



Assessment of semi-empirical mass transfer correlations for pervaporation treatment of wastewater contaminated with chlorinated hydrocarbons*

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Abstract: Assessment of mass transfer characteristics of pervaporation (PV) treatment of wastewater contaminated with chlorinated hydrocarbons is of great importance for water treatment plant operators conducting initial evaluation, process optimization, and process economics. While a membrane plays a central role in pervaporation processes and separation efficiency, the mass transfer in the liquid layer next to the membrane surface is of equal, if not greater importance. It is one of the few process parameters that can be adjusted in situ to manipulate the outcome of a pervaporation process. In this study, a bench scale pervaporation experiment of removing a common chlorinated hydrocarbon from water was carried out and the results of it were compared to the ones based on well-known semi-empirical correlations. The mass transfer coefficients from the experiments, ranging from 0.8×10^{-5} ~ 2.5×10^{-5} m/s under the operating conditions, are higher than those predicted by the correlation. The corresponding separation factors under varying flow velocities are determined to be between 310~950.

Key words: Chlorinated hydrocarbon, Mass transfer, Pervaporation, Wastewater treatment

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INTRODUCTION

Chlorinated hydrocarbons, a class of widely used dry-cleaning liquids, industrial organic solvents, and degreasers, increasingly find their way into drinking water sources, thus posing a very serious health and environmental problem (Love and Eliers, 1982). These organic solvents are known for their stability in the environment and cancer-causing potency and cannot be effectively and economically eliminated by current conventional treatment technologies. One of the few available techniques for removing chlorinated hydrocarbons from water involves the use of activated carbons. However, the process requires expensive re-generation process and,

sometimes merely turns a water pollution issue into a potential air pollution problem that has to be dealt with later when the air-stripping re-generation of activated carbons is considered. Naturally, researchers have been looking for solutions with membrane-based technologies, while in general, are energy efficient and compact/modular, which make them very easy to be integrated into existing water treatment processes. One currently promising membrane technology for removing chlorinated hydrocarbons is pervaporation (Dotremont *et al.*, 1993; Pereira *et al.*, 1998; Hunter and Oyama, 2000).

Pervaporation is a membrane separation process with a non-porous and permeation-selective membrane that allows solutes like chlorinated hydrocarbons in aqueous solution but limiting water to penetrate through the membrane, thus achieving material separations. The term is a contraction of the words of permeation and evaporation, which roughly describes

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two intertwined sub-processes working together to attain overall enrichment of one or more preferentially permeating species such as chlorinated hydrocarbons on the opposite side of the membrane. Pervaporation commences when a liquid stream containing two or more species is 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 upon exiting the membrane. The vapor is subsequently condensed and collected. Pervaporation is probably one of very few membrane processes where the state of the feed is different from that of the permeate on the other side of the membrane (liquid feed in and vapor permeate out). This unique characteristic indicates two important factors that are crucial for understanding pervaporation. One is that the process involves a phase change somewhere within or, as the authors believe, at the interface of the membrane and vapor phase on the permeate side of the membrane. The other is that the vapor pressure of the solute (e.g., chlorinated hydrocarbon) is higher than that of the background, the solvent (water). The former foretells the importance of feed temperature, rate of mass transfer of the solute in the membrane matrix, and the extent of partitioning of the solute between water phase and the membrane phase. And the latter determines how well the separation is achieved, which is summarized as selectivity of the process. Selectivity of and permeation flux of the solute are two key operational parameters for evaluating pervaporation process performance. The permeation flux is defined as:

$$J_i = k_i \rho_i (C_i^L - C_i^V), \quad (1)$$

while selectivity of the solute in PV is commonly expressed as separation factor, α :

$$\alpha_{ji} = \frac{(C_i/C_j)^V}{(C_i/C_j)^L}, \quad (2)$$

where k_i , ρ , C_i^L , and C_i^V are the overall mass transfer rate constant, density of feed, bulk liquid phase concentration (mass fraction), and bulk vapor phase concentration, respectively, for component i (Peng *et al.*, 2003). The separation factor, α , is analogous to

the relative volatility of the component (i and j) of a binary liquid mixture. Eq.(1) can be further simplified for chlorinated hydrocarbon removal from water since concentrations of these chemicals in water are in ppm scale due to their very low water solubility, thus C_i^V is very small:

$$J_i = k_i \rho_i (C_i^L). \quad (3)$$

Previous experimental studies have corroborated the above simplification (Jiang *et al.*, 1997). The linear relationship between J and C^L indicates that the mass transfer coefficient, k , is not concentration-dependent, thus highlighting the importance of k in the assessment of characteristics of mass transfer in a pervaporation process, which is the focus of this study.

