SEPARATION OF TRICHLOROETHYLENE FROM WATER BY SWEEPING-AIR PERVAPORATION

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Abstract

A preliminary experimental investigation was conducted to evaluate the performance of a commercial hydrophobic polydimethylsiloxane-polyethersulfone composite capillary module (SEM-PVG-G3) in the removal and/or concomitant recovery of trichloroethylene from water by sweeping-air pervaporation. The effect of feed flowrate, temperature and concentration and air moisture content and flowrate were expressed in terms of permeate flux and selectivity.

Keywords : air perstripping, trichloroethylene, pervaporation, environmental applications, polydimethylsiloxane

1. Introduction

Pervaporation is a membrane separation process which involves the simultaneous transfer of heat and matter from the liquid phase to the vapour phase through non-porous polymeric membrane, although microporous polymeric membranes have been used as well in some laboratory studies [1]. Traditionally-operated in vacuum, pervaporation is evolving into several variants to satisfy different intended applications. One such variant is the use of sweeping-gas or what is called as *air perstripping* [2], when air is used as the sweeping-gas.

As early as 1970, the potential of applying pervaporation to remove volatile pollutants from water using selective hollow fibers were already recognized by Cole and Genetelli [3]. It is believed that much of the inspiration in recent studies came from their foresight of this area of application - the treatment of industrial waste containing volatile organic compounds (VOCs).

VOCs comprise about half of the 129 United States Environmental Protection Agency (US EPA) priority pollutants and each is known to be toxic and/or carcinogenic. Thus, their removal from water is of prime public health and safety importance. Pervaporation can be profitably used not only to remove but also concentrate organic compounds for possible reuse from contaminated liquid streams like groundwater, leachate and industrial wastewater.

The chlorinated organic solvents which includes trichloroethylene are by far, the most problematic of all the VOCs as they are in ubiquitous and extensive use in metal and engineering industries, dry cleaning industry and to a lesser extent, for degreasing and deoiling processes in the textile, leather and electronic component industries. Their removal in the process stream would not only lessen the cost of further downstream processing but also of wastewater treatment.

The pervaporation performance is usually expressed in terms of flux or permeation rate and selectivity. Flux is the rate of mass transfer of a component(s) through the membrane. Flux is the rate of mass transfer of a component(s) through the membrane. Permeability is a function of both the permeant concentration and permeant diffusivity in the membrane. Dividing permeability by membrane thickness gives the flux density which is the amount of permeate per unit membrane area and unit time at the given membrane thickness. For a single species, flux can be expressed

