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VOC removal from contaminated groundwater through membrane pervaporation. (I): Water-1,1,1-trichloroethane system

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Abstract: 1,1,1-trichloroethane (TCA), a common chlorinated organic solvent and volatile organic compound (VOC), was removed from contaminated groundwater by using a bench-scale membrane pervaporation unit. The effects of TCA concentration, temperature, and flow rate on permeation flux and selectivity (α value) of the process were evaluated. In general, higher temperature leads to higher VOC flux but lower selectivity; higher flow rate of TCA feed stream results in higher VOC flux and selectivity, an indication of the effect of concentration polarization; higher TCA feed concentration produces higher TCA permeation, however, the selectivity was virtually unchanged.

Keywords: pervaporation; VOCs; groundwater remediation; 1,1,1-trichloroethane

Introduction

Rapid industrialization of the last century brought with huge environmental costs: vast quantities of organic solvents were disposed of in the oceans, rivers/lakes, and more likely in the soil (Hunter, 2000). Among all organic solvents that contaminate soil and consequently, the groundwater, is a group of chlorinated organic solvents that are particularly problematic (Love, 1982). These solvents have very low water solubility, low biodegradability, and higher density than that of water. As a result, these solvents settle through the water table until they reach a confined layer, where they serve as long-term source of contamination. 1,1,1-trichloroethane is one of these organic solvents that pose a health threat to the people who drink the contaminated water.

1,1,1-trichloroethane is classified as volatile organic compound (VOC) displaying high vapor pressure as well as a tendency to involve in photochemical reactions that destroy the ozone layer in the upper atmosphere. Consequently, researches related to removing VOCs like 1,1,1-trichloroethane from contaminated soil have been intensive and extensive (Nguyen, 1987; Dotremont, 1993; Goethaert, 1993; Jiang, 1997). The high vapor pressure and low water solubility of 1,1,1-trichloroethane render a high vapor-liquid partition coefficient commonly described by Henry's Law constant (H) in aqueous environment:

$$H_c = \frac{C_v}{C_L}, \quad (1)$$

where C_v and C_L are the vapor and liquid phase concentrations, respectively. The high value of H_c of TCA has long been utilized for its removal from the contaminated water by using air stripping. Another novel VOC removal technology involving taking advantage of the high H_c value of TCA is membrane pervaporation (Lee, 1989; Blume, 1990; Ji, 1995).

Pervaporation, whose term derives from the two major operations involved in the separation process, namely, permeation and evaporation, is defined as a separation process in which a liquid feed mixture is separated by means of partial diffusion-vaporization through a non-porous polymeric membrane. Pervaporation is usually carried out by placing a liquid stream containing two or more species in contact with one side of the membrane while a vacuum or sweeping gas is applied to the other side. The species, with various affinities to the membrane sorb into the membrane, permeate through it, and evaporate into the vapor phase. The vapor is then condensed. The membrane can be considered as a dense homogenous medium in which diffusion of species takes place in the free volume that is present between the macromolecular chains of the membrane material. Pervaporation has found increasing acceptance for use in

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diverse areas of practical operations ranging from flavor and aroma recovery from food processing (Karlsson, 1993; 1996), to volatile organic compound (VOC) removal from soil remediation fluids (Jiang, 1997). The driving force for pervaporation is the difference in chemical potential (or partial vapor pressure as a first approximation) of each component across the membrane. The chemical potential difference is generally maintained by either reducing total pressure on permeate side of the membrane (vacuum) or depressing the partial pressure of the component in the vapor phase below its vapor pressure in the feed (sweep gas). The net result is the same: the partial pressure in the vapor phase is kept below the vapor pressure of the component to be removed.

The performance of a pervaporation process is evaluated by examining the flux of the permeating species across the membrane and the selectivity of the species against one another (Jiang, 1997):

$$J_i = k_i \rho_i (C_i^L - C_i^V), \quad (2)$$

$$\alpha_{ij} = \frac{(C_i/C_j)^V}{(C_i/C_j)^L}, \quad (3)$$

where k_i , ρ_i , C_i^L , C_i^V are the overall mass transfer rate constant, molar density of feed, bulk liquid phase concentration (mole fraction), and bulk vapor phase concentration, respectively, for component i . Selectivity can be expressed in several ways. One common representation of selectivity, the separation factor, α , is analogous to the relative volatility of the component (i and j) of a binary liquid mixture. Sometimes, however, the enrichment factor, β_i , is used as an indication of the separation selectivity for component i :

