A Study on the Removal of Chloroform from Wastewaters by Means of Pervaporation

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ABSTRACT
Pervaporation is a membrane separation process in which the feed liquid mixture to be separated is placed in contact with one side of a dense selective membrane, producing an enriched vapor permeate on the other side of the membrane. One of the applications of pervaporation is the removal and recovery of organic compounds from contaminated industrial wastewaters.

In the present work the separation and recovery of chloroform from synthetic wastewaters was investigated. Experiments were conducted in two hollow fiber modules, using polydimethylsiloxane (PDMS) as membrane material. The effect of the volumetric flow rate and the thickness of the membrane were investigated.

The viability of the removal of chloroform from wastewaters was assessed. The results were analysed according to the continuity mass conservation equation, determining that the design parameter is the diffusion coefficient of chloroform in the aqueous phase. The value of D at 40°C is 1.51*10^-9 m^2/s.

Key words: Chloroform/ pervaporation/ industrial wastewaters/ diffusion coefficient
INTRODUCTION

Chlorinated hydrocarbons are used in numerous industrial processes due to their high solvent capacity and low flammability\(^{(1)}\). The uses of the chlorinated solvents include cleaning processes and degreasing (trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane), solvent extraction (dichloromethane, chloroform, 1,1,1 trichloroethane), additives in coatings and adhesives (dichloromethane, 1,1,1-trichloroethane), raw materials in drug synthesis, pesticides and polymers, dyes and solvent media in chemical reactions (carbon tetrachloride, dichloromethane)\(^{(1,2)}\).

However, according to recent studies some of these compounds are suspected to be potent carcinogens in humans. Also some of them are involved in the reduction of the stratospheric ozone layer\(^{(1,3-5)}\). As a consequence, the use of several chlorinated hydrocarbons is now limited if not prohibited by the Montreal protocol and its Adjustments and Amendments, such is the case of 1,1,1-trichloroethane.

Through air emissions and wastewaters discharges, large volumes of VOCs are released to the environment. The contamination of groundwater and surface water by VOCs is a worldwide environmental problem.

The aqueous effluents containing chlorinated hydrocarbons are characterised by their low concentration due to the low solubility of these organic compounds in water. However, their low biodegradability makes them specially dangerous, since they are easily spread in the hydrological cycle\(^{(6)}\). Environmental regulations, such as the EC normative, restrict the maximum content of several chlorinated hydrocarbons in the effluents of different manufacturing processes: chloroform, carbon tetrachloride, 1,2-dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.

According to\(^{(7)}\) membrane separation has become one of the emerging technologies for VOCs control. Three membrane processes have been demonstrated to be effective for removal of VOCs from wastewaters. These include membrane air stripping, vacuum membrane distillation and pervaporation.

Compared to the conventional VOC control technologies such as activated carbon adsorption and air stripping, pervaporation process has the following advantages:

- Selective removal of small amounts of pollutants
- Effective for a whole concentration range
• Recovery of solvent
• Easy integration with existing processes to form hybrid processes.

In this work we investigate the applicability of pervaporation to the removal of chloroform from industrial wastewaters. In the pervaporation operation the feed mixture is maintained into contact with one side of a dense membrane and the permeate is continuously removed from the other side in vapor form by a vacuum pump. The separation is determined by selective sorption and diffusion of the organic compound through the membrane. The flux is driven by the vapor pressure difference of the solute across the membrane, being the efficiency of the separation determined by the physicochemical structure of the membrane. By using organophilic membranes, chloroform can be concentrated at the permeate side and recovered by condensation. The condensed permeate liquid can be separated into two phases due to the limited solubility of chloroform in water. The organic phase can be treated for reuse and the aqueous phase saturated with chloroform can be recycled to the feed stream for reprocessing.