The mass transfer coefficient, k , is in fact an overall quantity that encompasses mass transfer coefficients in the membrane matrix and in the thin layer of liquid next to the membrane surface, often called the liquid boundary layer. By the definition of mass transfer coefficient, resistance to the mass transfer would be proportional to the reciprocal of the mass transfer coefficient, i.e., $1/k$. Under the steady state of PV operation, the following relation emerges:

$$\frac{1}{k_{ov}} = \frac{1}{k_b} + \frac{1}{k_m}, \quad (4)$$

where superscripts ‘ov’ and ‘b’ stand for “overall” and “boundary layer”, respectively. Eq.(4) is the well-known resistances-in-series model that is analogous to the one for heat conduction through different layers of materials with different thermal conductivities. The mass transfer coefficient in the membrane, k_m , is a very complex parameter that cannot be described precisely and confidently (it is related to many factors such as properties of the solute, properties of the polymer material and fillers in the membrane, structural characteristics of the membrane, temperature, permeate pressure, and so on). Many models (empirical, semi-empirical, and theoretical) have been proposed and none of them has been proven to be general enough to be useful. For a good survey of these models, a recent review paper is worth mentioning (Lipnizki and Trägårdh, 2001). The mass transfer coefficient, k_b , is a relatively “simple” pa-

parameter that is determined primarily by hydrodynamics in the boundary layer and permeation rate of the solute through the membrane. It is the parameter that can actually be “altered” by water treatment plant operators through varying certain operating conditions. The mass transfer coefficient, k_b , is mainly a function of flow velocity in the membrane module and diffusion coefficient of solute in the solution (Mulder, 1991) and can be expressed with semi-empirical expressions depending on flow regimes. Mulder (1991) gave the following relationships for a membrane channel:

$$\frac{k_b d_h}{D} = 1.85(Re \times Sc \times d_h / L)^{0.33} \text{ in laminar flow, (5)}$$

and

$$\frac{k_b d_h}{D} = 0.04 Re^{0.75} Sc^{0.33} \text{ in turbulent flow, (6)}$$

where Sc is Schmidt number and equal to ν/D ; Re is equal to $d_h v / \nu$; $d_h = 2Wh / (W+h)$. In these relationships, ν is kinematic viscosity, v is flow velocity, W is width of the channel, and h is height.

The objective of this paper was to assess the validity of the popular semi-empirical dimensionless correlations as shown in Eqs.(5) and (6) describing the mass transfer in the boundary layer of a pervaporation unit. These correlations are widely adopted for describing and scaling up several other membrane-based processes with “channel” configurations. The mass transfer coefficients were evaluated as a function of feed velocity with other operating conditions preset at constant values. The velocity was controlled so that the flow was within a laminar flow regime. Laminar flow regime is of particular importance because of the prevalence of such flows in several PV modules used in both lab and industrial scales that favor laminar flow for economical reasons. Additionally, mass transfer in laminar flows is easier to describe mathematically than that in turbulent flows.

MATERIALS AND METHODS

Materials

1,1,1-Trichloroethane (TCA) was used as a model chlorinated hydrocarbon: 99.5%, ACS reagent,

Sigma-Aldrich Company (Milwaukee, WI, USA), used as received. Methanol (GC grade) was procured from Fisher Scientific (Suwanee, GA, USA). Hydrophobic PDMS, also known as silicone rubber, flat sheet membrane (2-mm thickness) was acquired from Specialty Manufacturing Inc. (Saginaw, MI, USA).

Experiment setup and operating procedure

The diagram of the experiment setup is shown in Fig.1. A laboratory scale flat sheet membrane module with effective dimensions of the membrane holding cell of 2.4 cm by 16.4 cm, yielding an effective area of 39.36 cm², was used for all our experiments. Feed solutions first went through a heat exchanger to reach a steady temperature (30 °C unless otherwise stated) before entering the membrane module. The flow rate was controlled and indicated by a flow meter. Two cold traps were installed in parallel for condensing and collecting the vapor stream. The vacuum was kept between 0.266~0.400 kPa. Thermocouples were used for measuring temperatures of feed (before and after module) and vapor. A pressure sensor monitored pressure at the downstream. After about 3 h of initial operation, the steady-state separation was reached. The concentrations of feed and permeate samples were analyzed by GC. At the end of each run, the cold trap was taken out, capped, and stabilized in a draft cabinet for 2 min to remove condensed moisture at the out surface. The permeate was then weighed, diluted with methanol, and then transferred to a 10 ml volumetric flask. For each set of the operating parameters, two runs were performed to get replicate results.