$$\beta_i = \frac{(C_i)^V}{(C_i)^L}. \quad (4)$$

As the concentration of component i usually is very small, the concentration of component j in both feed stream and permeate will be close to 1. The separation factor will therefore be close to the value of the enrichment factor, β_i , for dilute solutions (Karlsson, 1993):

$$\alpha_{ij} \approx \beta_i. \quad (5)$$

It should be pointed out that permeation flux and selectivity are experimentally determined parameters, and Equations (1)–(4) are for data correlation purpose only because concentration polarization (discussed in the Results and Discussion section) often obscures computations of these parameters.

The objective of this study was to use a custom-made bench scale pervaporation unit using polydimethylsiloxane (PDMS), also called silicone rubber, membrane to remove/recover TCA from water and to examine the performance parameters of the pervaporation process under various operating conditions.

1 Experimental

1.1 Materials

1,1,1-trichloroethane (TCA): 99.5%, ACS reagent, Sigma-Aldrich Company, used as received; PDMS membrane: silicone rubber flat sheet with 0.0127 cm thickness from Specialty Manufacturing Inc, Saginaw, MI, USA; Methanol: GC grade, Fisher Scientific in the USA.

1.2 Bench pervaporation unit

The schematic diagram of the bench scale pervaporation unit is illustrated in Fig. 1. A 0.02 m³ stainless steel vessel served as the feed tank. The TCA concentration in the feed was adjusted by changing the amount of TCA in the solution. A magnetic stirrer was used for continuous uniform mixing. The feed mixture was circulated between the feed tank and the pervaporation membrane cell in a closed loop using a liquid pump. Liquid flow rate was measured with one of two rotometers. By passing the feed through a stainless steel coil heat exchanger the temperature of the feed liquid was adjusted. The liquid temperature before and after the membrane cell and the permeate vapor temperature were monitored by the

thermometers. The vapor side of the membrane was operated under vacuum, and the permeate was collected in a cold trap, cooled with liquid nitrogen. The permeate liquid collected over a specific time period is weighed and analyzed with gas chromatography(GC) to evaluate permeation flux and selectivity.

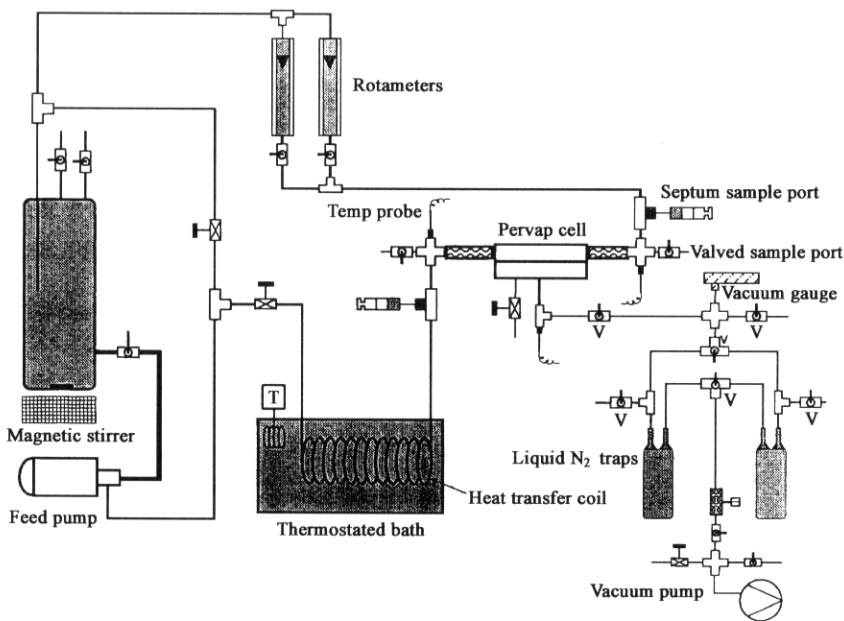


Fig.1 Schematic diagram of bench-scale pervaporation unit

The membrane cell is of rectangular shape so that the hydrodynamics within the cell can be well defined. The effective dimensions of the cell are 2.4 cm by 16.4 cm, yielding an effective area of 39.36 cm². The thin pervaporation membrane was supported by a porous stainless steel sheet of 100-micron grade (316L SS, Mott Industrial Co., USA). The cell consists of a top and a bottom compartments sealed by a Viton O-ring. Feed stream enters the cell from one end of the cell and exit at the other, flowing in one direction.