The influence of the thickness of the polydimethylsiloxane membrane has been investigated, working with two different hollow fiber modules. The study on the effect of the feed flow rate in the pervaporation unit was done by varying the flow rate through the modules in the range 0.02-0.105 l/min. The mass transfer analysis of the chloroform removal in hollow fiber pervaporation devices has been performed using the continuity mass conservation equation in unsteady-state conditions. The diffusion coefficient of chloroform in water at 40°C has been determined.

**EXPERIMENTAL**

Two pervaporation modules were tested. The properties of the membrane modules are given in table 1. Dense polydimethylsiloxane hollow fibers obtained from Dow Corning (Silastic laboratory tubing) were used to assemble the membrane module in the laboratory. The feed solution was introduced through the bore side of the fibers. Two lateral openings were practiced in the glass shell in order to connect to the module the vacuum pump and a sensor for absolute pressure.

The experimental set-up is shown schematically in Figure 1. A standard pervaporation system obtained from Sulzer Chemtech was used, although several modifications were performed in order to improve its characteristics and to adapt the system to the hollow fiber module.
Table 1. Properties of the pervaporation module

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Polydimethylsiloxane, non-porous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Housing material</td>
<td>Glass</td>
</tr>
<tr>
<td>Sealant</td>
<td>Dow Corning 732</td>
</tr>
<tr>
<td>Length of the module, m</td>
<td>Module 1: 0.37</td>
</tr>
<tr>
<td></td>
<td>Module 2: 0.38</td>
</tr>
<tr>
<td>Inside diameter of the shell, m</td>
<td>4 x 10^{-3}</td>
</tr>
<tr>
<td>Inside diameter of the hollow fibers, m</td>
<td>3.05 x 10^{-4}</td>
</tr>
<tr>
<td>Thickness of the membrane wall, m</td>
<td>1.65 x 10^{-4}</td>
</tr>
<tr>
<td>Number of hollow fibers</td>
<td>Module 1: 15</td>
</tr>
<tr>
<td></td>
<td>Module 2: 7</td>
</tr>
<tr>
<td>Total membrane area, m²</td>
<td>Module 1: 0.053</td>
</tr>
<tr>
<td></td>
<td>Module 2: 0.053</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of the experimental set-up
Aqueous feed solutions were prepared in the laboratory using reagent grade chloroform (Probus) in deionized ultrapure water. The initial concentration of chloroform in the feed was 500 mg/l unless otherwise stated. Materials in contact with the synthetic wastewater were stainless steel while all seals were made of Teflon or Viton. The aqueous feed is introduced in a jacketed vessel with a capacity of 2 liters. The temperature of the feed is controlled by pumping through the jacket a heat carrier liquid from a constant temperature immersion circulator (Hakke, Germany). Experiments at temperature below 40 because of the energy added by the feed pump, using either tap water or a cryogenic bath (Polyscience digital temperature controller, model 9510). A centrifugal pump was used to recirculate the feed from the feed tank through the pervaporation unit. The feed was split into two streams. One stream was passed through the pervaporation unit while the second one was directly recirculated to the feed vessel, providing enough mixing without mechanical agitation. The feed flowrate through the membrane module was monitored using a rotameter. During the experiments, the feed side of the membranes was maintained at atmospheric pressure and a needle valve and a vacuum pump (Telstar 2P-3) controlled the downstream pressure. A pressure meter (1-180 mm Hg) was used to measure the downstream pressure. Permeate was collected in a cold trap, cooled with liquid nitrogen. The experiments were run batchwise over a time interval of at least 3 hours.

The pervaporation system is provided with a feed sampling valve, allowing the collection of a few milliliters of liquid samples at regular intervals of time. In order to minimize losses of the volatile chloroform the capillary spiral was immersed in a cooling fluid during the feed sampling and the first 10 ml of the feed sample were discarded. The permeate was collected, weighted and analyzed at the end of each experimental run.

