

EMERGING TECHNOLOGY REPORT
CROSS-FLOW PERVAPORATION SYSTEM
FOR REMOVAL OF VOCs FROM
CONTAMINATED WASTEWATER

by

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The primary purpose of this guide is to provide standard guidance for designing and implementing a biodegradation treatability study in support of remedy selection testing. Additionally, it describes a three-tiered approach that consists of 1) remedy screening testing, 2) remedy selection testing, and 3) remedial design/remedial action testing. It also presents a guide for conducting treatability studies in a systematic and stepwise fashion for determination of the effectiveness of biodegradation in remediating a site regulated under the Comprehensive Environmental Response, Compensation, and Liability Act. The intended audience for this guide includes Remedial Project Managers, On-Scene coordinators, Potentially Responsible Parties, Consultants, Contractors, and Technology Vendors.

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ABSTRACT

The U.S. Federal Register of April 17, 1987, contains a list of priority pollutants found at Superfund Sites. About half of these are volatile organic compounds (VOC's), which are known to be toxic and/or carcinogenic in nature. Pervaporation is a membrane technology utilizing a dense non-porous polymeric film to separate the contaminated water from a vacuum source. A membrane is used that preferentially partitions the VOC organic phase used in this test. This process has proven to be an alternative to conventional technology because it removes the amount of VOC's without requiring any pre/post treatments. Pervaporation is a cost-effective method of removing VOC's.

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EXECUTIVE SUMMARY

Water contaminated with volatile organic compounds is encountered throughout industry and in many groundwater and site remediation applications. Conventional technologies such as air stripping and activated carbon treatment do not always provide a complete and economic solution for some of these wastewater applications. Previous work has demonstrated that pervaporation is a potentially suitable remediation method for such applications. The primary objectives of this project have been to develop an improved membrane and module design to make pervaporation a more cost-effective method of removing volatile organic compounds from contaminated water, and to compare the improved pervaporation module and membrane design to other remediation technologies as well as other pervaporation module and membrane designs for the removal of organics from contaminated water.

Improved modules and membranes were developed, and a system was designed to test these pervaporation modules. Testing was carried out by U.S. EPA accepted methods. Testing confirmed that the transverse flow pervaporation module using a thick membrane provided improved performance. In addition, important variables such as Reynolds Number, operating temperature, permeate pressure and organic volatility were considered in pervaporation testing and the effect of such variables were quantified at bench-scale. These results confirmed the validity of existing models for predicting pressure drop through membrane modules and, for estimating the rate of removal of organics from water by pervaporation. Removal rates and selectivities were higher in this work using a transverse flow pervaporation module than reported elsewhere for conventional modules. The bench-scale results were also verified at pilot-scale using a transverse flow pervaporation module with 0.5 m² of surface area

Models for mass transfer and pressure drop in a closely packed array of hollow fibres were used to carry out sensitivity and optimization analyses. These analyses identified optimum operating conditions for pervaporation operation. Some of these results were reported in Environmental Progress (Lipski and Côté, 1990). Optimization indicated that pervaporation operation with transverse flow modules would be most effective using thick membranes at higher Reynolds Numbers and higher operating temperatures

1.0 **INTRODUCTION**

This is the final report for the unsolicited proposal entitled “Development and Evaluation of a Cross-Flow Pervaporation System for Removal of Volatile Organics from Contaminated Water”, Contract #09SE.KE405-8-6385. This work was funded by Environment Canada through the Department of Supplies and Services.

The purpose of this work was to develop a cost effective pervaporation membrane module and system to remove volatile organic compounds from contaminated water. Pervaporation has the potential of replacing conventional technologies such as activated carbon adsorption and air stripping.

The project was broken down into 8 tasks:

- | | |
|--------------------------|--------------------------|
| 1. Membrane Requirements | 5. Qualification Testing |
| 2. Module Requirements | 6. System Optimization |
| 3. System Requirements | 7. System Evaluation |
| 4. System Construction | 8. Final Report |

Amendment #1 dated January 18, 1991 was to; 1) redefine the work statement of Task 5 to allow for modification of existing test equipment rather than building new equipment, and 2) eliminated field work from Task 7.

This project was also supported under the US Environmental Protection Agency SITE Emerging Technology Program. One of the requirements of EPA was the development of a Quality Assurance Project Plan that served as a guideline to obtain reliable experimental information. A Quality Assurance section (Section 5.2.2 in this report) discussed the results of this Quality Assurance Program

This report is organized in 7 sections. In Section 2, relevant background information is presented and supports the statement of project objectives in Section 3. The pervaporation equipment developed in the project is described in Section 4. Testing results are presented in Section 5 while ways to optimize the process are outlined in Section 6. Recommendations and conclusions are presented in Section 7.

Several publications have been produced in the course of this project. Copies of these are included in the Appendices.

2.0 BACKGROUND

2.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are common contaminants in wastewater, leachate and contaminated groundwater. About half of the 129 US EPA priority pollutants are VOCs and are known to be toxic and/or carcinogenic. VOCs are emitted in large quantities (1,600,000 to 5,000,000 metric tons per year) from waste treatment, storage and disposal facilities (Shen *et al.*, 1988). VOCs are also present at abandoned industrial sites. The U.S. Federal Register of April 17, 1987 contains a list of priority pollutants found at Super-fund sites. A number of these contaminants can be removed by pervaporation. These are presented in Table 2.1.

2.2 Pervaporation

Pervaporation has been considered (Brun, 1981; Eustache & Histi, 1981; Nguyen & Nobe, 1987) as an alternative technology for removal of volatile organic compounds from contaminated water. The contaminated water may be an industrial process water, groundwater or leachate. Pervaporation is a membrane technology utilizing a dense non-porous polymeric film to separate the contaminated water from a vacuum source (Figure 2.1). The volatile organic compounds contained in the liquid phase are adsorbed onto the membrane and diffuse through to the other side where they are drawn off by a vacuum. A membrane is used that preferentially partitions the VOC from the water (much like an organic phase used in extracting organics from water samples in liquid/liquid extraction). For water treatment applications, the membrane is made of an organophilic polymer such as silicone rubber which exhibits good permeability for the organic compounds while allowing very limited passage of water. A typical VOC concentration gradient across the membrane is shown schematically in Figure 2.1. Although permeability through silicone rubber may be four times higher for water than it is for VOCs, the preferential partitioning of VOCs at the membrane/liquid interface provides an overall enrichment of VOC on the permeate side of the membrane. Most organic compounds are concentrated in the permeate by orders of magnitude compared to the aqueous waste. The organics and some water which passes through the membrane are condensed. The condensed permeate often separates into an aqueous and an organic phase, offering industrial applications the possibility of recovering the organic fraction. A continuous pervaporation process is illustrated schematically in Figure 2.2.

**Table 2.1: Volatile Organic Compounds from the Federal Register
List of Priority Pollutants (April 17,1987)**

Contaminant	CAS#	Vapor Pressure @ 25°C [mm Hg]
Priority Group 1		
Chloroform	67663	208
Benzene	71432	95
Vinylchloride	75014	2660
Dichloromethane	75092	438
	79016	75
	106647	1
	127184	19
Priority Group 2		
Carbon tetrachloride	56235	113
Chloroethane	75003	1200
Bromodichloromethane	75274	59
Dichloroethylene (1,1)	75354	630
Dichloropropane (1,2)	78875	40
Trichloroethane (1,1,2)	79005	25
Tetrachloroethane (1,1,2,2)	79345	7
	107062	82
Toluene	108883	30
	542881	30
Priority Group 3		
Trichloroethane (1,1,)	71556	123
Chloromethane	74873	3830
Bromoform	75252	6
Dichloroethane(1,1)	75354	234
Ethyl benzene	100414	10
Acrolein	107028	244
Acrylonitrile	107131	114
Chlorobenzene	108907	12
Chlorodibromomethane	124481	18
Dichloroethene (trans)	158606	200
Priority Group 4		
Bromomethane	74839	1250
Carbon disulfide	75150	366
Trichlorofluoromethane	75694	796
Dichlorofluoromethane	75718	5000
Dichlorobenzene (1,2) (-p)	95501	2
Dioxane (1,4)	123011	37
Dichlorobenzene (1,3) (-m)	541731	2

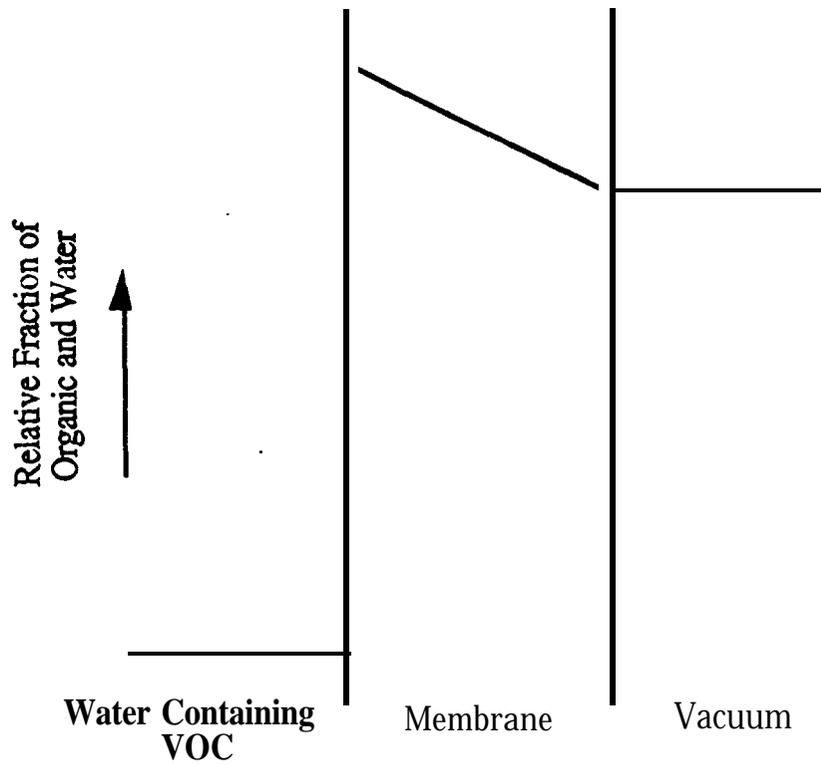


Figure 2.1 - Typical VOC Concentration Gradient from Membrane to Vacuum for Pervaporation Operation

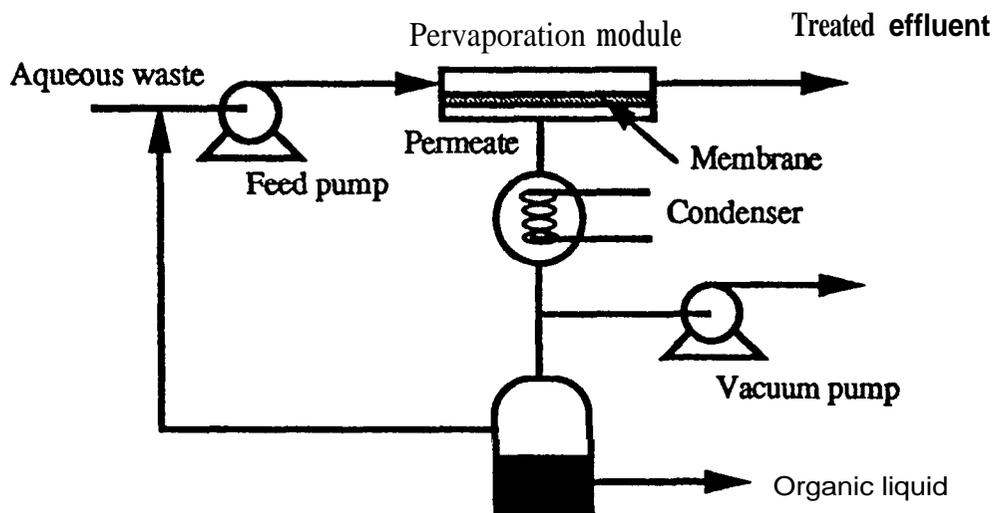


Figure 2.2 - Schematic of the Pervaporation Process

There are three companies that have developed pervaporation membrane modules for the removal of organic compounds from water : GFT (Germany) with a plate-and-frame module, GKSS (Germany) with a cassette type module, and Membrane Technology and Research (CA, USA) with a spiral-wound module. At this point, these membranes and modules are under evaluation in pilot- studies; no full scale application has been reported These systems are however not suitable for applications involving low concentrations of VOCs which are typical of contaminated groundwater due to poor economics and technical limitations (Lipski and Côté, 1990).