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mathematically as

$$J = DC^a \frac{(1 - p/p^e)}{\delta} \qquad (1)$$

There are two ways of expressing selectivity: by the separation factor α or the enrichment factor ß, both being dimensionless quantities:
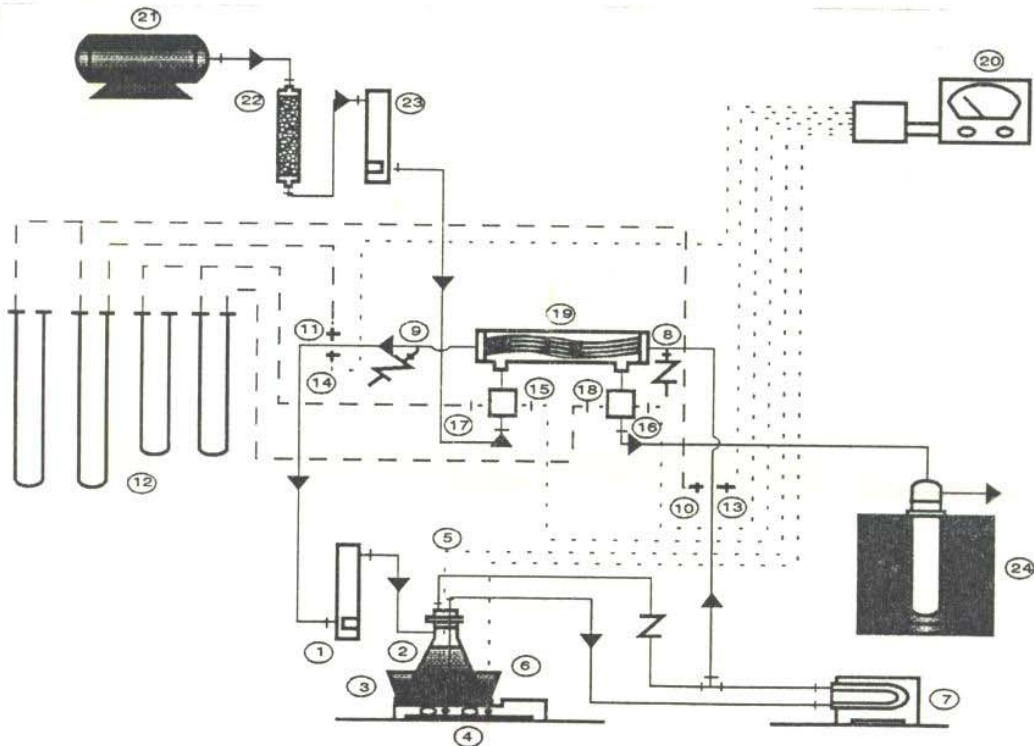
$$\alpha = \frac{[C_a/C_b]_{permeate}}{[C_a/C_b]_{feed}} \qquad (2a)$$

$$\beta = \frac{[C_a]_{permeate}}{[C_a]_{feed}} \qquad (2b)$$

For low organic concentrations in the liquid and vapor, the separation factor α is equivalent to the enrichment factor ß.

2. METHODOLOGY

Description of Test Apparatus

Figure 1. Schematic diagram of the experimental set-up. (1) liquid flowmeter (2) feed reservoir (3) constant-temperature water bath (4) stirrer-hot plate (5) feed temperature detector (6) water bath temperature detector (7) variable-speed pump (8) & (9) valves for liquid sampling (10) & (11) pressure tap (liquid inlet and outlet) (12) U-tube manometer (13) & (14) thermocouple (liquid inlet and outlet) (15) & (16) thermocouple (air inlet and outlet) (17) & (18) pressure tap (air inlet and outlet) (19) pervaporator (20) tempereture indicator (21) air compressor (22) silica gel column (23) air flowmeter (24) cold trap

Air System

Air was blown through the air lines via an air distribution line connected to a compressor through a silica gel column to absorb moisture in the air. Flow regulation was accomplished by manually-operated valves. Except for the valves which were made of brass, the air lines were either made of plastic tubings, or PVC pipes and fittings to minimize heat loss. The downstream portion of the line was directed to a cold trap cooled by liquid nitrogen for the collection of the permeated vapor.

Solution System

The TCE-water solution passed through two manifold blocks each housing a thermocouple, a pressure trap and a valve for sampling. A water bath was used to maintain the feed temperature at 25°C. Heating of the feed solution was accomplished by a magnetic stirrer-hot plate at ±1.0°C of the specified feed temperature.

Pressure Instrumentation

The air and liquid pressures were measured by a double-leg type mercury manometers, as were the air and liquid pressure differentials .

Temperature Instrumentation

All temperature were measured by means of single-junction copper-constantan thermocouples that allowed the temperature to be estimated within ±0.5°C.

Flow Metering

Air flow was measured by an air flowmeter with a range of 2 to 22 liters air per minute. Liquid flow was measured by a liquid flowmeter with a range of 0.05 to 0.5 liter per minute.

