Removal of trichloroethylene and trichloroethane using a novel hollow-fibre gas-permeable membrane

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Abstract In order to evaluate effects of operational parameters on the removal efficiency of trichloroethylene and 1,1,1-trichloroethene from water, lab-scale experiments were conducted using a novel hollow-fibre gas-permeable membrane system, which has a very thin gas-permeable membrane held between microporous support membranes. The permeation rate of chlorinated hydrocarbons increased at higher temperature and water flow rate. On the other hand, the effects of the operational conditions in the permeate side were complex. When the permeate side was kept at low pressure without sweeping air (pervaporation), the removal efficiency of chlorinated hydrocarbon, as well as water permeation rate, was low probably due to lower level of membrane swelling on the permeate side. But when a very small amount of air was swept on the membrane (air perstippling) under a low pressure, it showed a higher efficiency than in any other conditions. Three factors affecting the permeation rate are: 1) reduction of diffusional boundary layer within the microporous support membrane, 2) air/vapour flow regime and short cutting, and 3) the extent of membrane swelling on the permeate side. A higher air flow, in general, reduces the diffusional boundary layer, but at the same time disrupts the flow regime, causes short cutting, and makes the membrane dryer. Due to these multiple effects on gas permeation, there is an optimum operational condition concerning the vacuum pressure and the air flow rate. Under the optimum operational condition, the residence time within the hollow-fibre membrane to achieve 99% removal of TCE was 5.25 minutes. The log (removal rate) was linearly correlated with the average hydraulic residence time within the membrane, and 1 mg/L of TCE can be reduced to 1 µg/L (99.9% removal).

Keywords Air-perstrippling; chlorinated hydrocarbons; gas-permeable membrane; groundwater contamination; pervaporation; trichloroethylene; 1,1,1-trichloroethane

Introduction

Groundwater contamination due to chlorinated hydrocarbons has been a priority issue for safe water supply for more than two decades (Love and Eilers, 1982). Despite numerous researches and practical applications that have been implemented since the early 1980s, the problem gradually spreads from industrialized countries to the developing world. Since a complete clean-up requires a huge budget and a long period, it is very common to take a countermeasure in water treatment plants. One of the common treatment methods in potable water treatment processes is air-stripping using packed stripping towers (David et al., 1986). Packed tower stripping (PTA) methods, however, require large stripping towers to achieve a high removal rate, and consequently chlorinated hydrocarbons removed from groundwater contaminate the ambient air (Stenzel and Gupta, 1985). Thus an alternative process to remove volatile chlorinated hydrocarbons from contaminated groundwater is needed, especially in densely populated urban areas.

Pervaporation and air-perstrippling are methods to separate organic solvents at high concentrations using mass-transfer through a gas-permeable membrane. A number of experimental studies have been carried out on pervaporation and air-perstrippling processes for the removal of chlorinated hydrocarbons (Semmens et al., 1989; Zander et al., 1989;
Brown et al., 1993; Castro and Zander, 1995). These processes have an advantage in containing off-gas in line, and thus making it easy to treat either by an adsorption process or physicochemical degradation processes. Recently a number of new gas-permeable membranes were tested for the removal of chlorinated hydrocarbons though at comparatively high concentrations using a simple membrane configuration (Hoshi et al., 1998, 1999; Johnson et al., 1999a,b; Yeom et al., 1999; George et al., 2000). However, in order to apply this process for the treatment of drinking water it is necessary to evaluate the removal efficiency at lower concentrations with fabricated membrane modules.

A novel hollow-fibre gas-permeable membrane (Mitsubishi Rayon MHF304KM) was developed to improve the efficiency of the gas permeation process. This membrane has a very thin gas-permeable layer (0.4 µm) sandwiched between two 42 µm-thick polyethylene support membranes. This structure makes the effective thickness of gas-permeation membrane very thin without losing mechanical strength. In addition hollow-fibre membranes have very large membrane surface area in a unit volume of membrane housing, which can make water treatment units smaller. Experimental studies were carried out using this membrane and synthetic groundwater in order to investigate the efficiency and operational factors affecting the removal of very low levels of chlorinated hydrocarbons from water. The membrane system was operated either in dead-end vacuum-driven (pervaporation) or vacuum- or pressure-driven air stripping (air-perstripping) modes.