2.3 Activated Carbon and Air Stripping

Current VOC treatment methods generally utilize activated carbon adsorption and/or stripping to remove low concentrations of organic contaminants from water. These methods have been used as a basis for comparison to evaluate the potential of pervaporation for similar applications. Other technologies which can remove VOCs include biological treatment and liquid or gas phase oxidation (e.g. W-ozone). However, these technologies are not as widely used as carbon adsorption and stripping for VOC removal, therefore they have not been considered in detail in this report. The following driving forces exist for the replacement of activated carbon and stripping:

- 1) elimination of carbon disposal/regeneration costs;
- 2) elimination of air emissions from the stripping processes.

A brief comparison of these technologies vs. pervaporation is presented in the following **subsection**.

2.3.1 Activated Carbon

Activated carbon offers very high activation energies for most VOCs. Activation energy is defined as the amount of energy required to release the VOC from the active material. For most VOCs on carbon, this high activation energy requires heat (either direct fired or from steam) to release the VOCs and regenerate the carbon. On the other hand, pervaporation takes advantage of the lower activation energy offered by organophilic polymers compared to carbon by offering continuous release of the VOCs to vacuum. Because of its high activation energy, activated carbon can not be regenerated by vacuum

In activated carbon, organic compounds compete for adsorption sites and therefore the removal efficiency decreases as **these** sites become saturated Certain compounds, such as ethylene dichloride (EDC) and methylene chloride although adsorbed by activated carbon, are quite often "displaced by" other organic compounds which have higher activation energies for the activated

carbon, Unlike carbon adsorption, there is no competition between organic compounds in pervaporation. Compounds which diffuse through the polymer membrane are continuously removed on the vacuum side and can not be released back into the aqueous stream.

Carbon adsorption is cost-effective for low concentration applications but becomes expensive at higher concentrations because spent carbon must be disposed of or regenerated more frequently. In addition, the effectiveness of carbon declines each time it is regenerated, In pervaporation, since there is continuous release of the VOCs to the vacuum, the membrane never becomes saturated and therefore never needs to be regenerated. In pervaporation, the permeate, which is primarily organic liquid, must be disposed of as a hazardous waste if it cannot be reused in an industrial process stream. This volume is, however, much reduced compared to the initial wastewater allowing for more economical off-site transport to an approved hazardous waste incinerator for destruction. Likewise, as carbon is regenerated, organic liquids recovered from regeneration must be disposed of as a hazardous waste if not suitable for reuse. Finally, pervaporation does not consume reagents or exhaustible sorbents. As landfill costs increase for disposal of activated carbon (considered a hazardous waste), carbon will tend to be used only in applications where other technologies prove to be ineffective.

2.3.2 Air Stripping

Air stripping is limited to the removal of compounds that preferentially partition into air compared to water (i.e. high Henry's law constant). Furthermore, water containing dissolved solids often promotes fouling of stripping columns due to iron oxidation and/or carbonate precipitation, reducing process efficiency and resulting in increased maintenance costs. In pervaporation, fouling is minimized because air is not added to the water being treated

In addition to the above limitations, unless the off-gas is treated, air stripping merely turns a water pollution problem into an air pollution problem. A recent survey of 177 air stripping installations at remedial sites in the U.S. showed that only 17 had any off-gas treatment, and for most of these, data was not available on the efficiency of the process (Radian Corporation, 1987). It is anticipated that the U.S. Clean Air Act will make off-gas treatment compulsory, greatly increasing the complexity and cost of air stripping. The most popular method for off-gas treatment is carbon adsorption, which has the same limitations described above for water treatment. In contrast, for pervaporation, the organic compounds permeating through the membrane are contained by condensation, thus providing an opportunity for the recovered organic phase to be reused

2.4 Relative Costs of Technologies for VOC Removal

Typical treatment costs for air stripping and activated carbon were presented in a recent publication (Lipski and Côté, 1990). This case study considered a 167 litres/min. system which contained 10 ppm trichloroethylene (TCE) which was to be reduced by 99%. Air stripping alone would cost **\$0.10/m³**. The cost of combining air stripping with granular activated carbon (GAC) in various configurations, varied from **\$ 0.40/m³** for air stripping and vapour-phase GAC, to **\$ 0.80/m³** for liquid phase GAC alone. These costs include regeneration or disposal of activated carbon. By comparison, the cost of pervaporation would be in the order of **\$ 0.56/m³** using the membrane and module design developed in this project. This cost was estimated from energy requirements and amortization of assembly costs and component costs and indicates that pervaporation is cost competitive with existing technologies.

Compared to competing technologies, pervaporation features the following benefits :

- Process is completely enclosed thereby **minimizing** direct and fugitive emissions;
- suitable for concentrations ranging from ppb to **g/L**;
- no requirement for chemicals or adsorbents;
- systems are compact, modular and easily transportable;
- low operating costs;
- opportunity for recovering concentrated organics for recycle/reuse.

2.5 Previous Pervaporation Work for Removal of Volatile Organic Co-

There has been some prior work in the **removal** of VOCs from water by pervaporation. Examples of organic compounds which have been effectively separated from water using different membranes are presented in Table 2.2. The separation factor, α , which is a measure of the increase in the concentration of the VOC in the permeate relative to the feed concentration, varies significantly in the range 80 to 21,500. Use of mass transfer coefficients (MTCs) is a convenient means used to describe the relative effectiveness of different membranes in terms of rate of removal of VOCs from water.

Separation factors for all the systems are high and provide a measure of enrichment of the VOCs in the permeate over the feed. In fact, most of the systems show separation factors that are high enough to allow for collection of a super-saturated permeate which undergoes phase separation.

Table 2.2 Summary of Pervaporation Results for Organic Compound Removal from Water

Reference	Membrane	Thickness (μm)	Water Flux ($\text{g}/\text{m}^2/\text{h}$)	Compound Separation Factor (Δ)	Coeff.	
					(Δ)	($\mu\text{m}/\text{s}$)
Eustache & Histi, 1981	Plane polyester coated with silicone rubber (Rhone Poulenc TS605)	100	27	Benzene	11100	N/A
				chloroform	6800	N/A
				Dichloroethane	4300	N/A
				Vinyl chlorid.	9000	N/A
Brun, 1981	Butadiene styrene/acrylonitrile copolymer	195	1.7	chloroform	21500	10
Nguyen & Nobe, 1987	Silicone rubber fiber Dow Corning	165	13	chloroform	9400	34
				Bromomethane	7200	26
				Di chloromethane	4760	17
Pswne, 1984	Plane polysulfone coated with silicon rubber	0.8	530	Chloroform	200	29
				Trichloroethylene	80	12
					630	
	Plane polysulfone coated with silicon rubber	15	160	Chloroform	355	29
				Trichloroethylene		16
	Silicone rubber fiber Dow Corning	165	14	Trichloroethylene	5000	3-27*
Radnoff & Lipski, 1988	Polyethylene	50	40	1,2-Dichloroethane (4100 ppm)	320	3.6
			14	1,2-Dichloroethane (2500 ppm)	750	2.9

*Range obtained for Reynolds numbers varying from 2 to 200

Preferential permeability plays a minor role in the separation of most of the compounds from water by pervaporation. As illustrated in Figure 2.1, water may be preferentially permeable compared to the VOC, yet the membrane can demonstrate excellent separation towards the VOC. The differences in gas permeabilities of most VOCs range by no more than a factor of ten, with water being slightly more permeable, through silicone, than most VOCs. Other polymeric materials exist which have demonstrated higher permeabilities towards VOCs than water (Nijhuis, 1990).

Preferential partitioning from the water to the membrane surface plays the critical role in defining the effectiveness of pervaporation for the removal of a certain VOC from a particular water stream. Henry's Law constant is a useful parameter for estimating partitioning of a VOC from water. Octanol/water partition coefficients also offer good indication of partitioning from the water to the membrane surface. Henry's Law constants are however more readily available in the literature.

The preliminary work in pervaporation was sufficient to demonstrate that this technology is applicable to VOC removal from contaminated water. However, it soon became clear that the module design and consequently the liquid film resistance (LFR) represented the rate controlling mechanism (CM and Lipski, 1988) in this pervaporation application.

2.6 Importance of Liquid Film Resistance

Several groups, Yang and Cussler (1986) and **Lévêque** (1928), have demonstrated the importance of liquid film resistance (LFR) in heat and mass transfer applications. In pervaporation, **Côté** and Lipski (1988) and Nijhuis (1990) were able to show that, in most instances, removal of the VOCs from water is limited by LFR for mass transfer. It has been demonstrated that although chlorinated organic compounds have a very high affinity for silicone rubber compared to water, LFR is often rate controlling and reduces the rate at which organics may be removed from the water. In fact, Nijhuis demonstrated that separation would be increased by 3 or 4 times (for either toluene or trichloroethylene with 60 - 240 μm thick silicone rubber) if there was no LFR.

The relative magnitude of the LFR compared to the membrane resistance can however be reduced by using a thicker membrane to achieve the higher separation factor. The thicker membrane typically offers reduced water flux with no significant decrease in VOC removal. Improving hydrodynamic conditions (as described below) also increases the separation factor and has the added benefit of improved VOC removal. Since there is a practical ceiling to improvement of hydrodynamic conditions, it is apparent that membrane thickness should also be optimized for a given hydrodynamic condition in order to provide high VOC removal and good selectivity. In addition to improving the selectivity, using a thick membrane to reduce the water flux, without sacrificing organic removal, has operational advantages. Reducing water flux (quite often, the major permeate component) reduces vapour handling requirements and condensing duties (estimated to be one of the highest sources of energy consumption in typical pervaporation systems).

To overcome hydrodynamic limitations, Lipski and **Côté** (1990) were able to reduce liquid film resistance and significantly increase removal of the target compound by using a transverse flow module. Furthermore, improving hydrodynamic conditions, which reduced the liquid film resistance, improved the removal of the organic compound even with a thicker membrane which resulted in reduced water flux. Increasing the rate of VOC removal while significantly reducing the water flux has significant advantages due to reduced vapour handling requirements and operating costs. The impact of these effects on treatment cost was investigated in a sensitivity analysis. It was concluded that a system utilizing a transverse flow module design offered the most cost effective technique for VOC removal by pervaporation.

3 . 0 **PROJECT OBJECTIVES**

The principal objective of this project was to develop an improved pervaporation treatment process to remove volatile organic compounds from waste streams. Secondary objectives include:

- 1) Development of hollow fibre membranes with the active polymer coated on the outside.
- 2) Optimization of the membrane thickness and hydrodynamic conditions to maximize process efficiency.
- 3) Development of a transversal-flow prototype module with improved mass transfer characteristics.
- 4) Testing of the pilot-plant with several VOC contaminated wastewater solutions to determine the performance and provide scale-up data.
- 5) Carry out technical and economic analysis of the process compared to conventional VOC removal processes.

EQUIPMENT DEVELOPMENT

The three major tasks of the project involved development of the membrane, the module which houses the membrane and, the pervaporation system which enables the module to perform effectively are summarized in the following subsections:

The Membrane

The objective of membrane development work was to develop and test a hollow fibre with a pervaporation membrane on the outside surface of a supporting layer. This development work was aimed at defining a method for making a membrane on a fibre support to allow subsequent testing to be carried out with liquid flow transverse to the fibre axis.

A number of criteria were used to define the requirements of the membrane and its supporting layer. The membrane and support material had to be resistant to a wide variety of solvents that may be encountered in typical contaminated groundwaters. These materials also had to be suitable for testing at elevated temperatures up to **60°C**. The support fibre needed sufficient strength to allow pervaporation testing with high liquid velocities orthogonal to the fibre direction. Previous

work indicated that a thick (at least 30 μm) silicone membrane would be most suitable for pervaporation testing. Other polymeric membranes, such as polyethylene or polypropylene, etc., were also identified as being suitable for use as pervaporation membranes. Finally, the membrane material used to coat the fibres had to be suitable for potting in order to allow the fibres to be sealed in a water-tight module.

Several options were available to allow testing of pervaporation fibres with transverse liquid flow. Pure silicone fibres were considered since they were commercially available and used in previous work. Although these fibres are readily available as a source for pervaporation membranes, they are relatively expensive. Silicone fibres also require a support material to provide a means of handling and orienting the fibres into the desired configuration.

Celgard fibre, available from Hoeschst Celanese Corporation, was retained as the support material as it provided solvent resistance and was temperature stable to **70°C**. This was a microporous polypropylene fibre with a wall thickness of 30 μm . The microporous material had a benefit in this application as it allowed the membrane to anchor itself into the support. Silicone rubber was chosen as a membrane material since it is available in a two component base and catalyst which provided easy polymer fabrication without need for any complex polymer fabrication equipment. Potting is a critical step in the module manufacturing process since silicone rubber can not be potted with available epoxies, membrane coating after module construction was considered first. Coating was first attempted by pouring silicone over a potted module array of fibres, then allowing

the silicone to drain. The silicone material proved to be too viscous and did not allow sufficient drainage. Coating was then attempted on a potted module array, but this time by filling the micropores of the support material from the inside of the hollow fibre. Since the pores were relatively large and allowed passage of the silicone, the silicone was pushed (at 25 psig) through the pores to form a layer of silicone on the outside of the fibre. The bore of the fibre was then purged with gas to remove the silicone prior to cross-linking. The coating thickness on the outside of the fibre was controlled by adjusting coating time. Coating thickness on the inside of the fibre was controlled by adjusting purge time. This method proved effective for producing membranes from 30 μm thick (the thickness of the Celgard fibre wall) up to 150 μm thick. Membrane thickness was also controlled by addition of solvent (such as pentane) to reduce membrane thickness upon application.