1.3 Experimental conditions

The operating parameters include concentration, flow rate and temperature. Their ranges are shown in Table 1.

1.4 Experimental operation

Experiments were run in such a manner that the system operating parameters: feed flow rate, feed temperature, and permeate(vacuum) pressure were maintained at stable levels in each run and monitored every 30 min. Prior experience has determined that it takes approximately 3 h for the system to reach steady-state operation. Two cold traps were installed in parallel

for the purpose of collecting the vapor stream over a fixed time interval. At beginning the pervaporation unit was operated in the unsteady state regime and the vapor stream was transferred to the first cold trap. After about 3 h of initial operation, the steady-state permeation collection was started by switching immediately to the second cold trap. At the end of the run, the vapor stream was switched back to the first cold trap right away, followed with the stopping of the experiment. The liquid recovered in the second cold trap was the permeate collected over a fixed time interval. This cold trap vessel was allowed to warm up to room

Table 1 Operating parameters for all experiments

Operating parameters	Variation range
Feed concentration, mg/L	50—350
Feed flow rate, L/min	1—1.2
Temperature, °C	30—50
Permeate pressure(vacuum), Pa	400

temperature and weighed, the permeate sample was then dissolved in a small amount of methanol, transferred to a 10 ml volumetric flask, diluted to 10 ml with methanol to the engraved mark, and shaken. This sample would be used for subsequent analysis and the gas chromatography(GC) procedure for sample analysis is shown in the next section.

Two feed samples were taken for each run of the permeate collection, one at the start and another at the end of the experiment. The reported feed concentration was the average of these two samples. Feed samples were taken directly from the sample port on membrane cell into a 20 ml vial. Then a 0.1—1.0 ml portion (depending on the concentration of the feed) was taken from this vial and injected into 10.0 ml water and shaken. The diluted samples were further diluted with methanol and final sample was transferred immediately to two 2 ml vials capped with Teflon-lined septa. These two vials were analyzed as duplicates in the GC.

1.5 GC analysis

GC Varian 3500 with flame ionization detector was used and the column was a J&W Scientific DB-1 60 m × 0.32 mm with film thickness of 3 μm, detector 300°C; column temperature was held at 180°C, carrier gas helium flow rate in the column was 3 ml/min, injection amount 1 μl, split ratio 12.7, column pressure 12.7 psi at starting of the column temperature programming process. Column temperature programming was held for 2 min at 35°C, increasing to 50°C at 5°C/min, then held for 16 min. Internal standard retention time was 14.5 min; TCA retention time was 17 min. In analyzing feed samples, the column was raised to 180°C at 20°C/min and held for 30 min.

1.6 Experimental error

The relative percent difference was calculated on duplicate analyses, according to:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{[(C_1 + C_2)]/2},$$

where *RPD* is the relative percent difference; C_1 is the larger of the two values; C_2 is the small of the two values. The maximum experimental error was found within 10%.

2 Results and discussion

2.1 Effect of feed concentration on pervaporation performance

The driving force of pervaporation operation is chemical potential difference between two sides of the membrane. At the vacuum side the concentration of TCA is almost zero because of high degree of vacuum. The increase in feed concentration would increase driving force for pervaporation, thus increasing the flux and permeate amount of TCA. This was observed in our experiments, as shown in the following figures. Linear regression was made passing through the origin. At both 30°C and 40°C, the fluxes of TCA increased linearly with feed concentration. As for separation factor, α , it was not found to be a function of feed concentration. As long as the flow was kept steady within a laminar flow regime and a certain range of feed concentration variations, α values should be constant if no interaction between membrane and solute occur. At 30°C, 0.3 gallon/min (1.1356 L/min or 0.0681 m³/h, equivalent to 0.39 m/s mass average velocity within module) flow rate and feed concentration being up to 350 ppm separation factor was found to be around 2840. At 40°C, 0.1 gallon/min (0.0227 m³/h) flow rate and similar concentration, the α was about 1200. The reason of using 0.1 gallon/min rather than 0.3 gallon here was to make sure that the effect of feed concentration would not be masked by the factors resulting from a turbulent flow.