The permeation flux of chloroform was determined by analyzing the feed samples by gas chromatography (Hewlett-Packard 6890 model) via an electron-capture detector. Aqueous samples were injected cool on column, using He as carrier gas at a constant flow of 2.6 ml/min. A retention gap 5 m in length (HP 19095-60610) was inserted before the semicapillary column (length 30 m, nominal diameter 530 μm, model HP 19095Z-123). The retention time of chloroform was 5.3 min. Calibration curves in the range of concentration 0-5 mg/l were prepared using standard solutions. A HP Chemstation performed integration and data treatment.
RESULTS

The study on the effect of the feed flowrate in the pervaporation unit was performed at 40-0.02-0.105 l/min. Figures 2 and 3 give the evolution with time of the dimensionless concentration of chloroform in the feed tank as a function of the feed flowrate in the two membrane modules under investigation.

It can be noticed that the yield of chloroform removal is considerably poorer at low feed flowrates. This fact demonstrates that the mass transfer resistance of the liquid boundary has a strong influence on the flux of chloroform.

Figure 2. Concentration courses in the feed tank when testing module 1. Influence of the feed flowrate. Feed temperature: 40
The analysis by means of the fundamental equations separates the effects of the operation variables such as the hydrodynamic conditions and the geometry of the system from the mass transfer properties of the system, described by the diffusion coefficient in the aqueous phase and the membrane permeability. Raghunath and Hwang* presented a similar analysis to describe the separation of benzene, chlorobenzene and toluene with PDMS hollow fibers, but solving the continuity equation under steady-state conditions.

The aqueous solution containing chloroform flows in fully developed, one-dimensional laminar flow. At \( z = 0 \), the fluid contacts the membrane. At this point the concentration of the solute is uniform and equal to \( C_o \). Chloroform removal takes place by diffusion through the solid PDMS membrane, as described in figure 4. Axial diffusion is neglected compared to axial convection. Under these approximations, the nonsteady-state mass conservation equation for the solute species and the associated boundary conditions will be
Figure 4. Schematic diagram of the system and hollow fiber

**Tank mass balance**

\[ \nu \frac{dC}{dt} = F(C_{in} - C) \]  
(1)

\[ t = 0 \quad C = C_{in} \]  
(2)

**Mixing point**

\[ (1 - \alpha)FC + \alpha FC_{z=L} = FC_{in} \]  
(3)

**Module mass balance**

\[ \frac{\partial C^m}{\partial t} + 2\nu \left[ 1 - \left( \frac{r_i}{r} \right)^2 \right] \frac{\partial C^m}{\partial z} = D \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial C^m}{\partial r} \right] \]  
(4)
B.C.1: \( t = 0 \quad C^m = C_0 \quad \text{for all } r \text{ and all } z \) (5)

B.C.2: \( z = 0, \quad C^m = C, \quad \text{for all } r \) (6)

B.C.3: \( r = 0 \quad \frac{\partial C^m}{\partial r} = 0, \quad \text{for all } z \) (7)

B.C.4: \( r = r_i \quad -D \frac{\partial C^m}{\partial r} = k_m \left( C_{\text{membrane}}^1 - C_{\text{membrane}}^2 \right), \quad \text{for all } z \) (8)

The fourth boundary condition imposes the continuity of flux of chloroform at the fluid/membrane interface. The left-hand side of the equation gives the solute flux arriving at the membrane wall from the bulk due to radial diffusion. The right-hand side of the equation accounts for the transport of solute through the membrane due to the diffusion in the solid PDMS. Assuming that the low pressure of the permeate side allows to consider \( C_{\text{perm}} = C^2_{\text{membrane}} = 0 \), when the membrane resistance to mass transfer is negligible the fourth boundary condition can be replaced by

B.C.4: \( r = r_i \quad C^m = 0, \quad \text{for all } z \) (9)

Equation (9) is valid when the pervaporation membrane shows a high affinity for the organic solute, as in the case of the polydimethylsiloxane-chloroform system(9).