4.2 The Module

The objective of this phase was to develop a transverse flow, hollow fibre, lab scale prototype module.

The module was required to contain capillary fibres (less than 1 mm diameter) which were suitable for transverse flow operation. The fibres had to be arranged in a pattern such that liquid flow outside the fibres is orthogonal to fibre direction, and channelling is minimized by the fibres which are pulled taut and spaced in an ordered, repeating matrix.

Several options provided means of satisfying these requirements. Weaving fibres to form a mesh of membrane fibres amongst guide fibres (made of non-membrane material) was considered as a method of orienting fibres to provide a form suitable for manipulation and subsequent potting. Direct fibre placement onto a grid network was also considered for module preparation. Weaving of fibres was contracted out to determine feasibility for fibre preparation as a part of module production. Arrays of woven fibres did not however possess well defined and repetitive spaces between fibres and would be prone to fouling and channelling of liquid flow.

Direct placement of hollow fibres onto grooved plastic strips was retained as the method of fibre preparation to provide an orderly fibre pattern. Fibres were **sandwiched between two grooved** plastic strips which were glued to secure fibre orientation as shown in Figure 4.1. Two sets of glued strips acted to form an element which could be physically handled and built up into a cartridge. Cartridges were built up into a module. Progression of construction is illustrated in Figures 4.2 through 4.4.

The modules used for testing purposes are described in the following table. The fibre length of 5 cm was the same for all testing applications (Table 4.1).

Table 4.1: Description of Modules and Fibres Used for Testing and Determining Hydrodynamic Conditions Applicable for a Transverse Flow

Module	Use	Characteristics
1	Heaclloss analysis	4800 fibres 460 μm OD 30 μm wall
2	Pervaporation testing to investigate feed velocity effect	890 fibres 540 μm OD 125 μm wall
3	Pervaporation testing to investigate the effect of temperature, permeate pressure and organic type	672 fibres 540 μm OD 125 μm wall
4	Pilot testing to verify effect of operating parameters on pervaporation performance	5760 fibres 540 μm OD 125 μm wall

4.3 The System

A pervaporation system was required to evaluate these new modules and to quantify the effects of certain operating parameters. This system required means of controlling feed flow rate, feed temperature and vacuum pressure in order to test all operating parameters typical of pervaporation operation.

Several options existed to provide methods for evaluating module performance. Two existing systems were available to Zenon for testing module performance. The specifications of the two existing systems are provided in Table 4.2. One system was a bench unit constructed by Zeton Technologies Corporation for the Wastewater Technology Centre and the second system was a pilot unit constructed by Zenon Environmental Inc. for the River Road Environmental Emergencies Division of Environment Canada.

Since the bench unit provided better automation and control of system variables, it was used for pervaporation testing. The unit was retrofitted to allow quantifying module performance with the transverse flow module and for determining the effect of certain process parameters on overall pervaporation performance. However, the pilot unit was also retrofitted to permit testing of a full-scale module under typical pervaporation conditions that would be expected in field operation.

The bench pervaporation system was used to establish optimum hydrodynamics conditions for pervaporation. A detailed description of the pervaporation system is provided in the Quality Assurance Project Plan (QAPP) accepted by EPA (Appendix A) and will not be described further in this report. One correction to the QAPP, however, must be noted. The system volume as measured by the addition of a tritium spike solution and measurement of the subsequent dilution factor indicated that the system volume was in fact 10.3 L and not 6.0 L as stated in the QAPP. Measurement of several tritium concentrations also indicated that complete mixing was achieved within one minute. A schematic of the pervaporation bench scale system is provided in Figure 4.5.

A schematic of the pilot system is provided in Figure 4.6. This system was used to verify scale up parameters. The membrane area for pilot operation is 100 times greater than the area used for the bench testing work.

QUALIFICATION TESTING

The purpose of this section is to report the testing results for the transverse flow module and to assess its potential for the removal of VOCs from water.

Feed Pressure Loss

For estimating pressure drop through a bank of fibres, correlations for transverse flow are available from the Engineering Sciences Data Unit (ESDU) series (1974). The pressure drop can be estimated by

$$AP = 0.5KN_1V_{\max}^2$$

where N_1 is the number of rows in a module, V_{\max} is the velocity of the Liquid at greatest constriction between the fibres and K is the friction factor coefficient and can be estimated from

$$K = a (\log(\text{Re}))^2 + b (\log(\text{Re})) + c$$

where Re is the Reynolds number calculated using the outside fibre diameter, and the coefficients a, b and c are dependent on the spacing between fibres and the spacing between rows. For the current module design, the spacing (centre-to-centre fibre diameters) between fibres is 2.17 and K may be estimated from the Table 5.1 by linear interpolation for each velocity. This estimate of K is applicable for the range of Reynolds numbers from 10 to 1000.

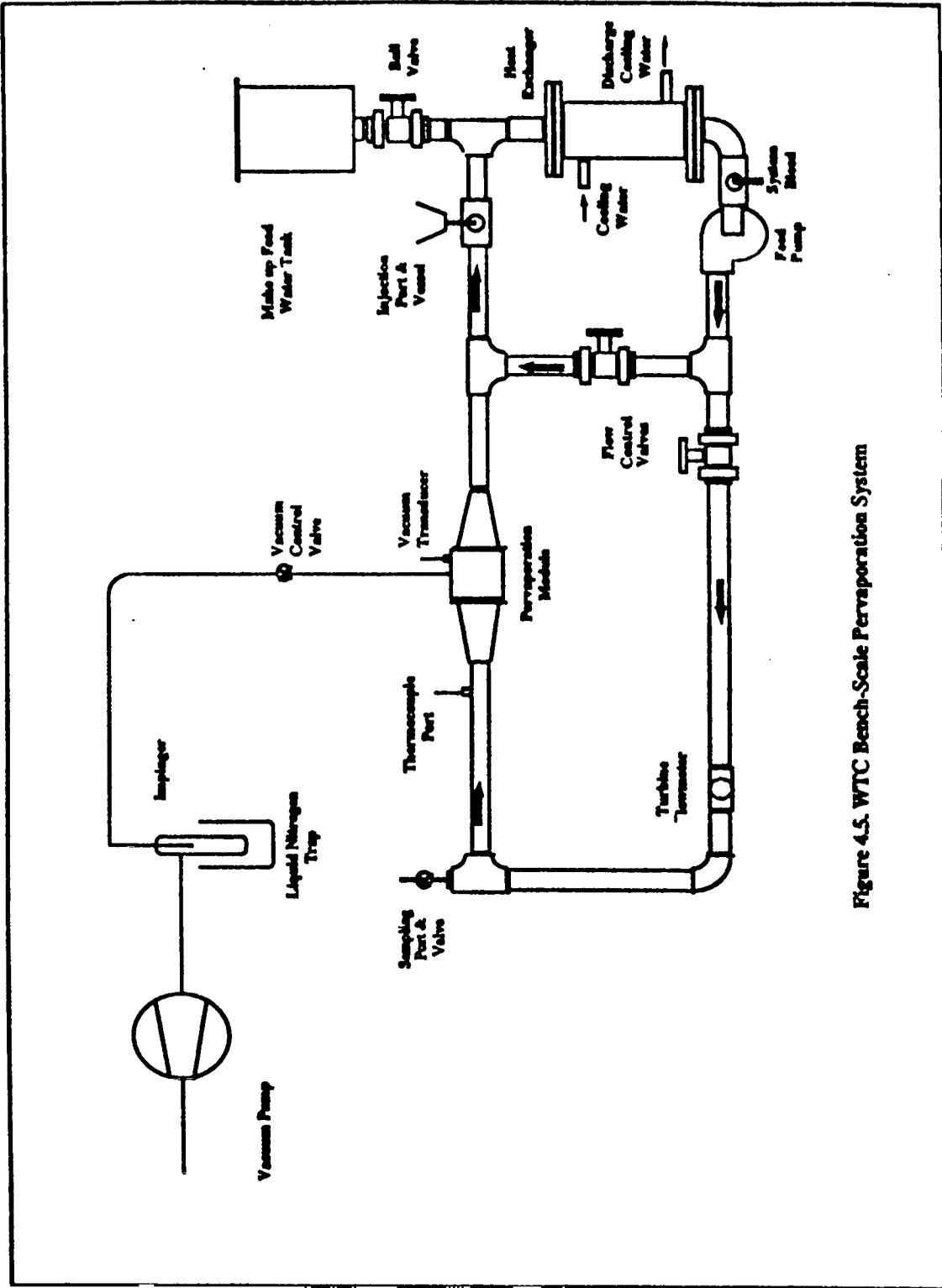
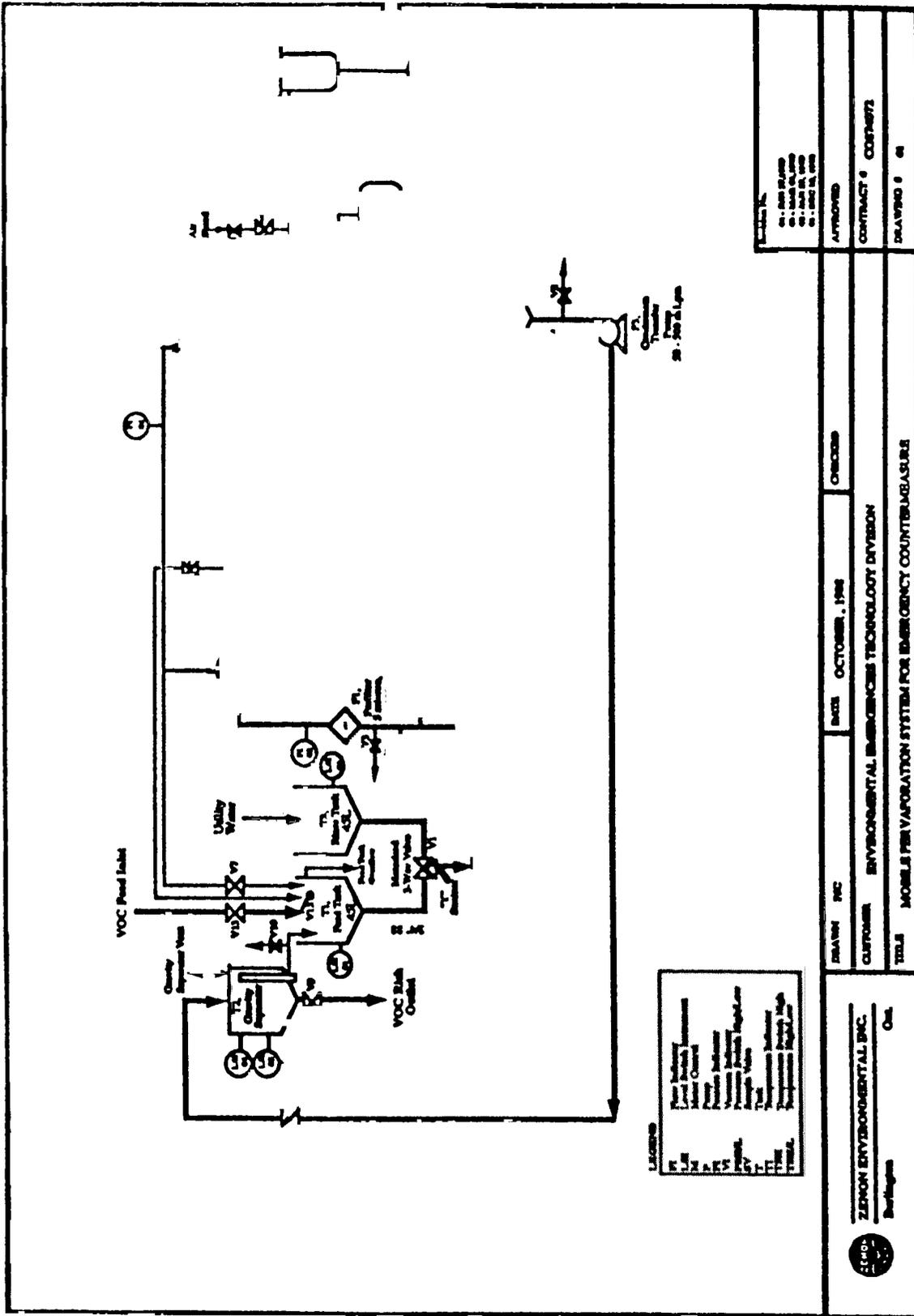


Figure 4.5. WTC Bench-Scale Pervaporation System



APPROVED CONTRACT # C0374873 DRAWING # 48

DRAWN BY: MC DATE: OCTOBER, 1988 CHECKED:

CUSTOMER: ENVIRONMENTAL EMERGENCIES TECHNOLOGY DIVISION TITLE: MOBILE PERVAPORATION SYSTEM FOR EMERGENCY COUNTERMEASURES

ZENON ENVIRONMENTAL, INC. Berthelton, Ont.

