of the membrane. Following 3 days of recirculation of a suspended cell culture of MEK degraders, the green side was flushed with sterile L-salts at a rate of 7 cm^3/min (single-pass) and 33 cm^3/min (recirculated) L-salts. This minimized the retention of cells on the green side and maintained vigorous mixing of the fluid in the unit. The red side was exposed to L-salt medium containing 250 ppm MEK, recirculated to a 2L tank. After 17 days of biofilm growth, the biofilm thickness was approximately 80 microns in thickness. The Minitan™ unit was then connected to two reservoirs, as shown in the following schematic.



First, both green and red sides contained L-salts medium, and MEK was transferred from the red to the green side of the membrane. However, samples of the green side fluid indicated no MEK, so the transfer of MEK out of the red side fluid was completely consumed by the biofilm, exhibiting a degradation rate of 80 mg MEK/ m^2 h. The Minitan™ was then stored overnight with L-salts on both red and green side. The L-salts recirculating on the red side were then replaced with octanol containing MEK. MEK did accumulate on the green side, and the observed biodegradation rate was 60 mg MEK/ m^2 h. This reduction in rate may be due to consumption of octanol by the biofilm, but a more likely explanation is

that the biofilm culture was starved during the overnight storage between experiments, and biofilm activity decreased as a result.

Finally, the hollow fiber unit was used to determine whether mass transfer rates for MEK were enhanced by the presence of an active biofilm. The Liqui-Cel® unit was operated with a single-pass aqueous phase on the shell side and recycled octanol (2L mixing vessel) on the tube (fiber) side. For the biofilm experiment, a 2 day old biofilm was established on the shell side. All experiments began with 5000 ppm MEK in the octanol phase. The experimental configuration and results are shown in the following table.

Liqui-Cel® Mass Transfer of MEK				
Experiment Type	Abiotic			Biofilm
Aqueous phase	Filtered tap water			L-salts
$Q_{aqueous}$ (cm^3 /min)	116	301	598	301
$Q_{octanol}$ (cm^3 /min)	290			
MEK in octanol (ppm)	5000			
Mass transfer rate (g/ m^2 h)	1.8	2.1	4.5	3.0

The results indicate that the presence of an active biofilm increased the transfer rate of MEK by nearly 50% (mass transfer rate of 3.0 g/ m^2 h with biofilm vs. mass transfer rate of 2.1 g/ m^2 h without biofilm), and this result has been verified in subsequent experiments.

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The overall objective is to validate and further develop a cost-effective VOC control system for painting facilities that meets the requirements of the Aerospace NESHAP, an 81 percent reduction in VOCs from non-compliant coatings. This will be accomplished using the partitioned recirculation flow reduction technique and a novel VOC concentrating and biological treatment process.

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