The computer program yielded values for the solute concentration in the module as a function of \( r \) and \( z \). The bulk concentration of the flowing stream at the exit of the membrane module is calculated by averaging the concentration profile as

\[
C_{\text{mean}}^m(z = L) = \frac{\int_0^R v_z(r) C^m(r, L) r \, dr}{\int_0^R v_z(r) r \, dr}
\] (10)

Equations (1)-(10) can be solved simultaneously using the numerical integration package gPROMS (10,11). The values of the parameter \( D \) referring to the diffusivity of chloroform in the aqueous phase were obtained by comparing experimental with simulated results, using the weighted standard deviation as optimization function defined as

\[
\sigma_w = \sqrt{\frac{\sum_{i=1}^N \left( \frac{C_{\text{exp}} - C_{\text{sim}}}{C_{\text{exp}}} \right)^2}{N - 1}}
\] (11)

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Diffusivity values are shown in figure 5 as a function of the Reynolds number of the aqueous stream. As expected the parameter D remains nearly constant when changing the linear velocity of the fluid.

![Figure 5. Diffusivity of chloroform in water at 40](image)

It is also observed that the resulting value of D is the very similar in the two modules under investigation. The main difference among both modules is the thickness of the wall of the hollow fiber pervaporation membranes. Thus the initial assumption of negligible mass transfer resistance of the membrane (eq. 9) is confirmed, since the unique parameter D is found to be independent on the thickness of the membrane.

An average value of the diffusion coefficient at 40 

| Table 2. Diffusivity of chloroform in water, 40 |
|-----------------|-----------------|-----------------|
| $D_{av}$, Module 1 | $D_{av}$, Module 2 | $D_{WILKE\ CHANG}$ |
| $1.55*10^9$ | $1.46*10^9$ | $1.53*10^9$ |
CONCLUSIONS

It has been found that the removal of chloroform from wastewaters by means of pervaporation is a viable process. The initial concentration of 500 mg/l of chloroform in the feed was reduced to 150 mg/l in 150 min of batch operation. Experiments were conducted in hollow fiber modules, a membrane geometry that can provide high membrane area per volume of equipment ratios. The influence of the flow rate of the aqueous feed (0.02-0.105 l/min) and the thickness of the pervaporation membrane (1.65 x 10^-4 m and 2.79 x 10^-4 m) were investigated.

A mathematical model resulting from the solution of the continuity equation of the feed phase flowing in laminar regime through the hollow fiber module in unsteady-state conditions was proposed. The diffusivity of chloroform in aqueous solutions was the only parameter required to describe the separation rate values obtained at different flow rates and different temperatures.

The value of the parameter (D) at each membrane thickness was obtained from the comparison of experimental and simulated results with the proposed model, and the resulting value of the diffusion coefficients were compared to the values predicted by the Wilke-Chang correlation observing a good agreement. An averaged value D(40) = 1.51*10^-9 m^2/s was calculated.

It was found that the polydimethylsiloxane membrane does not exert an outstanding influence on the chloroform separation rate and that the resistance to mass transfer is located in the liquid phase.

LIST OF SYMBOLS

C: chloroform concentration in the feed tank, mol/m^3
C^n: chloroform concentration in the feed along the membrane module
C^a: concentration of the fluid at the entrance to the feed tank
C^o: initial chloroform concentration in the feed
D: diffusivity, m^2/s
F: total volumetric flowrate of the feed
$k_m$: membrane mass transfer coefficient

$N$: number of experimental points

$r$: radial coordinate

$r_i$: inner radius of the hollow fiber, m

$t$: time, s

$v$: average linear velocity of the fluid, m/s.

$v_a(r)$: axial velocity of the fluid inside the hollow fiber, m/s

$V$: volume of the feed, m$^3$

$z$: axial coordinate

**Greek letters**

$\alpha$: portion of the total volumetric flowrate that circulates along the module ($0 < \alpha < 1$)

$\alpha_w$: weighted standard deviation.

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**REFERENCES**