In dilute TCA concentrations water flux in pervaporation should not be affected by TCA feed concentration as its value is only determined by its solubility and diffusivity within the hydrophobic PDMS membrane. The water flux found at 30°C and 40°C are about 35 and 50 g/(m²·h) respectively (Fig. 2, 3, 4 and 5).

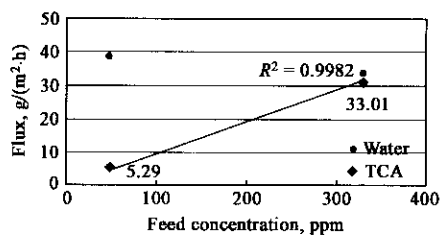


Fig. 2 Effect of TCA concentration on TCA and water flux at 30°C , 0.3 GPM

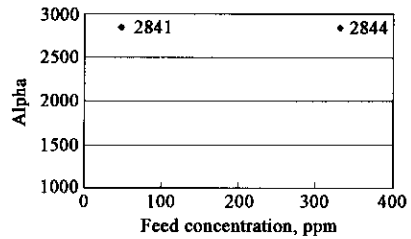


Fig. 3 Effect of TCA concentration on separation factor at 30°C , 0.3 GPM

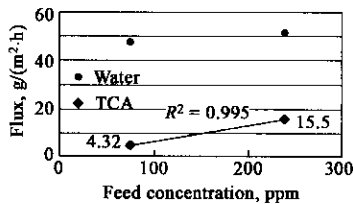


Fig. 4 Effect of TCA concentration on TCA and water flux at 40°C , 0.1 GPM

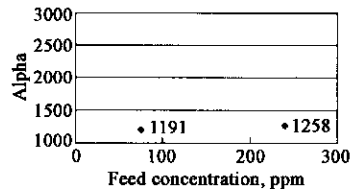


Fig. 5 Effect of TCA concentration on separation factor at 40°C , 0.1 GPM

2.2 Effect of feed velocity(flow rate) on pervaporation performance

The flow dynamics in the membrane cell affects pervaporative mass transfer. The feed-side boundary layer of the membrane has huge influence on overall mass transfer resistance. At feed side near the membrane surface there exists not only momentum boundary layer, concentration boundary also exists, which creates concentration polarization phenomenon. When feed velocity was increased within laminar flow regime, there was a corresponding increase in TCA flux as well as separation factor, indicating that concentration polarization effect(the TCA concentration difference between the bulk liquid phase and the region near the membrane, often resulting in a lower flux rate predicted based on the bulk concentration) was alleviated by increasing flow rate. In the experiment, the TCA fluxes at 0.1 through 0.3 gallon/min ranged from 19 to 46 g/(m²·h) respectively, showing a 2.5-fold increase. The separation factors also showed differences ranging from 1258 to 2772. The water flux was not influenced by the flow rates and was almost constant at 50 g/(m²·h)(Fig.6 and 7).

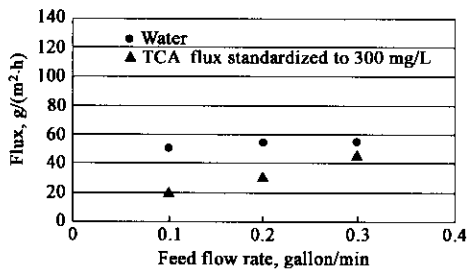


Fig. 6 Effect of feed flow rate on TCA and water flux at 40°C

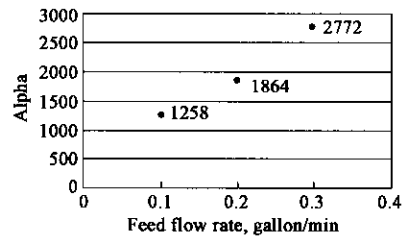


Fig. 7 Effect of feed flow rate on separation factor at 40°C

2.3 Effect of feed temperature on pervaporation performance

The effect of temperature on pervaporation operation is illustrated in Fig. 8 and 9. Both TCA and water fluxes showed higher values at high temperatures though TCA flux did not keep up with the increase rate of water flux. As a result, the separation factor decreased at higher temperatures, from 2844 at 30°C to 2469 at 48°C.