Description of the Pervaporator Module

The module was a commercial composite membrane of polyethersulfone and silicone (SEM-PVG-G3) made and purchased from SEMPAS Membrantechnik GmbH, Germany. It is composed of 15 capillary fibers potted with silicone potting in a glasshouse 360 mm long and 20 mm in diameter. With inner diameter of 1.2 mm, each fiber has a theoretical silicone coating 0.6 μm thick for a total effective area equal to 150 cm^2.

Experimental Methods and Conditions

Pervaporation rates were measured using TCE-water feed solutions prepared from reagent-grade trichloroethylene and distilled water. With several interdependent parameters studied, experimental runs were organized as presented in Table 1.

In all runs, initial TCE concentrations were maintained at the solubility limit ($\approx$ 1100 mg/L). One hundred twenty-mL serum bottles capped with Teflon-lined rubber septum and Teflon sheet were used to contain the ten-mL liquid samples collected.

Prior to head-space analysis [4], samples were placed inside a rotary-shaker incubator set at 25°C and 40 rpm for at least one hour. After equilibration, 250 μL or 0.25 mL of the head-space gas was taken-out using air-tight syringe and then injected to a gas chromatograph equipped with a flame ionization detector (Shimadzu 14-A) connected to an integrator. The stainless steel column was packed with Carbopack B (mesh 60/80)/1% SP-1000. The temperature of the column, injector and detector were set at 190 °C, 210 °C and 230 °C respectively. The air, hydrogen, primary carrier and secondary carrier gases were set at gas pressures of 0.5, 0.5, 2.0, and 1.0 kg/m^2 respectively.

Table 1. Summary of Experimental Conditions

| Parameters	Test values	Other conditions
Feed temperature (°C)	25, 30, 35, 40	Feed rate = 0.5 L/min Air flowrate = 13.75 L/min Air temperature = 29 - 32 °C
Feed rate (L/min)	0.2, 0.3, 0.4, 0.5	Feed temperature = 25 °C Air flowrate = 13.75 L/min Air temperature = 26 - 32 °C
Air flowrate Moisture-laden air (L/min)	11.0, 12.5, 13.75, 15.5, 17.0	Feed temperature = 25 °C Feed rate = 0.5 L/min Air temperature = 28 -32 °C
Dry air (L/min)	11.0, 12.5, 13.75, 15.5, 17.0, 18.5, 20.0	Feed temperature = 25 °C Feed rate = 0.5 L/min Air temperature = 24 - 32 °C
Optimization - Air flowrates (L/min)	9.0, 11.0, 12.5, 13.75, 15.5	Feed temperature = 40 °C Feed rate = 0.5 L/min Air temperature = 29 - 34 °C

3. RESULTS AND DISCUSSIONS

3.1 Comparison of Moisture-laden and Dry Sweeping-air Pervaporation

It seems that when a hydrophobic membrane (like PDMS) is used, sweeping-air pervaporation (or air perstripping) employing moisture-laden air is as effective in removing trichloroethylene from water as the one employing dry air. Unlike when using a hydrophilic membrane like cuprophan, where the moisture content of the air limits the effectiveness of the membrane by allowing the transfer of moisture to the solution at relative humidities of the air greater than the moisture content of the solution [2], the moisture content of the air seemed not to affect the removal of TCE by the hydrophobic PDMS membrane. Presumably, there must have been an almost nil, if not zero, mass transfer resistance imposed by the moisture in the air at the membrane-vapor interface for the desorption of the permeated vapor from the membrane. The higher flux value for the moisture-laden sweeping-air pervaporation was obviously due to the moisture in the air but this effect was negated by a lower selectivity primarily because of dilution of the permeated vapor and possibly, by incomplete condensation of the permeated vapor.