Materials and methods

Synthetic groundwaters were made by spiking trichloroethylene (TCE) and/or 1,1,1-trichloroethane into double-distilled water at a concentration of 80 to 1,000 µg/L. A 5.68-L glass bottle filled with synthetic groundwater was connected to the membrane module with Teflon® tubing. The permeate side of the membrane, i.e. the gas-phase side, is either suctioned by a vacuum pump, or swept with clean air after passing through a silica-gel column and activated carbon columns for moisture and contaminants removal, respectively. Thus the chlorohydrocarbons in the aquatic phase are driven to the gas-phase as the water passes through the hollow-fibre membrane. A small fraction of water vapour also passes through the membrane into the gas-phase at the same time. During the experiments, the concentration changes in the raw water tank, water flow-rate, air flow-rate, humidity in the off-gas, vacuum pressure and temperature were measured. Operational conditions were varied by changing the water recycling rate, the air flow-rate, and also the concentration and species of chlorinated hydrocarbons.

The water temperature was maintained at 30°C ± 1°C except for run 6, and pH was adjusted at 7.5 ± 0.1. The air temperature was between 30°C and 33°C, the same or slightly higher than the water temperature. A summary of the experimental conditions is given in Table 1. 10-mL water samples were withdrawn from the top of the water bottle by a glass syringe, and the concentration of chlorohydrocarbons was determined by GC-ECD (Shimadzu GC-14B, attached with a packed column Chromasorb W-HP (60–80 mesh) coated by 20% silicone DC550).

Results and discussion

The effects of water flow rates and the operational temperature were evaluated in runs 1 and 6, respectively. The higher the water flow rate and the operational temperature, the more efficient the TCE permeation is. These are the effects of reduced feed-side boundary layer resistance and a higher mass-transfer rate, respectively. The results obtained in this study were consistent with others (Semmens et al., 1989; Slater et al., 1990).

The effects of the operational conditions in the permeate side were more complex. Figures 1 and 2 show the results of pervaporation and pressure-driven air-
perstripping experiments, respectively. By comparing these two figures it is obvious that air-perstripping showed better TCE removal efficiencies than pervaporation. However, the effect of air flow rates on the removal efficiency was not straightforward. Up to an air flow rate of 10 L/min, the removal rate goes up probably by reduced mass transfer resistance within the support membrane; but then at the maximum flow rate of 12.5 L/min, the removal efficiency slightly decreases. This may be due to a higher rate of water vapour removal on the permeate side, and resultant reduced membrane swelling, which limit the overall rate of mass transfer within the gas permeable membrane. The water vapour pressure slightly increased for the first 3 to 5 minutes, and then reached plateaux in all the experiments. However, as the incoming air was dry the plateau level differed in each run. As the air flow rate increased from 5 L/min to 12.5 L/min, the water vapour pressure decreased from 2.2 kPa to 1.27 kPa, or from 52% saturation to 30% saturation. This difference in the water vapour pressure in the permeate side may have affected the extent of membrane swelling, resulting in lowering of the TCE mass transfer through the membrane.

Semmens et al. (1989) demonstrated that plug flow assumption in both air and water flow in the membrane module leads to a constant ratio between the TCE concentration in the inlet and outlet of the membrane, which further makes it possible to derive a first-order reduction of the TCE concentration in the glass reservoir. Figure 3 shows the comparison of different initial TCE concentrations. Although the initial TCE concentration differed

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**Table 1** Experimental conditions

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Chloro-hydrocarbon</th>
<th>Concentration (mg/L)</th>
<th>Water flow rate (L/min)</th>
<th>Air flow rate (L/min)</th>
<th>Air pressure kPa*</th>
<th>Water temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TCE**</td>
<td>0.8–1.0</td>
<td>2, 5, 8, 10</td>
<td>7.5</td>
<td>&gt;1</td>
<td>30°C ± 1°C</td>
</tr>
<tr>
<td>2</td>
<td>TCE</td>
<td>0.8–1.0</td>
<td>5</td>
<td>36.9, 62.7, 94.9</td>
<td>30°C ± 1°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TCE</td>
<td>0.8–1.0</td>
<td>5</td>
<td>7.5, 10, 12.5</td>
<td>142.5–145.5†</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>101.4–131.7‡</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TCE</td>
<td>0.8–1.0</td>
<td>5</td>
<td>7.5, 10, 12.5</td>
<td>19.4, 34.3, 48.5†</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TCE</td>
<td>0.8–1.0</td>
<td>5</td>
<td>7.5</td>
<td>145.45†‡</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>101.4‡</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TCE</td>
<td>0.8–1.0</td>
<td>5</td>
<td>7.5</td>
<td>142.5–147.6†</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>101.4†</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TCE+1,1,1-tri-chloroethane</td>
<td>0.8–1.0</td>
<td>5</td>
<td>7.5</td>
<td>145.45†‡</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>101.4†</td>
<td></td>
</tr>
</tbody>
</table>