LEGEND 1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.

Figure 4.6 Pervaporation Pilot System

Liquid pressure drop tests were conducted with modules that contained approximately 4800 fibres. An air/water manometer was used to measure pressure drop. A flow meter was used to monitor the flow of water through the module.

The pressure drop for water flowing orthogonal through the array of fibres is shown in Figure 5.1. Tests were conducted at 20.7 °C. Results compare very well with the model (ESDU data) in Figure 5.1 for such a configuration.

Table 5.1: Coefficients for Estimation of Pressure Drop in Transverse Flow of Water Across a Bank of Fibres

Fibre Spacing (diameters c/c)	a	b	c
2	0	-0.213	0.348
3	0	-0.161	0.013

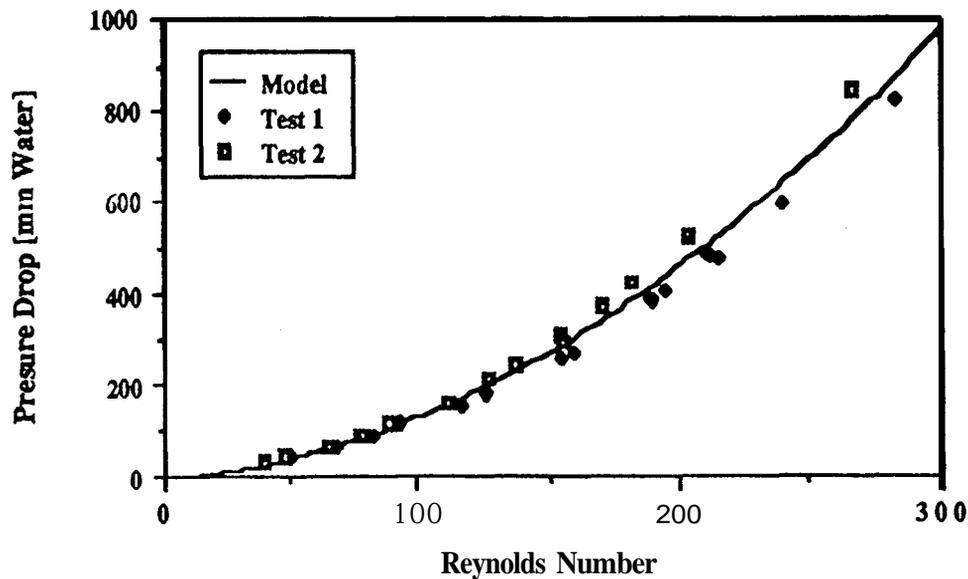


Figure 5.1 - Pressure Drop Through Array of 4800 Fibres

5.2 Pervaporation Results (Bench Scale)

5.2.1 Pervaporation Results

The results of the pervaporation tests are summarized in this section. All data included in this section are used in a manner which satisfies the guidelines **summarized** in the QAPP regarding data **acceptance** including whether data are used for verification or calculation purposes. In this Section, the data represented in the figures is used for quantification only if the symbols or bars are solid. Open symbols or bars indicate that data was only used for verification purposes.

The following major system variables were tested in the experimental program:

- Feed flow velocity
- operating temperature
- Permeate** side vacuum pressure
- Type of organic compound

All run conditions and results are **summarized** in Table 5.2. Runs **1,2** and 3 were conducted with module 2. Subsequent use of module 2 was under conditions which damaged the fibres. A different module (Module 3) **was used** for all other runs. The characteristics of Modules **2 and 3** are given in Section 4.

Table 5.2: Pervaporation Test Results for Bench Scale Program.

Run #	YOC	Date	Run Time [hour]	Vacuum [Pa]	Feed Flowrate [L/min]	Permeate Flowrate [USGPM]	Feed Temp [°C]	Permeate Conc. [g/L]	Water Flux [L/m ² ·hr]	Re Bo Flux [L/m ² ·hr]	VOC Flux [L/m ² ·hr]	Separation Factor	MTC [m/s]	S.R.
1	Toluene	Nov 26/90	0.47	129	6.49	1.72	24.94	0.0033	0.0112	42	0.0003	20802	6.49E-05	90%
2	Toluene	Nov 26/90	0.53	160	25.85	6.83	24.75	0.0059	0.0116	246	0.0008	31310	9.69E-05	115%
3	Toluene	Nov 29/90	0.47	151	50.33	13.35	24.72	0.0099	0.0097	490	0.0019	41158	1.11E-04	115%
4	Toluene	Feb 1/91	0.50	115	5.41	1.43	25.01	0.0051	0.0031	44	0.0008	31251	5.22E-05	108%
5	Toluene	Feb 1/91	1.05	2195	5.33	1.46	25.22	0.0087	0.0035	45	0.0003	14041	1.32E-05	69%
6	Toluene	Feb 5/91	0.57	156	6.25	1.65	25.04	0.0080	0.0090	51	0.0008	20404	5.15E-05	91%
7	Toluene	Feb 5/91	1.27	1936	6.06	1.80	25.06	0.0083	0.0040	49	0.0002	11883	1.27E-05	71%
8	Toluene	Feb 6/91						0.0046	0.0046					
9	Toluene	Feb 7/91	1.10	1818	5.77	1.52	25.30	0.0088	0.0046	47	0.0003	11132	1.28E-05	79%
10	Toluene	Feb 7/91	0.80	548	6.22	1.64	24.86	0.0081	0.0046	50	0.0008	17618	3.56E-05	97%
11	Toluene	Feb 7/91	1.57	1130	6.39	1.66	24.64	0.0096	0.0041	51	0.0006	17118	2.58E-05	109%
12	Toluene	Feb 12/91	0.57	135	6.32	1.67	24.88	0.0099	0.0032	51	0.0009	23119	5.46E-05	99%
13	Toluene	Feb 12/91	1.17	643	6.25	1.65	25.02	0.0085	0.0031	51	0.0006	19522	3.03E-05	112%
14	None	Feb 13/91	0.82	138	5.43	1.43	24.65	0.0083	0.0033	44				
15	None	Feb 13/91	1.65	157	5.60	1.48	25.01	0.0083	0.0033	45				
16	EDC	Feb 14/91	0.98	141	5.75	1.52	24.78	0.0086	0.0032	46	0.0001	5546	1.27E-05	69%
17	EDC	Feb 14/91	1.57	137	5.72	1.51	24.99	0.0081	0.0019	46	0.0001	6169	1.42E-05	92%
18	None	Feb 19/91	1.28	508	6.36	1.68	25.08	0.0095	0.0075	52				
19	None	Feb 19/91	0.88	2105	6.09	1.61	24.82	0.0093	0.0035	49				
20	TCB	Feb 20/91	0.72	154	6.17	1.63	24.86	0.0094	0.0015	50	0.0004	22664	5.31E-05	94%
21	TCB	Feb 20/91	1.15	153	6.09	1.61	25.04	0.0093	0.0016	49	0.0005	20302	4.66E-05	93%
22	None	Feb 27/91	1.45	155	6.87	1.82	25.14	0.0094	0.0074	54				
23	None	Feb 28/91	0.67	135	6.58	1.74	17.79	0.0056	0.0056	46				
24	None	Feb 28/91	0.92	880	6.66	1.76	17.89	0.0032	0.0032	46				
25	None	Feb 28/91	0.57	155	6.74	1.78	20.29	0.0106	0.0106	61				
26	None	Feb 28/91	0.55	1009	6.74	1.78	20.33	0.0083	0.0083	61				
27	Toluene	Mar 5/91	0.55	182	7.06	1.86	33.39	0.0049	0.0028	68	0.0008	16102	6.19E-05	118%
28	Toluene	Mar 5/91	0.63	1237	6.85	1.81	33.54	0.0045	0.0041	66	0.0008	14985	4.62E-05	108%
29	Toluene	Mar 5/91	0.65	1036	6.85	1.83	33.08	0.0046	0.0031	67	0.0005	19907	3.11E-05	54%
30	TCB	Mar 12/91	0.52	181	6.70	1.77	31.08	0.0031	0.0016	62	0.0008	13807	4.19E-05	63%
31	TCB	Mar 12/91	0.63	2867	6.42	1.70	31.13	0.0034	0.0022	59	0.0002	14311	2.46E-05	70%
32	TCB	Mar 12/91	0.72	1125	6.42	1.70	31.00	0.0038	0.0038	59	0.0003	15446	2.96E-05	83%
33	TCB	Mar 18/91	0.38	198	5.98	1.58	33.46	0.0067	0.0141	60	0.0008	12547	4.85E-05	69%
34	TCB	Mar 18/91	0.63	2326	5.94	1.57	33.54	0.0094	0.0081	60	0.0009	14049	3.54E-05	83%
35	TCB	Mar 18/91	0.75	1241	5.90	1.56	33.63	0.0101	0.0102	60	0.0011	14073	4.81E-05	97%
36	TCB	Mar 20/91	0.57	192	5.90	1.56	34.39	0.0078	0.0043	58	0.0008	17722	4.82E-05	94%
37	TCB	Mar 20/91	0.65	1372	5.89	1.56	35.25	0.0095	0.0115	59	0.0012	14806	4.78E-05	100%
38	TCB	Mar 20/91	0.88	2306	5.68	1.50	35.21	0.0105	0.0088	57	0.0009	12735	3.13E-05	80%
39	TCB	Mar 26/91	0.62	2289	5.87	1.55	35.19	0.0014	0.0089	59	0.0001	13409	3.58E-05	80%
40	EDC	July 4/91	0.62	149	4.99	1.52	35.30	0.0028	0.0296	50	0.0001	2133	1.71E-05	64%

* Same or all samples maintained for analysis.
 -- Units: L/m² · hr; kg/m² · hr

Results are best expressed as a separation factor and overall mass transfer coefficient. The separation factor, α , is a measure of the effectiveness of separation and is estimated by

$$\alpha = \frac{(Y_{\text{VOC}}/Y_{\text{water}})}{(X_{\text{VOC}}/X_{\text{water}})}$$

where Y is the concentration of the the indicated component in the permeate and X is the concentration of the component in the liquid feed. Since α is dimensionless, X and Y may be any convenient but consistent concentration unit. Although the separation factor is a convenient way of communicating effectiveness of separation, it provides no useful information required to design a pervaporation system

The MTC (or k , with units of m/s) is calculated by

$$k = J / C$$

which defines the VOC removal rate and provides a method for calculating membrane area for a pervaporation system J (expressed as $\text{kg/m}^2\text{s}$) is the VOC flux and C (expressed as kg/m^3) is the concentration of the VOC in the water. The MTC allows flux data to be compared independently of feed concentration.

The measured separation factor ranged from 2135 for EDC to a maximum of 41,000 for toluene. This corresponds to mass transfer coefficient ranging from 1.71×10^{-5} to 11.1×10^{-5} m/s. The significance of these results is given in the following section, grouped by important process parameters.

The results of the pervaporation testing are included in Table 5.2. The reduced analytical and system data is shown in Table 5.3. Data is included for both the module tested at increased Reynolds Numbers as well as the module which was tested at other adjusted operating conditions. Also included in these tables is the data for the pure water runs as it provides insight into system operation. Runs marked with an asterisk (*) signify that some or all of the samples had to be resubmitted for analysis due to lack of precision, In most cases this lack of precision was a direct result of several aliquots measured as not ‘useful’ (as defined in the QAPP), which reduced the sample space and therefore increased the variance beyond the precision requirements specified in the QAPP.

5.2.2 Quality Assurance

This section documents the results of the Quality Assurance (QA) program required to validate the findings of this study.

Table 5.3: Reduced Analytical and System Data for Petvaporation Testing.