3.2 Effect of Air Flowrate

With initial TCE concentrations around the solubility limit ($\approx$ 1100 mg/L), a maximum flowrate which effected the highest percent removal can be identified from the inverted "U" curve of Fig. 2. On the other hand, the plot of enrichment factor β and permeate flux J after 6 hours of operation shows decreasing trends for both parameter, in contrast with the observations based on a study on sweeping-gas pervaporation using ethanol-water systems [5]. These seeming deviations can be attributed to the very high air flowrates that were used in the process i.e., the permeated vapor was not condensed completely but was carried away by the outgoing air instead. Likewise, a closer examination of the downstream pressure developed at each flowrate revealed that a build-up of pressure inside the tube (i.e., an increase in the pressure difference between the inlet and outlet of the capillary tube as the air flowrate increases) have caused the lowering of the flux at higher air flowrates. NGUYEN [6] reasoned that this build-up appears most likely to occur if the permeation rate of the membrane is high (due to high content of the preferential solvent in the feed, for example) and the volume available for vapors is small. In a later study [7], he concluded that, in a module, the downstream compartment
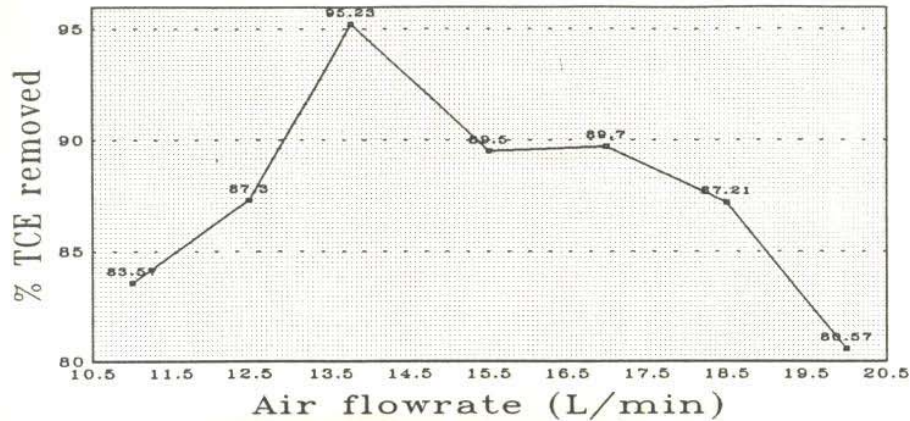
feed rate = 0.5 L/min
feed temperature = 25 °C
air temperature = 24 — 32 °C

**Figure 2. Effect of air flowrate on TCE removal**

should be designed in such a way as to avoid any vapor build-up: a permeate draining system with low pressure drop and many pumping outlets should be chosen, especially near the feed entrance, since the permeation flux is highest in this region.

3.3 Effect of Feed Rate

High feed flowrate favors high removal of TCE. Since flowrate is directly proportional to axial Reynolds Number, the data collected were consistent with previous observations made by other researchers that mass transfer increases with increasing Reynolds number [8, 9, 10]. However, ultimately, based on the resistance-in-series model, the optimum situation for best performance, i.e, least resistance to mass transfer, can be achieved by considering not only the hydrodynamics of the process (boundary layer resistance) but also the thickness of the membrane (membrane resistance) [11]. In an earlier paper [8], they suggested that for non-volatile pollutants, modules should be designed to operate in the laminar range and make use of thin layers of highly-selective polymers while for volatile pollutants, modules should be designed to operate in the turbulent regime and make use of a thick active layer. However, although concentration polarization is frequently minimized by operating with turbulent crossflow, this results in low net separation per unit length of membrane. In such cases, Colman and Mitchell [12] suggest pulsation of a low mean crossflow in a baffled channel to achieve high mass transfer which they described with a pervaporation membrane being commercialized by *Kalsep*. Furthermore, for sweeping-air pervaporation, it is inferred that an additional consideration should be made: the quality of the sweep gas (its temperature, moisture content and flowrate).