*: absolute pressure, **: trichloroethylene, †: inlet, ‡: outlet

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**Figure 1** TCE removal by pervaporation operation (vacuum pressure = 36.9 kPa)  
**Figure 2** TCE removal at different air flow rates (pressure-driven, air-perstripping)
12 times (73 mg/L and 880 mg/L), the rate of TCE concentration reduction was almost the same. The independence of the log(removal rate) of the TCE concentration indicates that the TCE removal can be explained by the above-mentioned plug flow model. However, the semi-log plots drawn in Figures 2, 3 and 4 show that the overall trends of the TCE removal deviate slightly from linear lines, though they in part fit into linear lines. One of the reasons that can explain the reason for this deviation is the discrepancy from the plug flow hypothesis of the air. The Reynolds numbers for these experimental conditions were between 3,800 for the air flow rate of 5 L/min and 9,490 for 12.5 L/min, which indicate that the flow was turbulent in all experiments. The membrane system is operated in the counter-current mode between water and air flows in order to maintain a good TCE permeation rate. Back-mixing of TCE vapour, however, significantly reduces the gas permeation rate near the water outlet, especially at lower TCE concentrations. Another reason for the discrepancy of the model may be short cutting of the vapour pathway, which in part produces a stagnant vapour within the membrane module. When we want to achieve a high TCE removal rate, it is necessary to deal with these factors that may reduce the gas permeation rate.

Figure 4 shows the comparison of different air flow rates in vacuum-driven air-perstripping operation. Unlike the results of pressure-driven air-perstripping experiments, Figure 4 shows that the TCE removal was the most effective at the lowest air flow rate of 5 L/min. The difference was more significant at lower TCE concentrations as the log(TCE concentration) reduced linearly following the above-mentioned model at the air flow rate of 5 L/min, whereas the log concentration curve deviated from linear lines at all other air flow rates. It is also important to point out that with the air flow rate of 5 L/min the TCE concentration was brought down to less than 1 µg/L, achieving 99.9% removal. It is important to identify exactly what has made this operational condition the most efficient in the future study, but some of the possible reasons are: 1) the seeping air can be maintained in plug-flow mode better at lower flow rate and lower as evidenced by the linear regression line in Figure 4, and 2) a lower permeate side pressure makes it easy to reduce the diffusional resistance in the support membrane even at a low air flow rate. To support 1), the Reynolds number for the air flow rate of 5 L/min was calculated to be 520, whereas it varied from 1,370 at 7.5 L/min and 4,830 at 12.5 L/min. While the plug flow is also assumed by others (Ito et al., 1990) in pervaporation process, it deviates from the ideal flow when the air/vapour pressure and flow rate increase. As for 2), Duan et al. (2001) also pointed out the importance of reducing the mass transfer resistance within a porous membrane.
Similar experiments on 1,1,1-trichloroethylene removal were also carried out with and without TCE. The removal characteristics of trichloroethylene were almost the same as those of TCE. Co-existence of two chlorinated hydrocarbons did not affect the permeation rates of each other, indicating that the permeation model developed for a single solute removal can be applied to a multiple solute removal process.

**Conclusions**

The permeation rate of chlorinated hydrocarbons increased at higher temperatures due to enhanced diffusion and at higher water flow rates due to reduction of liquid-side diffusion resistance. On the other hand, the effects of the operational conditions in the gas-phase (permeate side) were complex. When the permeate side was kept at low pressure without sweeping air (pervaporation), the efficiency of chlorinated hydrocarbon, as well as water permeation rate, was low probably due to lower level of membrane swelling on the permeate side. But when a very small amount of air sweeps on the membrane (air perstipping) under a low pressure, it showed the highest efficiency than in any other conditions. Three factors affecting the permeation rate are: 1) reduction of diffusional boundary layer within the microporous support membrane, 2) air/vapour flow regime and short cutting, and 3) the extent of membrane swelling on the permeate side. A higher air flow, in general, reduces the diffusional boundary layer, but at the same time disrupts the flow regime, causes short cutting, and makes the membrane dryer. Due to these multiple effects on gas permeation, there is an optimum operational condition of the vacuum pressure and the air flow rate. Under the optimum operational conditions of this experiment, the residence time within the hollow-fibre membrane to achieve 99% removal of TCE is 5.25 min (apparent residence time based on the volume of the membrane module is 21.5 min), and the off-gas volume was 23 m³/m²-water at the standard temperature and pressure, which is still considerably high. The log(removal rate) is linearly correlated with the average hydraulic residence time within the membrane, and 1 mg/L of TCE can be reduced to 1 µg/L (99.9% removal). Since significant difference was found in the removal efficiency and the off-gas volume of chlorinated hydrocarbons depending on the operational conditions, it is important to further optimise the design and operational conditions of the gas-permeable membranes. As for the membrane used in this study, it is recommended to reduce the thickness of both the feed-side and permeate-side support membranes as far as possible to reduce the permeation resistance.

**References**


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