Run #	Module Pressure (torr)	SD_MP	RSD_MP	Feed Temp. (°C)	SD_FT	RSD_FT	Feed Flowrate (USGPM)	SD_Alc	SD_MJ	Feed Conc. (µg/L)	SD_F	Retentate Conc. (µg/L)	SD_R	Permeate Conc. (µg/L)	SD_P
1	0.97	0.11	11.3%	24.9	0.11	0.4%	1.72	0.029	0.004	0.0033	0.010	0.0016	0.013	0.43	0.029
2	1.20	0.06	5.0%	24.8	0.06	0.2%	6.83	0.027	0.007	0.0039	0.007	0.0016	0.013	1.15	0.027
3	1.14	0.08	7.0%	24.7	0.09	0.4%	13.4	0.029	0.004	0.0039	0.006	0.0015	99.000	1.18	0.029
4	0.86	0.05	1.9%	25.0	0.14	0.6%	1.43	0.046	0.007	0.0051	0.035	0.0031	0.033	0.89	0.022
5	16.47	0.47	2.6%	25.2	0.04	0.2%	1.46	0.046	0.007	0.0067	0.014	0.0043	0.104	0.63	0.110
6	1.17	0.15	5.0%	25.0	0.31	1.2%	1.65	0.015	0.009	0.0060	0.005	0.0031	0.013	1.08	0.007
7	14.54	0.66	4.1%	25.1	0.10	0.4%	1.80	0.015	0.003	0.0063	0.008	0.0040	0.005	0.69	0.005
8*								0.051	0.006	0.0068	0.000	0.0046	0.011		99.000
8	13.65	0.27	1.7%	25.3	0.26	1.0%	1.52	0.167	0.003	0.0068		0.0046		0.67	0.005
9*								0.038	0.003	0.0081	0.107	0.0046	0.004	1.36	99.000
9	4.11	0.08	1.4%	24.9	0.08	0.3%	1.64	0.167	0.003	0.0081		0.0046		1.41	0.004
10*								0.038	0.003	0.0093	99.000	0.0041	0.013	0.91	0.300
10	8.49	0.20	2.0%	24.6	0.45	1.8%	1.66	0.167	0.006	0.0084	0.011	0.0041		2.06	0.006
11	1.01	0.05	2.0%	24.9	0.07	0.3%	1.67	0.013	0.005	0.0059	0.015	0.0032	0.025	1.16	0.004
12*								0.013	0.005	0.0062	99.000	0.0031	0.006	1.64	0.039
12	4.83	0.11	1.8%	25.0	0.16	0.7%	1.65	0.014	0.006	0.0065	0.020	0.0031		1.64	
13	1.19	0.06	2.4%	24.7	0.10	0.4%	1.43								
14	1.17	0.05	2.1%	25.0	0.32	1.3%	1.48								
15	1.06	0.09	1.9%	24.8	0.19	0.8%	1.52	0.091	0.019	0.0036	0.005	0.0025	0.026	0.32	0.078
16	1.08	0.07	2.7%	25.0	0.22	0.9%	1.51	0.088	0.018	0.0031	0.017	0.0019	0.026	0.47	0.044
17	4.04	0.09	1.6%	25.1	0.53	2.1%	1.68								
18	15.80	0.58	3.4%	24.9	0.22	0.9%	1.61								
19	1.16	0.05	1.8%	24.9	0.15	0.6%	1.63	0.075	0.049	0.0034	0.026	0.0015	0.014	0.75	0.009
20	1.15	0.07	2.8%	25.0	0.23	0.9%	1.61	0.075	0.049	0.0032	0.011	0.0016	0.014	1.40	0.039
21	1.16	0.07	2.8%	25.1	0.13	0.6%	1.82								
22	1.02	0.02	0.7%	17.8	0.19	1.1%	1.74								
23	6.68	0.08	1.0%	17.5	0.02	0.1%	1.76								
24	1.16	0.02	0.9%	30.3	0.19	0.6%	1.78								
25	13.74	0.17	1.1%	30.3	0.18	0.4%	1.78								
26	1.36	0.05	1.7%	33.4	0.05	0.2%	1.86	0.074	0.004	0.0049	0.011	0.0028	0.010	1.09	0.004
27	9.21	0.16	1.5%	33.5	0.11	0.3%	1.81	0.074	0.004	0.0065	0.008	0.0041	0.009	1.14	0.003
28	13.78	0.12	0.8%	33.1	0.16	0.5%	1.83	0.065	0.008	0.0066	0.034	0.0031	0.007	0.81	0.007
29	1.36	0.03	0.9%	31.1	0.20	0.6%	1.77	0.048	0.004	0.0031	0.042	0.0016	0.012	0.42	0.007
30	15.52	0.20	1.2%	31.1	0.11	0.3%	1.70	0.048	0.004	0.0034	0.006	0.0022	0.004	0.38	0.006
31*								0.048	0.004	0.0038	0.001		99.000	0.55	0.002
31	8.45	0.12	1.2%	31.0	0.08	0.2%	1.70	0.048	0.004	0.0038		0.0023	0.024	0.55	
32	1.49	0.04	1.4%	35.5	0.43	1.2%	1.58	0.025	0.007	0.0067	0.005	0.0029	0.082	1.11	0.014
33	17.46	0.23	1.2%	35.3	0.05	0.1%	1.57	0.025	0.007	0.0094	0.018	0.0058	0.010	1.32	0.006
34	9.32	0.12	1.1%	35.6	0.12	0.3%	1.56	0.025	0.007	0.0101	0.016	0.0055	0.023	1.85	0.010
35	1.44	0.04	1.6%	34.3	0.27	0.8%	1.56	0.023	0.018	0.0078	0.021	0.0042	0.037	1.36	0.070
36	10.30	0.12	1.0%	35.2	0.04	0.1%	1.56	0.023	0.018	0.0095	0.011	0.0052	0.022	1.89	0.006
37*								0.023	0.018	0.0095	99.000	0.0050	99.000	1.80	0.075
37	17.40	0.75	4.0%	35.2	0.25	0.7%	1.50	0.023	0.005	0.0105	0.002	0.0053	0.056	1.80	0.075
38	16.58	0.42	2.4%	35.2	0.30	0.9%	1.55	0.023	0.005	0.0014	0.027	0.0008	0.008	0.19	0.009
39	1.05	0.80		35.3	0.42	1.2%	1.32	0.009	0.009	0.0028	0.044	0.0020	0.023	0.25	0.031

Legend
SD Standard Deviation
RSD Relative SD
MP Module Pressure
FT Feed Temperature
Alc log(Area Count of Fluorobenzene in Aliquot)
F Feed Concentration
R Retentate Concentration
P Permeate Concentration
* Some or all samples reanalyzed for analysis

The results of the QA objectives for precision and completeness are shown in Table 5.4. Completeness of test runs (approximately 85%) was lower than expected (90% expected) and represents the fraction of the number of acceptable test runs divided by the total number of runs. For a test run to be acceptable, the criteria outlined in the QAPP had to be satisfied. The two criteria set in Table 2.1 of the QAPP included 1) Precision and 2) Accuracy. The precision results for each test are included for each test in Table 5.3. Accuracy results were obtained by estimating closure in mass balance and by submitting lab prepared standards in unmarked bottles along with samples in order to get an unbiased estimate of the recovery error. 80% of the test runs closed the mass balance to within the precision guidelines of the QAPP. A sample calculation for percent recovery is shown in Appendix B. The recovery error for the program is reported in Table 5.4. Both an average absolute and an average actual recovery error are provided to illustrate maximum deviation. As the number of standards submitted (21 in total) for analysis increased, the average actual recovery error tended towards zero and was not a good indication of equipment fluctuation from test to test. Since the average actual recovery error does tend toward zero, it is an indication that in the long term, the equipment and procedures were within the precision requirements set in the QAPP.

For the samples analyzed, 91% were within the precision requirements set out in the QAPP for the standard deviation on aliquots submitted. Of all aliquots submitted, 82% of the samples had internal calibration standards within the guidelines set out in the QAPP.

The overall number of tests was increased from 24 (estimated in the QAPP) to 39 in order to compensate for the lower number of acceptable test runs as well as to provide some additional water runs. Precision data was not available for feed flow-rate due to limitations in a transducer used to convert a frequency signal to a variable current signal for the data acquisition system. This problem was only encountered at flow rates less than 11 L/min. (3 gpm). A totalizer on the flowmeter was however tested for precision in the range used for the low Reynolds Numbers pervaporation testing. The precision of the flowmeter was measured at 3.6% to 4.9% relative standard deviation for flows less than 11 L/min. using calibration runs independent of the pervaporation testing.

The QAPP was useful in identifying one problem area (correct estimation of system volume) in the pervaporation test program. Use of system volume holdup, as determined by simple drainage of the system, resulted in the inability to close a mass balance in the recovery of VOC's in the pervaporation testing. Action was taken to determine the actual system volume holdup. To better estimate system volume, a spike solution containing a measured quantity of tritium was added to the system and the volume was estimated by the extent of tritium dilution in the final system volume. Use of this system volume to estimate %R showed results that were within the objectives of the QAPP.

No recalibration of analytical or system instrumentation was required throughout the sampling program or the pervaporation testing. Daily analytical calibration checks were always within the precision requirements set at the beginning of this test program. No test was rejected due to poor precision or control of the operating parameters.

Table 5.4: Quality Assurance Precision and Completeness Results

Completeness	
Overall Number of Tests	85%
Samples Analyzed	91%
'Useful' Aliquots	82%
Percent Recovery for Mass Balance	80%
Recovery Error (avg. abs.)	0.026
Recovery Error (avg.)	0.003

Effect of Major Variables

Major process variables including feed flow velocity, operating temperature, vacuum pressure and the type of compound are discussed in this section. These results were obtained using the bench scale pervaporation system

Effect of Reynolds Number

The effect of Reynolds number on **the VOC removal rate (expressed as a mass transfer coefficient)** is illustrated in Figure 5.2. These results compare very well with the resistance in series model (also shown in Figure 5.2) which was reported in earlier work (Lipski and Côté, 1990). These results indicate that the models used for predicting mass transfer in transverse flow are in fact applicable to closely packed fibres. The curve is characterized by a quick rise in mass transfer followed by levelling off with increase in Reynolds number. The quick rise in mass transfer is a direct result of the effectiveness of module design which promotes excellent removal of VOC's from water even at low Reynolds numbers. Levelling off of the overall mass transfer coefficient occurs because the membrane resistance becomes significant compared to the LFR at the higher Reynolds numbers. To further increase VOC removal, at higher Reynolds numbers, membrane thickness should be reduced or organic compound volatility increased (discussed further in this section).

Replicate testing of **the high Reynolds Number pervaporation testing was not possible because the module was damaged at high velocity. The data were, however, adequate to confirm the models for widely spaced hollow fibres, and were useful in predicting VOC removal performance for closely spaced hollow fibres.**

5.3.2 Effect Feed Temperature

The VOC permeability is one membrane factor affecting the separation (and hence removal) of organics from water.

Increasing the feed temperature, increased the water flux through the silicone rubber membrane as shown in Figure 5.3. Water flux data was obtained for both runs with pure water on the feed side and water that contained VOCs. There was no measurable difference in these water fluxes. The linear relationship of the water flux as a function of the inverse absolute temperature, is typically found in pervaporation (as well as other physical systems which exhibit an Arrhenius-type relationship), and is a measure of the membrane/liquid interaction. These water fluxes were estimated both with and without organic contaminants, and showed no measurable difference in the water flux. From this linear relationship, it is possible to predict water fluxes at higher operating temperatures. The slope and intercept of this line were determined **by linear regression**.