3.4 Effect of Feed Temperature

The effect of temperature on the overall permeate flux and on membrane selectivity can be clearly seen from Fig. 3. It can be noted that higher enrichment factors and lower permeate fluxes were obtained at low temperatures than at high temperatures. According to the free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increases, the frequency and amplitude of the chain jumping (i.e., thermal agitation) increase and the resulting free volumes become larger. In pervaporation, the permeating molecules can diffuse through these free volumes. Thus, when temperature is high, the diffusion rates of isolated permeating molecules and associated permeating molecules are high, so that total permeate flux is high and the enrichment factor low. A correlation coefficient of $r^2 = -0.99$ for the exponential regression analysis of the average overall permeate flux against the reciprocal of absolute temperature indicates a strong adherence to the Arrhenius Law-type variation of flux with temperature. An activation energy
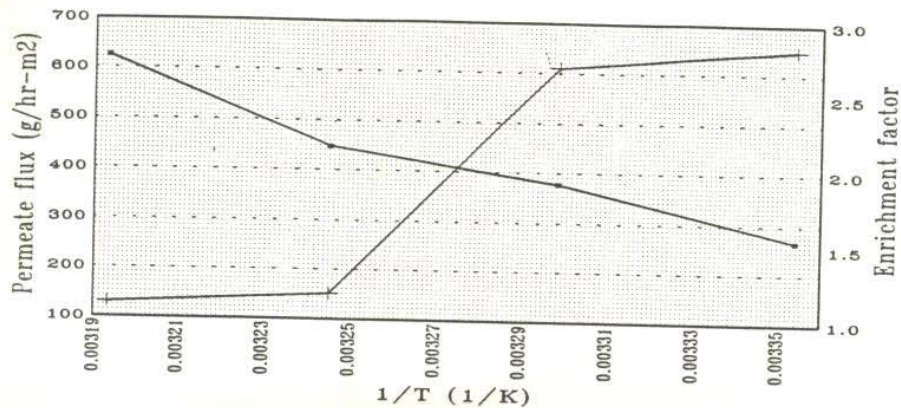
feet rate = 0.5 L/min
air flowrate = 13.75 L/min
air temperature = 29 — 32 °C

Figure 3. Effect of feed temperature on the average overall flux and on the enrichment factor

of 612 Joules/mole was also calculated which according to the permeation transport mechanism can be considered as composed of the energy for diffusion and the heat of sorption.

However, the TCE flux (component flux) did not follow the same trend. A mass balance of the process indicated that most of the TCE removed were not condensed and collected in the cold trap but were carried by the out-going air and vented into the atmosphere (see Table 2 below). This further confirms the earlier contention that limited condensation of the permeated vapor results from the very high air flowrate employed. It was also observed in this study that high temperature does not

Table 2. Trichloroethylene mass balance at each Feed Temperature

Mass Balance (Total volume ≈ 3000 mL)	Feed Temperature (°C)			
	25	30	35	40
g TCE in solution initially (a)	3.336	3.003	3.000	3.198
g TCE in solution after 2 hours (b)	0.8853	1.1210	0.9096	0.3934
g TCE removed after 2 hours (a - b)	2.4507	1.8820	2.0904	2.8046
% removal ({a - b}/a x 100 = c)	73.46%	62.7%	69.68%	87.70%
g TCE in the collected permeate (d)	0.019782	0.03039025	0.031405	0.0239765
% of removed TCE (d/c x 100)	0.81%	1.6%	1.5%	0.85%

necessarily results to maximum recovery or enrichment of TCE, in contrast with the observed upward trend for selectivity for the ethanol-PTMSP system [13] or at least a maximum selectivity at a particular temperature for the ethanol-PDMS system [14]. A possible reason for this is the high temperature of the out-going vapor (due to heat transfer) which added further limitation to the condensing capacity of the cold trap. Nevertheless, high feed temperature was efficient in faster and higher removal probably due to increased diffusivity and/or solubility in the membrane and to the faster volatilization of TCE in the feed reservoir. However, these observations may not be truly significant as the effect of temperature on selectivity is highly system (membrane/mixture) dependent [14]. It is also inferred that the relatively much higher initial concentration of TCE for the lowest

temperature might be the cause of the conspicuously high percent TCE removal after two hours of operation. Feed temperatures higher than 40°C were not tried because of possible damage that high temperature might cause the thin active layer.