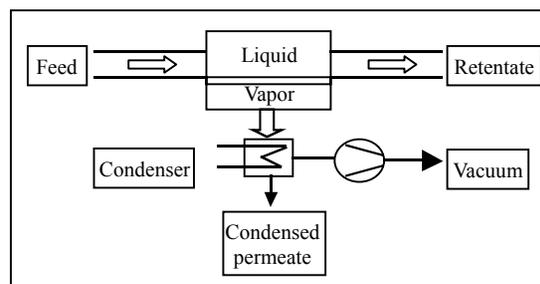


Fig.1 Schematic diagram of the experimental setup for PV experiments

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 psig 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.

RESULTS AND DISCUSSIONS

The results are presented in Fig.2 and Fig.3. The main focus of this research was on mass transfer occurring under laminar flow regime. However, the deviation of experimental results from the semi-empirical correlation [Eq.(5)] led to further investigations into transitional flow regime. In Fig.2, mass transfer coefficients calculated from the experimental data were compared with those of the empirical correlation results as described in Eq.(5). In the laminar flow mode, where the Re was below 2000, the experimental results showed reasonable agreement with the semi-empirical correlation. The range of the values of mass transfer coefficients in this flow pattern, i.e., from 0.81×10^{-5} to 2.1×10^{-5} m/s was at the high end of mass transfer coefficients in most PV experiments for organic solutes (Peng *et al.*, 2003). The experiments conducted under Re over 2000 showed that the mass transfer coefficients surpassed the values obtained from the semi-empirical correlation for laminar flow by almost 50%. Interestingly, the results were not up to the prediction by the semi-empirical correlation for turbulent flow regime [Eq.(6)]. Although it was initially intended to find a demarcation line where the turbulence would bring a sharp increase in mass transfer, the PV unit used in this research could only allow an average velocity of no more than 0.48 m/s, which is far short of a velocity that ascertains a definite turbulent flow. In this transitional flow regime, the mass transfer coefficients did not behave erratically when subject to different runs of experiments. This may imply that the process could be better described by a new correlation differing from both Eq.(5) and Eq.(6). When a statistical regression was performed with the experimental re-

sults, it was found that the mass transfer coefficients could be correlated to velocity (or Re) raised to the power of 0.46. This seems to give better predictions than those widely adopted semi-empirical correlations under laminar and turbulent flow regimes.

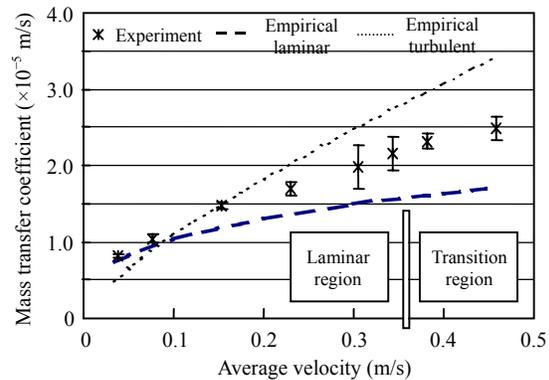


Fig.2 Mass transfer coefficients varied with feed velocity: semi-empirical correlations (laminar and turbulent) and experimental data

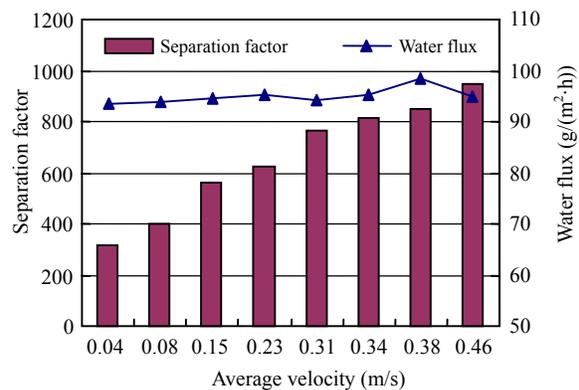


Fig.3 Separation factor and water flux under different velocities

As stated in the introduction, the overall mass transfer coefficient actually encompasses the effects of all the contributing factors influencing PV separation processes. The PV unit used in the experiments contained two turning angle at the entrance and outlet (155 mm length, 2 mm length module height), therefore introducing some extra motions for mass transfer at both entrance and outlet. This could partly explain the deviation observed in the experiments from Eq.(5). However, this could also be a result of underestimation of mass transfer coefficient by the semi-empirical correlations that were developed ini-