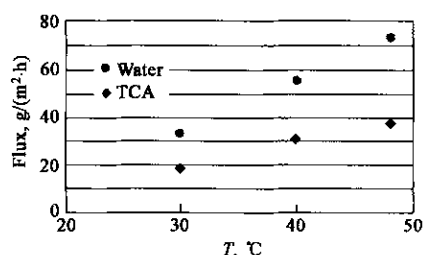


Fig.8 Effect of temperature on TCA and water flux at 0.3 GPM

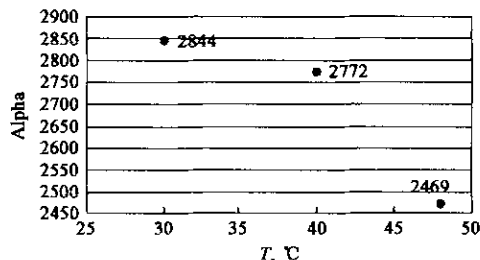


Fig.9 Effect of temperature on separation factor at flow rate of 0.3 GPM

3 Conclusions

The experiments of 1,1,1-trichloroethane(TCA) removal from water using a bench scale pervaporation unit was carried out and the effects of feed concentration, temperature, and flow rate(flow velocity) on permeation flux and selectivity were assessed. In general, increase in TCA feed concentration will increase TCA flux rate but not selectivity since the water flux also increases proportionally. One explanation was that the higher TCA concentration would result in increased membrane swelling and free volume within the matrix of the polymeric membrane, thus increasing water flux as a consequence. The effect of flow rate was somewhat predictable: the increase in the flow rate yielded an increase in TCA flux. The concentration polarization was evident in the data in the form of the linearity between flow rate and TCA flux as the diffusion of sparsely soluble TCA molecules in water(a polar solvent) is slower than that in the PDMS membrane matrix(a hydrophobic non-polar polymer). Also as expected the water flux under different flow rates showed no sign of changing one way or the other. This is because the TCA solution is made up of almost all water and the water permeation in the membrane was a slow diffusion process not subject to the influence by the flow dynamics in the system. The effect of temperature on pervaporation performance was more profound; the TCA flux increased as the temperature in the unit was raised, and so was the water flux. In fact, the rate of increasing in water flux was higher than that in TCA flux, resulting a decreasing selectivity(separation factor). The reason for this phenomenon may reside in the fact that the diffusion coefficient of water molecule in the PDMS matrix is more sensitive to the temperature than that of TCA in the PDMS matrix.

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References:

- Blume I, Wijmans J G, Baker R W, 1990. The separation of dissolved organics from water by pervaporation[J]. *J Membrane Sci*, 49: 253—286.
- Dotremont C, Goethaert S, Vandecasteele C, 1993. Pervaporation behavior of chlorinated hydrocarbons through organophilic membranes[J]. *Desalination*, 91: 177—186.
- Goethaert S, Dotremont C, Kuijpers M *et al.*, 1993. Coupling phenomena in the removal of chlorinated hydrocarbons by means of pervaporation[J]. *J Membrane Sci*, 78: 135—145.
- Hunter P, Oyama S Y, 2000. Control of volatile organic compound emissions: conventional and emerging technologies[M]. New York, USA: John Wiley & Sons, Inc.
- Ji W, Subhas K S, Hwang S T, 1995. Sorption, diffusion and permeation of 1,1,1-trichloroethane through adsorbent-filled polymeric membranes[J]. *J Membrane Sci*, 103: 243—255.
- Jiang J S, Vane L M, Sikdar S K, 1997. Recovery of VOCs from surfactant solutions by pervaporation[J]. *Journal of Membrane Sci*, 136: 233—247.
- Karlsson H O E, Trägårdh G, 1993. Pervaporation of dilute organic-waters mixtures. A literature review on modeling studies and applications to aroma compound recovery[J]. *J Membrane Sci*, 76: 121—146.
- Karlsson H O E, Trägårdh G, 1996. Applications of pervaporation in food processing[J]. *Trends in Food Science & Technology*, 7: 78—83.
- Lee Y M, Bourgeois D, Belfort G, 1989. Sorption, diffusion, and pervaporation of organics in polymer membranes[J]. *J Membrane Sci*, 44: 161—181.
- Love O T, Eilers R C, 1982. Treatment of drinking water containing trichloroethylene and related solvents[J]. *J Am Water Works Assoc*, 8: 413—425.
- Nguyen T Q, Nobe K, 1987. Extraction of organic contaminants in aqueous solutions by pervaporation[J]. *J Membrane Sci*, 30: 11—22.