3.5 Effect of Feed Concentration

Though was indirectly tested, the effect of concentration on pervaporation was rather obvious: higher fluxes result from higher feed concentrations. Corollary to that, it was noticed that the maximum rate of removal occurred during the first two hours of the run and that the rate of removal slowed-down as the run went to progression. These observations are traditionally interpreted in chemical engineering as due to the change in the driving force of the process, as can be deducted from the very familiar mass transfer equation derived from Fick's law of diffusion:

$$J = \kappa (C_1 - C_2) \tag{3}$$

With C_2 nearly constant and C_1 proportional to the bulk concentration in the liquid, an increase in the concentration in the bulk liquid would correspond to an increase in the flux.

Moreover, an increase in concentration would also correspond to an increase in interactions between the permeants and with the membrane material, which eventually leads to the following effects in the transport rates of the components of the solutions to be separated: a) a *free volume effect* which generally increases the diffusivity (i.e., plasticizing effect) and b) a *coupling effect* due to the remaining interactions between molecules in the polymer which can increase or decrease the diffusivity (i,e., interaction effect) [15]. In an organophilic membrane like PDMS, an increase in the organic concentration in the feed causes the amorphous regions of the membrane to become more swollen, and the polymer chains become more flexible thus decreasing the energy required for diffusive transport through the membrane (plasticizing effect). This is another reason for the increase in flux at higher TCE concentrations. Likewise, as the free volume due to the plasticizing effect of TCE increases, the possibility of the permeation of interacted molecular pairs as well as isolated molecules of water and TCE through the membrane becomes higher. Thus, the membrane has a lower selectivity at higher organic concentration in the feed mixture.

4. CONCLUSIONS

Although the moisture content of the air have not affected the degree of removal of TCE, efficient concentration was not achieved as the moisture in the air diluted the collected permeate. Furthermore, air perstripping is deemed to be especially attractive when the temperature of the sweeping-air is higher than the temperature of the solution as the air becomes the source of the latent heat of vaporization for the phase change .

Air flowrate affected the removal of TCE by increasing the activity gradient between the upstream and downstream sides of the membrane as the air flowrate was increased. However, the pressure build-up inside the tube as the air flowrate increases negated this effect. Likewise, very high air flowrates did not favor complete condensation as water and TCE were carried along with it. Thus, the flowrate of the sweeping-air is a critical consideration in the choice of process objective : recovery, removal or both.

High feed flowrates favored high removal of TCE underlining previous observations that mass transfer can be increased by increasing the Reynolds number. However, a system approach is deemed more appropriate as hydrodynamics analysis alone is inadequate. Optimum conditions should be established for each intended applications and process conditions.

Opposing trends for permeate flux and membrane selectivity were observed as feed temperature was increased from 25 to 40 °C : overall flux increased while selectivity decreased. However, component (TCE) flux showed a different trend which was attributed to the incomplete condensation

of TCE as the temperature of the downstream air increased due to heat transfer.

Similar to the temperature effect, opposing trends for permeate flux and membrane selectivity were observed as the feed concentration decreased : overall flux decreased while selectivity increased. These observations were explained both by the increase in the driving force and in the interactions between the permeants and with the membrane material.

List of symbols

a, b	Components of a solution
C, c	Concentration, μg/liter
D	Diffusion coefficient, m^2/s
e	Equilibrium
J, J$_p$	Flux, m^3/m^2-s
k	Mass transfer coefficient
m	Membrane
p	Partial pressure

Greek Characters

α	Separation factor, dimensionless
β	Enrichment factor, dimensionless
σ	Membrane thickness, μm

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