tially not for membrane-based separations. A more insightful fundamental study of the hydrodynamics in the boundary layer of a pervaporation membrane module and its effect on the mass transfer coefficient in the layer is needed. Currently, a detailed study of hydrodynamic effect is being carried out by the authors using computational fluid dynamics (CFD) approach and will be reported in the near future.

The relationship between the mass transfer coefficient in the boundary layer and overall mass transfer coefficient deserves further discussion. The previous analysis on the data was based on the assumption that the membrane resistance was negligible (fast permeation rate), and accordingly mass transfer resistance in the boundary layer can approximately be equal to the overall resistance. It has been demonstrated in literature that PDMS shows a high degree of compatibility (permeability) with chlorinated hydrocarbon in the range of $0.9 \times 10^{-8} \sim 50 \times 10^{-8} \text{ m}^2/\text{s}$ for permeability (permeability is equal to the product of mass transfer coefficient in the membrane and membrane thickness). As the PDMS membrane used in our experiments was 2 mil ($5.08 \times 10^{-5} \text{ m}$), the mass transfer coefficient for the membrane material can be calculated as in the range of $1.8 \times 10^{-4} \sim 9.8 \times 10^{-3} \text{ m/s}$, which is far larger than those obtained from the experiments, therefore validating the assumption of negligible membrane resistance and the boundary-layer resistance representative of the overall mass transfer resistance. When the resistance in the feed side boundary layer limits mass transfer for a membrane process, the phenomenon is termed as concentration polarization and the operating parameters (mainly feed flow rate for a given membrane module) are considered to be of particular importance to overall efficiency of a PV separation process (Psaume *et al.*, 1988; Michaels, 1995).

The PV separation effectiveness is expressed by separation factor rather than by solute flux as the latter is directly affected by feed concentration. As shown in Fig.3, the increase in feed velocity from 0.04 m/s to 0.46 m/s increased separation factor for TCA from 310 to 950, which means 3 fold increase for the solute permeate with the same feed solution. The water flux during this feed velocity range showed relatively constant value of around $95 \text{ g}/(\text{m}^2 \cdot \text{h})$, indicating that the hydrophobic membrane matrix was structurally stable and did not undergo swelling

changes at the TCA concentration used in our experiments. Water flux is usually stable under a fixed operating temperature and barring extreme feed concentrations. When operating temperature is increased to increase the flux of target solute compounds, water flux usually will also increase at a higher rate, therefore leading to a decreasing separation factor although the solute flux was nevertheless increased.

CONCLUSION

Experiments carried out in the lab scale PV unit demonstrated the pervaporative mass transfer characteristics of a chlorinated hydrocarbon in the aqueous solution and shed some light on the usefulness of some widely adopted semi-empirical correlations for channel-form membrane modules. It was found that the correlations were generally in unremarkable agreement with the experimental data generated from a lab scale flat-sheet pervaporation membrane module commonly used for membrane evaluation and process assessment. As in the cases of other membrane process studies, the semi-empirical correlations, which have their roots in heat conduction in simple flow channel geometry, once again underestimated the mass transfer in the flow channel of a PV module. This study provides yet another argument for detailed study of hydrodynamics in the membrane module using computational fluid dynamics (CFD) simulation. Current computing power and numerical method research and enhancement should provide sufficient resources to process designers and plant operator to carry out this type of research in process evaluation and optimization.

The mass transfer coefficients were observed to fall between $0.8 \times 10^{-5} \sim 2.5 \times 10^{-5} \text{ m/s}$ in the tested flow velocity range that covered from laminar to transitional regions corresponding to Re of 200~2500. The relatively mild deviation of the observed experimental results from those from the empirical correlation supported the use of the general correlation when detailed analysis of hydrodynamics is not available. In large-scale pervaporation operations employed in environmental cleanup, process design and improvement based on the empirical correlation of pervaporative mass transfer coefficient ought to be

equally valid since the edge effects of a large membrane module imposes proportionally smaller distortion on calculations of overall mass transfer coefficients that typically ignore edge effects than those of a laboratory-scale one.

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