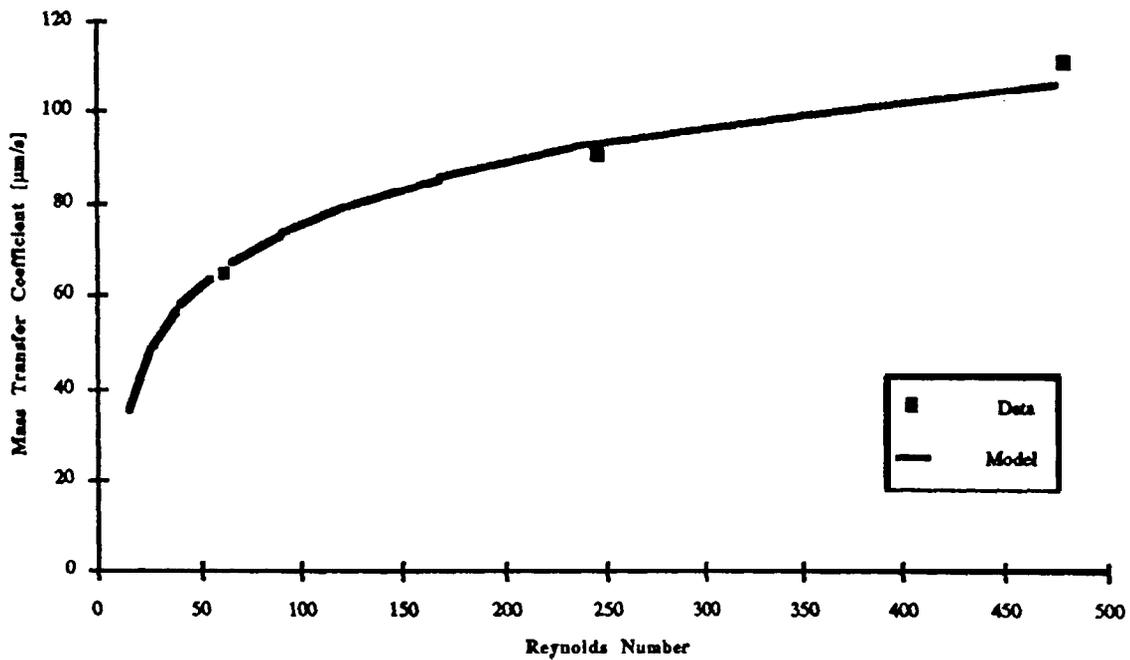


Figure 5.2 - Enhanced VOC Removal Promoted by Increase in Reynolds Number

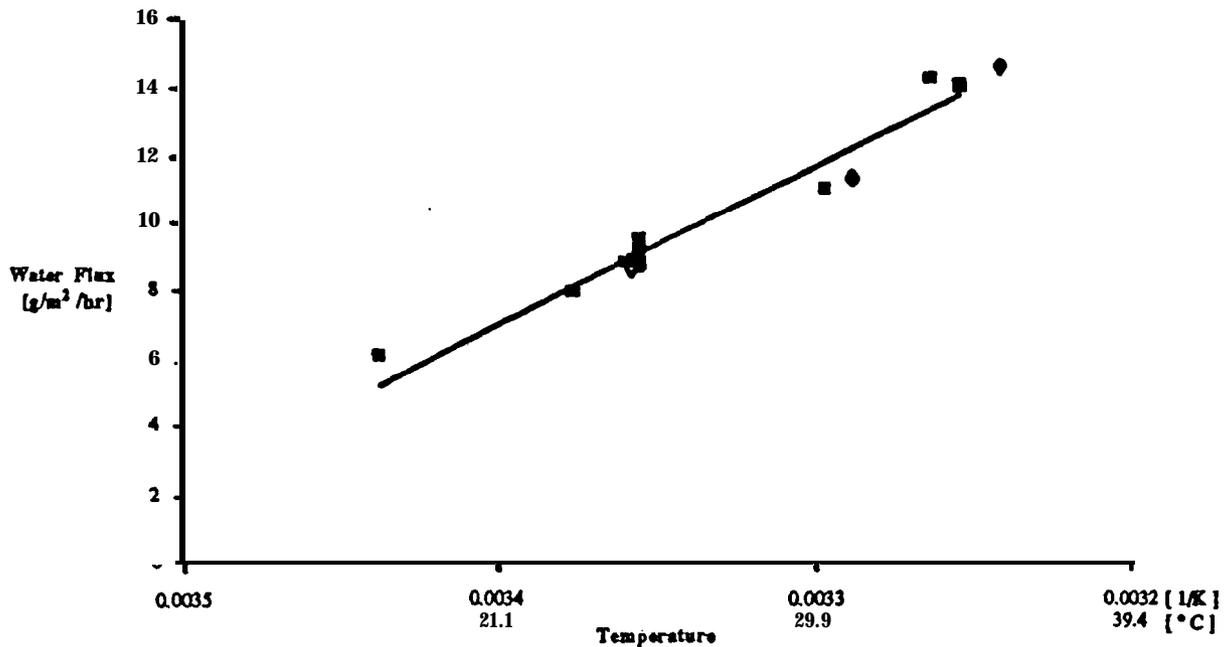


Figure 5.3 - Water Permeability Increased by Increasing Operating Temperature

This Arrhenius-type relationship for water flux was used in predicting operating performance in Section 6.2.

The Arrhenius relationship is also applicable for the VOC/membrane interactions. As the temperature increases, the VOC permeability through the membrane increases, just as for water. This increases the potential of the membrane to remove VOCs from water. Increased permeability could not however be shown experimentally at the low Reynolds Numbers due to liquid film resistance (LFR) that controls the rate of VOC removal. To illustrate, Figure 5.4 shows that the removal of VOC at 25°C and 35°C are not significantly different at low Reynolds number for either TCE or toluene, due to LFR. Toluene removal increased from approximately 50 $\mu\text{m/s}$ to 60 $\mu\text{m/s}$ while it dropped for TCE from 50 $\mu\text{m/s}$ to 48 $\mu\text{m/s}$. These differences are not outside the limits of the precision of the study and do not represent any significant change in the rate of VOC removal. Although demonstration of higher permeabilities at higher temperatures, should be expected at higher Reynolds Numbers, poor fibre stability at higher temperature and Reynolds numbers did not allow testing under these conditions.

Higher operating temperatures have an adverse affect on the separation factor for systems that are liquid film controlled. Increases in temperature cause increased water permeability with no increase in removal of VOCs. The increased water fraction in the permeate actually dilutes the

permeate, resulting in a net decrease in the separation factor as illustrated in Figure 5.5. For VOCs such as EDC that are not liquid film controlled, increasing feed temperatures also reduces the separation factor, but not to the same extent as VOCs that are LFR controlled.

In summary, it may be generalized that operation at higher temperatures in a pervaporation system that is liquid film controlled does not increase the removal of the VOC for high vacuum operation. It is therefore necessary to adjust other conditions such as increasing Reynolds number or increasing the membrane thickness in order to regain the high separation factors while at the same time derive the benefits from operation at higher temperatures (see Section 4.25).

5.3.3 Effect of Different VOCs

As indicated earlier, the removal of VOCs through a membrane is dependent on the preferential partitioning of the VOCs out of the water and in this case onto the membrane surface. Some organic compounds are more volatile and partition more readily than other compounds. Differences in Henry's Law constant rather than permeability of VOCs through the membrane itself (see Section 24) are better used to describe the effectiveness of removal. As such, it was important to quantify the rate of removal as a function of volatility. Three compounds tested are provided in Table 5.5 (Montgomery and Welkom, 1990). TCE doubles in volatility from **25°C** to **37°C** and at **25°C**, TCE is approximately 30% more volatile than toluene. TCE is 10 times more volatile than EDC at **25°C**. The results in Figure 5.4 indicate that the overall mass transfer coefficients (at high vacuum) for TCE (at 25°C and **35°C**) and toluene are indistinguishable. In addition, TCE and toluene removal is only three to four times higher than the removal rate for EDC, although EDC is only one-tenth as volatile as TCE. This is in agreement with the resistance-in-series model which generalizes that for very volatile compounds, the liquid film boundary layer becomes rate controlling and that rate of removal is independent of the membrane and VOC properties. On the other hand, the less volatile EDC is not partitioned readily to the membrane surface and, therefore, LFR does not play a critical role in defining VOC removal. Hence, removal of EDC from water was increased by increasing temperature from **25°C** to **35°C** as shown in Figure 5.4. Testing at temperatures above 35°C with the transverse flow module was not possible with the current support fibre without collapsing the fibre.

Just as increases in the permeability (illustrated in Section 4.2.2) had no effect on organic removal, enhanced partitioning at the higher temperatures does not aid in removal of the VOC in a system that is liquid film controlled. For TCE and toluene, removal of the VOC from the bulk liquid is governed by module hydrodynamics. Even if Henry's Law Constant for TCE is doubled, by

increasing the feed temperature to 35°C (from 25°C) the TCE removal is not measurably changed because removal is limited by LFR.

Table 5.5: Organic Compounds Considered for Removal by Pervaporation at Various Operating Temperatures

Compound	Temperature [°C]	Henry's Law Constant [atm·m ³ /mol]
Toluene	25	0.0067
TCE	25	0.0091
	37	0.0196
EDC	25	0.00091

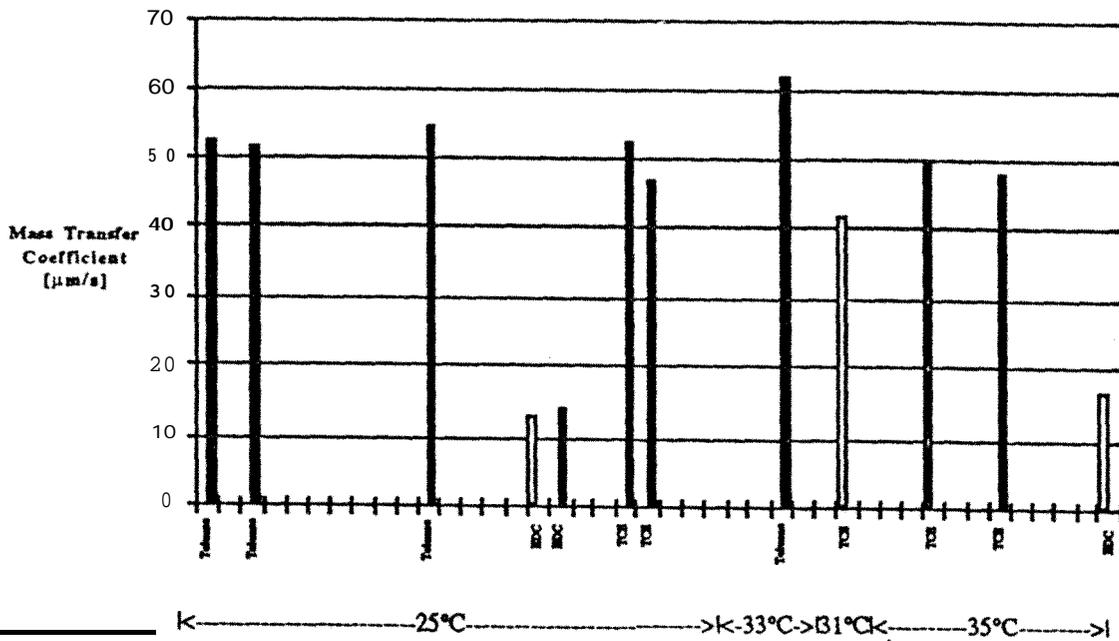


Figure 5.4 - VOC Removal for Toluene, TCE and EDC @ 25 Through 35°C Using a Transverse Flow Pervaporation Module **Operating** Under High Vacuum and a Water Side Reynolds Number of 40 to 60

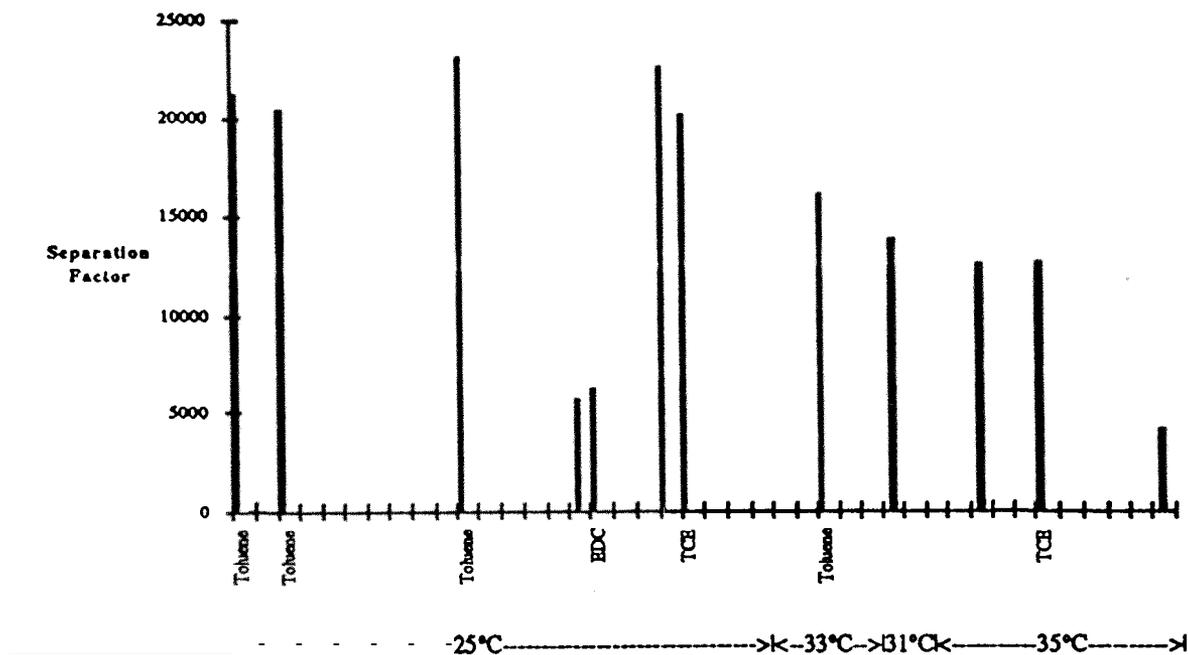


Figure 5.5 - Separation Factors for VOC Removal for Toluene , TCE and EDC @ 25 - 35°C Using a Transverse Flow Pervaporation Module Operating Under High Vacuum and a Water Side Reynolds Number of 40 to 60

5.3.4 Permeate Pressure

Vacuum pressures of 1000 Pa or greater are typically employed in pervaporation applications. Most vacuum pumps can however provide vacuum pressures much less than 1 Pa. Operating vacuum pressures greater than 500 Pa are termed ‘rough vacuum’ in the vacuum pump industry. The ultimate vacuum achieved in typical pervaporation applications is not controlled by the vacuum pump, but rather by the condenser upstream of the vacuum pump (Figure 2.2). The temperature in the condenser determines the system vacuum pressure (as governed by vapour pressure of the permeate components trapped in the condenser). The reduction in flux through the membrane caused by system operation away from the ultimate vacuum is considered a vapour side restriction, (VSR), in the pervaporation process.

In order to simulate an industrial application of pervaporation, permeate flow was constricted to obtain a rough vacuum in the range from 100 Pa to approximately two-thirds of the saturation pressure (calculated at the feed temperature) of the water. The effect of the permeate pressure on the water flux is shown in Figure 5.6. The vapour pressure fraction is estimated from the total permeate pressure, P , divided by the vapour pressure, P_{vap} , of water at the feed temperature. The reduction in water flux is defined as 100% reduction when the flux is zero and 0% reduction at

high vacuum where flux is maximized for a given temperature. The linear model suggested by Lipski *et al.* (1991) estimates, quite reasonably, the reduction in flux due to VSR's. The data was obtained for operating temperatures in the range of 18°C up to 35°C for pure water and water that contained up to 10 ppm organic compounds. There was no measurable difference in water flux in the presence of VOCs.

The reduction in the organic flux due to VSR is shown in Figure 5.7. Similar to Figure 5.6, this organic flux is linearly dependent on the vapour pressure of the water (at the membrane) rather than the vapour pressure of the organic compound. Since **the** organic compound is the minor component in the permeate, the water vapour acts to sweep away the organic from the membrane surface and thus reduce the partial pressure of the VOC, effectively by dilution. If the water vapour is considered as a plug of material that may contain some fixed quantity of VOC, then increasing the flow of that plug increases the removal of VOCs from the membrane and the water (It was estimated that the permeate vapour was saturated with **the** VOC in all cases where removal of VOCs from water was observed and VSR had an effect). In effect, the quicker the water can be removed from the membrane surface, the faster the organic can be swept away from the membrane surface and greater removal of the VOC from water can be achieved. On the other hand, if the vapour pressure at the membrane approaches the downstream pressure, the plug of water vapour becomes stagnant and VOC removal effectively stops since the VOC must diffuse through the water vapour to leave the membrane surface. This diffusion velocity is very small compared to the sweep (bulk flow) velocity which is generated if the water vapour can be removed from the membrane surface. In most cases, however, sweep of the water vapour and reduction of the VOC partial pressure is maintained to provide continuous removal of VOCs. Furthermore, pervaporation is not limited to removal of VOCs at ppm levels. Since the water vapour acts to dilute the VOC in the permeate, and so long as the water is being swept away from the membrane surface, removal of ppb levels of VOCs is possible (Côté and Lipski, 1991).

5.3.5 Effect of Feed Temperatures for R o u g h V a c c u m O p e r a t i o n

As stated above, the permeate side pressure is a function of the condenser temperature. Since ice buildup in condensers poses a handling problem, condenser temperatures should be maintained above freezing. Typical condenser pressures as a function of condenser temperature are illustrated in Figure 5.8. Choosing a condenser temperature of say 5°C, the condenser pressure (estimated **from** vapour pressure data available for the organic and aqueous phase) is estimated at approximately 16 torr. Given a **fixed** permeate pressure (2,000 -2,500 Pa), increased VOC removal, shown in Figure 5.9, was demonstrated in this study by increasing the feed temperature. **Removal was increased by 3 to 4 times when the feed temperature was increased from 25°C to**

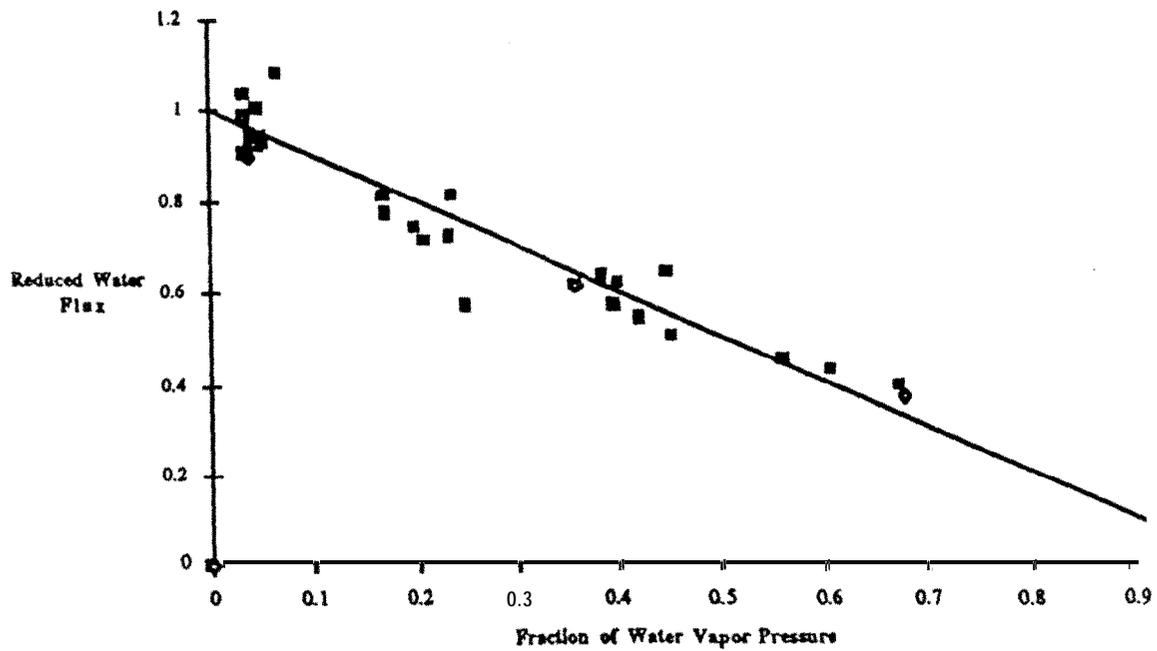


Figure 5.6 - Reduction in Water Flux with Increase in Module Permeate Pressure

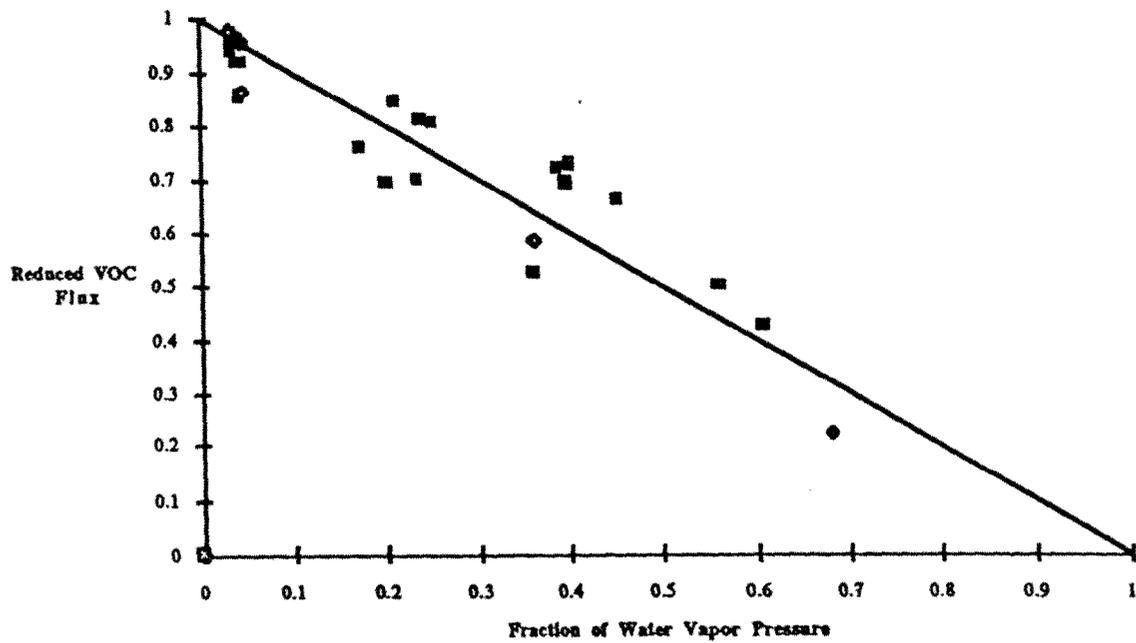


Figure 5.7 - Reduction in VOC Flux with Increase in Module Permeate Pressure

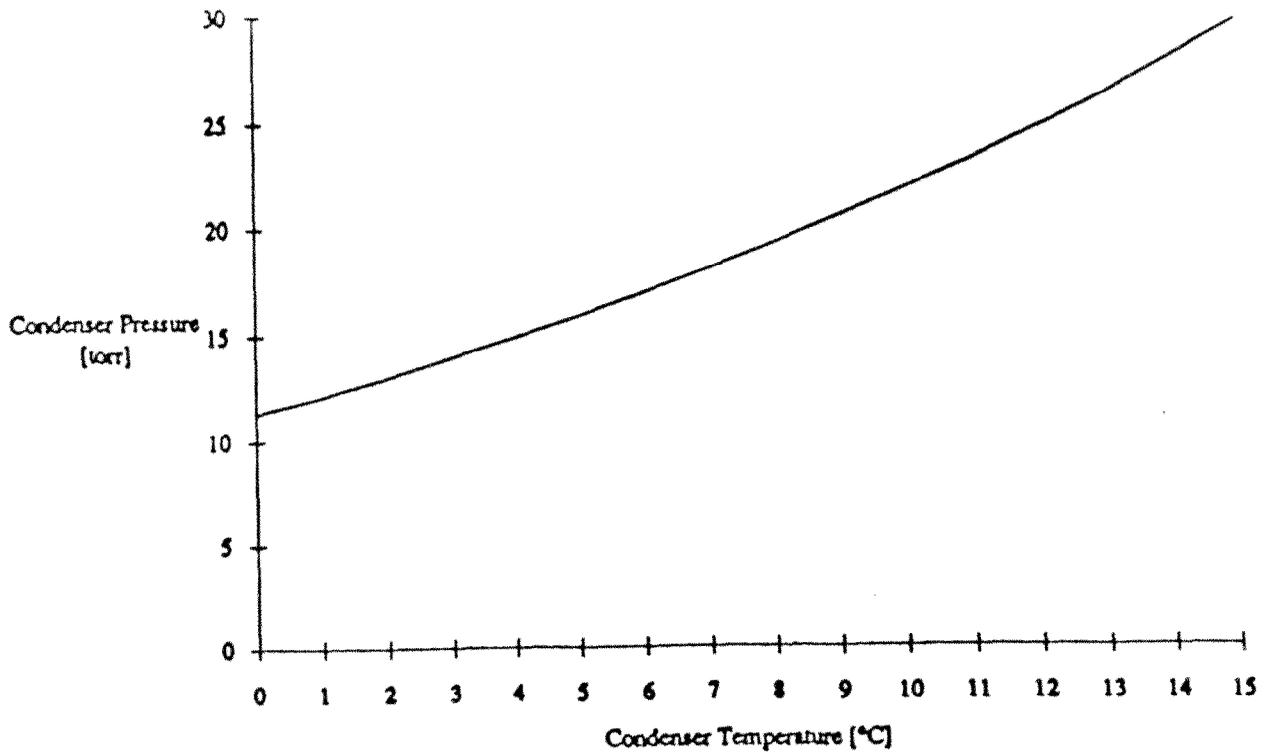


Figure 5.8 - Condenser Pressure Estimated as a Function of Condenser Temperature for a Saturated Toluene/Water Liquid

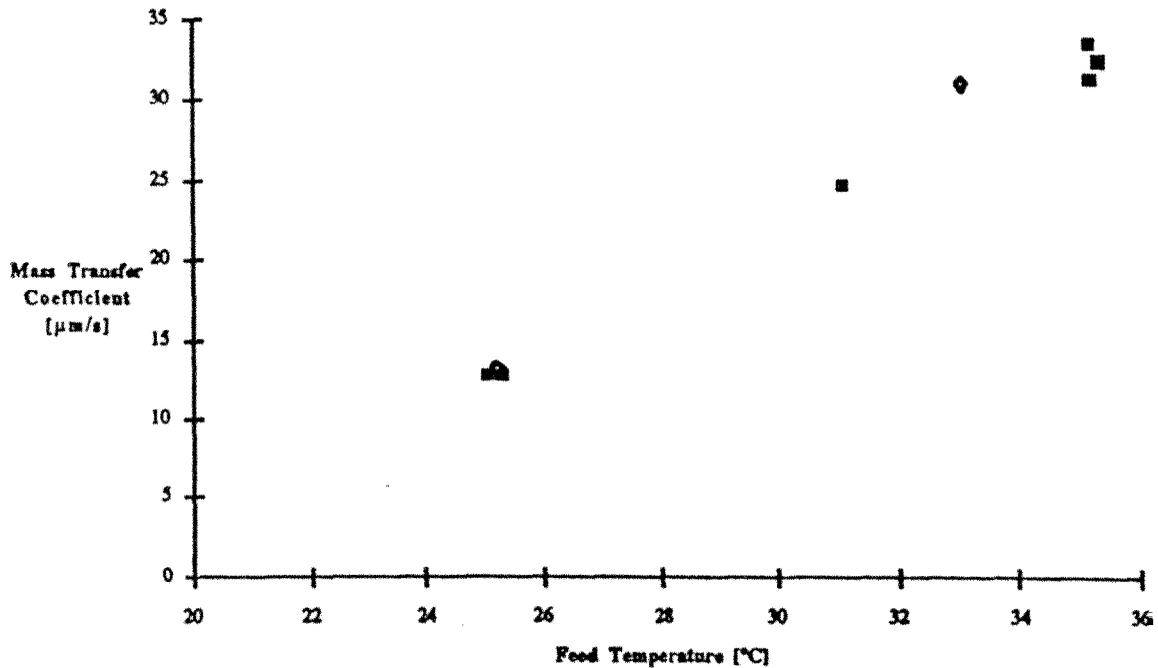


Figure 5.9 - Increased VOC Removal at High Temperature for Rough Vacuum Operation

35°C for simulated rough vacuum operating conditions. This increased removal, in rough vacuum operation, is directly attributed to reducing the VSR for water at the higher feed temperature. As the VSR is minimized, removal rates will increase until rates are comparable to rates achievable under high vacuum operation.

It is apparent that for rough vacuum, the effective rate of removal of a VOC from water may be increased by increasing the feed temperature. Increasing the feed temperature (which increase the vapour pressure at the feed), increases the driving force from the feed to the condenser (the condenser being at a constant temperature and pressure). Extrapolating, VOC removal can be improved to within 5% of the maximum removal defined by the LFR and the membrane resistance by operating at feed temperatures of **75°C**. The 5% shortfall in maximum VOC removal is due to VSR. Although operation at higher temperature does not increase removal rates due to higher partition coefficients or membrane permeabilities removal is enhanced for systems by reducing the VSR

Improved performance can, however, be realized for EDC and other semi-volatiles by operation at higher feed temperatures. As feed temperatures increase and volatility increases (i.e. Henry's Law Constant for EDC more than doubles from room temperature up to **37°C, 0.00225 atm·m³/mol**), greater removal can be achieved for these compounds which were not liquid film controlled at the lower operating temperatures. As with removal for the volatile compounds, removal rates can only be improved for semi-volatiles to a rate where LFR becomes rate controlling. At such a temperature, removal rates of semi-volatiles will be comparable to removal rates for volatiles.

5.4 Pilot Scale Operation

The River Road pervaporation pilot unit was tested on a synthetic wastewater. The synthetic wastewater contained approximately 3 ppm toluene in tap water. The system was operated under conditions that allowed accurate monitoring of process parameters. Flowrates were adjusted to provide 1) reasonable toluene removal, and 2) effluent concentrations well above the method detection limit for toluene analysis. Accurate analysis of toluene concentration was critical in assessing the actual rate of removal by pervaporation.

One pervaporation test was conducted using a module that contained 5760 fibres providing a surface area of 0.5 m². Operating conditions for this test are provided in Table 5.6. Feed and retentate samples were taken at the beginning, middle and end of the run to compare to expected pervaporation performance. The model (for estimating removal rate as a function of Reynolds Number and other process parameters) which was verified in Section 5.3 was again used to estimate toluene removal now using a module with ten times greater surface area. The measured toluene removal was in very good agreement with the model and was well within the analytical precision limits. This test indicated that models used in Section 5.3 are accurate for scale-up purposes. Although removal of more than 90% could be achieved by increasing the membrane surface area or reducing the volumetric flowrate, such removal could not be verified analytically, and, no such tests were performed.

Verification of these models confirms that the technico-economical analysis (Lipski and Côté, 1990) used for estimating effectiveness of removal can be used for scale-up purposes.

**Table 5.6: Operating and System Parameters for Pilot Testing
of a Pervaporation Module**

Membrane Area (m²)	0.5
Operating Feed Temperature (°C)	35
Condenser Temperature (°C)	-10
Condenser Pressure (torr)	3.5
Influent Flowrate (litres/min.)	2.2
Reynolds Number	20
Removal Rate (%)	
At start of test	42
In middle of test	41
Endof test	47
Removal predicted by Model (%)	42

6.0 PROCESS OPTIMIZATION

The purpose of this section is to outline design and operating conditions that will maximize pervaporation performance. The basic model used to perform the optimization is illustrated by Lipski and Côté (1990). The results will only be summarized here.

6.1 Operating

To increase removal rates, higher Reynolds numbers should be developed to overcome liquid film resistance (LFR) and higher feed temperatures should be utilized to reduce the vapour side restrictions (VSR). In addition, higher operating feed temperatures will allow removal of semi-volatile compounds from water. For operation at increased Reynolds number or operating temperature the substrate fibre material must be strengthened. In addition, permeate pressure should be minimized to reduce VSR. A case study considering these system conditions will be illustrated in Section 6.2

6.2 Case Study

The benefits of employing the changes in system's operation which were recommended in Section 6.1 are compared to the current capability of the existing pervaporation module. The significant

limitation of the existing module is that operation is limited to low Reynolds Numbers and feed temperatures. A computer model was used to provide capital and operating requirements for the available system (used in this study) and compare them with the requirements of an improved system. The current system is defined as having a ceiling temperature of **35°C** and a maximum Reynolds Number of 70, while an optimized module and system would have a ceiling temperature of **75°C** and be capable of achieving a Reynolds Number of 600. To provide an equivalent basis for comparison, capital equipment is considered that will provide and support 99% removal of toluene from a water stream. For purposes of comparison, support equipment (i.e. condensers, feed and vacuum pumps) for both systems were identical. Membrane thickness was increased in the high temperature application that would provide an equivalent water flux in comparison to the low temperature constraint and thus call for an identical vacuum pump and condensation train.

Pervaporation operation was considered at the high feed side Reynolds number represented in Figure 5.2 and operating at a feed temperature of 75°C extrapolated from Figure 5.3 and using available Henry's Law data. The results of such a case study is provided in Table 6.1. The model considered two systems, each to provide 99% removal of toluene from a 34 litre/min. water stream. The condenser temperature was **5°C** which would provide a vacuum pressure of 16 torr.

The significant component in the capital cost is the membrane cost. The reduced membrane requirement at the higher Reynolds Numbers and feed temperature, directly impacts on the capital cost of the pervaporation system. Since a significant component of the operating cost includes capital depreciation, reducing capital cost reduces the operating cost directly. Energy requirements for both systems are however equivalent and are approximately 0.17 kWh/m³. These costs are in line with previous cost schedules for pervaporation (Lipski and Côté, 1990).

6.1: Benefits of Operation of Pervaporation System at Optimum Conditions

Feed Temperature (°C)	35	75
Reynolds Number	52	633
Mass Transfer Coefficient (µm/s)	43	268
Flux Reduction (VSR, %)	38	6
Membrane Requirement (m ²)	98	10
Capital Cost (\$K)	217	31
operating Cost (\$/m ³)	4.35	0.57

6.3 Technical and Economic Analysis

To carry out an economic analysis, a case study considered a 167 litre/min. system which contained 10 ppm trichloroethylene (TCE) that was to be reduced by 99%. Pervaporation was compared with existing technologies (including assumptions) such as air stripping and activated carbon (Lipski and CM, 1990). The estimated cost of treatment by air stripping alone was estimated at \$0.10/m³. The cost of combining air stripping with granular activated carbon (GAC) in various configurations, varied from \$ 0.40/m³ for air stripping and vapour-phase GAC, to \$ 0.80/m³ for liquid phase GAC alone. These costs include regeneration or disposal of activated carbon. By comparison, the cost of pervaporation would be in the order of \$ 0.56/m³ using the membrane and module design developed in this project. This cost was estimated from energy requirements and amortization of assembly costs and component costs and indicates that petvaporation is cost competitive with existing technologies.

Incineration costs are not included in the above costs. Since it is necessary to incinerate only the organic phase of the pervaporation condensate or from the carbon regeneration, incineration costs would represent a fractional **increase** in the overall operating cost. If incineration costs of up to \$1/liter (depending on fuel value) are assumed treatment costs would increase by only \$0.10 /m³ if effluent concentrations are up to 100 ppm and only the organic phase is sent off for incineration. For industrial applications where the effluent contains a single organic there exists the potential for organic reuse and these incineration costs are not applicable.

To obtain and optimize treatment costs for pervaporation a computer cost model package was developed (Lipski and Côté, 1990). A sensitivity analysis was carried out to identify critical variables and to optimize these variables.

Technically, pervaporation has several advantages over carbon as described below. Since air stripping alone is not suitable for groundwater remediation and requires carbon adsorption for controlling off-gas emissions, air stripping alone can not be compared to pervaporation. It must however be mentioned that pretreatment is often required to avoid precipitation and fouling in air stripping columns. Some of the major advantages that pervaporation can offer over carbon adsorption are:

- 1) Pervaporation uses no sorbents which must be regenerated
- 2) Continuous monitoring is not necessary for effluent breakthrough.

- 3) Pervaporation is continuous and offers immediate recovery of solvents for industrial applications.
- 4) Pervaporation is suitable for both high and low concentration VO contaminated water.
- 5) Pervaporation offers removal of moderately soluble compounds such as ethylene dichloride which can not be removed by carbon.

Carbon adsorption is however applicable in certain instances. Use of activated carbon is best suited for water contaminated at low VOC concentrations as monitoring for breakthrough and column saturation will be infrequent. Used downstream of pervaporation, carbon will be effective for removal of any residuals not suitable for pervaporation as well as removal of any traces of VOCs without significant loading on a carbon bed.

7.0 **CONCLUSIONS AND RECOMMENDATIONS**

The work in this project has developed and identified improved pervaporation operation for VOC removal as compared to use of pervaporation modules existing on the market prior to this study. This improvement was measured as a reduced membrane requirement for any given application and a more energy efficient pervaporation system. Secondary objectives which were accomplished in order to deliver these results are included below.

Hollow fibres were developed with a thick and selective layer on the outside of a hollow fibre. This active silicone rubber layer was thick and continuous from the inside to the outside of the hollow fibre and used a microporous membrane as a support to facilitate membrane preparation. This membrane thickness (125 μm) was optimized to provide a strong and selective active layer.

A prototype transverse flow module was developed in this work. This module consisted of hollow fibres (540 μm OD) spaced 1 mm centre to centre in both lateral and longitudinal direction. These modules were used to test pervaporation performance. Throughout the testing program, there was no evidence of fouling or channelling of feed in the transverse flow modules. Removal rates were shown to increase beyond the rates reported in previous work. Mass transfer and pressure drop correlations available for widely spaced tubes were validated for closely packed hollow fibres. Hydrodynamic conditions were optimized to provide long membrane and module life and good VCK! removal. Although VOC removal could be enhanced under very turbulent conditions, such operation reduced fibre life. Bench testing also indicated that rate of removal is independent of temperature and type of VOC for the more volatile compounds (such as TCE and

toluene) for low Reynolds Numbers and under conditions of very high vacuum. Removal was more effective with increase in Reynolds Number or by increasing feed temperatures for rough vacuum operations. Limited testing at pilot scale confirmed the bench-scale results.

Models and equations describing hydrodynamic conditions, developed for other applications, were confirmed in this work and could be used as a tool for estimating performance under all hydrodynamic conditions. A computer model was developed using these equations and enabled identification of key operating parameters for pervaporation operation. Optimization of key system variables led to identification of process conditions for improving pervaporation performance:

- Semi-volatile compounds such as EDC and methylene chloride can be removed more effectively by pervaporation at higher feed temperatures.
- . To improve overall performance of a transverse flow pervaporation system, a module should be developed for operating at a Reynolds Number above 600 and at a temperature of at least **75°C**.

These module improvements should be implemented prior to any field testing.

Field testing of pervaporation will be required before commercialization of pervaporation can be exploited as an alternative site or industrial remediation process for VOC removal. Since peavaporation has distinct advantages over other technologies when considering high concentration VOCs, initial demonstration and field testing should focus on high concentration effluents. In particular, single component VOCs which have some reuse value should be considered in order to demonstrate the VOC recovery potential of pervaporation.

Commercialization of pervaporation will require scale-up of pervaporation modules so that membrane costs may be reduced Other areas for improvement in pervaporation systems will be identified at pilot scale.

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