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Mass transport in the membrane air-stripping process using microporous polypropylene hollow fibers: effect of toluene in aqueous feed[☆]

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Abstract

Membrane air-stripping (MAS), using microporous polypropylene hollow fiber membrane modules, is one of the most promising processes for removal and recovery of volatile organic compounds (VOCs) from water/wastewater. In this work, aqueous feed containing VOCs was allowed to cross-flow on the shell side, whereas air flowed through the lumen of fibers. Chloroform, toluene and their mixture were used as model VOCs. The effects of presence of toluene alone and in mixture with chloroform in aqueous feed on the mass transport of VOCs through the membrane are reported. It was found that Henry's law constants (HLCs) for toluene as well as chloroform did not change significantly in mixtures. The tests showed that higher toluene adsorption than that of chloroform on the fibers. It appeared that toluene blocked the pores partially, due to its strong affinity for the membrane material, resulting in substantially reduced mass transport.

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Keywords: Membrane air-stripping; Organic separations; Water treatment; Microporous membranes; Partitioning

1. Introduction

Conventional treatment methods for removal and recovery of volatile organics include air-stripping,

adsorption, advanced oxidation, anaerobic/aerobic biological methods and distillation. All these techniques, in general, have at least one major disadvantage [1] and have been reviewed in detail by Mahmud et al. [2]. Liquid-phase adsorption is economical only at low part per billion (ppb); volatile organic compound (VOC) concentrations due to the high cost of adsorbent replacement and/or regeneration, while distillation is economical only at higher VOC concentrations. The effectiveness of advanced oxidation is compound dependent and it can form new products that could be more harmful than the original ones. Packed-tower aeration (PTA) is the most economical and hence the most widely used process for removal

Abbreviations: CI, confidence level; HLC, Henry's law constant; GC(P&T), gas chromatograph (Purge & Trap); GC6890, gas chromatograph (HP 6890 series); MAS, membrane air-stripping; ppb, parts per billion; ppm, parts per million; PTA, packed-tower aeration; TC, total carbon; TOC, total organic carbon; VOC, volatile organic compound

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Nomenclature

a	surface to volume ratio (m^2/m^3)
C_V	coefficient of variance
C^*	liquid-phase concentration that would be in equilibrium with the air phase concentration (ppm)
C_{aa}	concentration of the VOC in the system after adsorption (ppm)
C_{ba}	concentration of the VOC in the reservoir before adsorption (ppm)
C_f	final concentration of the loss test after 24 h (ppm)
C_i	initial concentration of the loss test (ppm)
C_o	estimated initial concentration of the VOC in the liquid-phase after loss (ppm)
C_t	VOC concentration in the reservoir at time t (ppm)
C_0	VOC concentration in the reservoir at time 0 (ppm)
C_1	measured initial concentration (ppm)
d_i	inner diameter of the hollow fiber (ppm)
d_o	outer diameter of the hollow fiber (m)
D_w	diffusion coefficient of compound in water (m^2/s)
D_c	continuum (ordinary) diffusion coefficient of compound in air phase (m^2/s)
D_{eff}	effective diffusion coefficient of compound in air (m^2/s)
D_{Kn}	Knudsen diffusion coefficient of compound in air (m^2/s)
H	dimensionless Henry's law constant
h	length of the hollow fiber module compartment (0.5 l) (m)
k	rate constant (min^{-1})
k_a	local air-phase mass transfer coefficient (m/s)
k_L	local liquid-phase mass transfer coefficient (m/s)
k_m	membrane mass transfer coefficient (m/s)
K_{La}	overall volume specific mass transfer coefficient (h^{-1})
K_L	overall liquid-phase based mass transfer coefficient (m/s)
L	hollow fiber length (m)
Q_a	air flow rate (m^3/s)

Q_w	water flow rate (m^3/s)
r_{in}	outer radius of the center tube (m)
r_{out}	inner radius of the membrane module (m)
R	stripping factor = $Q_w/Q_a H$
Re	Reynolds number ($d_o u^w/\nu$)
Sc	Schmidt number (ν/D_w)
Sh	Sherwood number ($k_L d_o/D_w$)
t	time (s)
u^a	air velocity in the lumen of the hollow fiber (m/s)
u^w	aqueous solution velocity on the shell side of the hollow fiber (m/s)
V_a	volume of the air (m^3)
V_L	volume of the liquid (m^3)
V_T	total volume of solution in the system (m^3)
V_w	reservoir volume (m^3)
X	equilibrium mass concentration of the component in the air phase (ppm)
x	fraction of the pore filled with air
$(1 - x)$	fraction of the pore filled with water

Greek letters

δ	pore length, m
ε	fiber porosity (dimensionless)
ν	kinematic viscosity of air/water (m^2/s)
τ	pore tortuosity (dimensionless)

of ppb levels of VOCs from drinking water and regarded as the best available technology (BAT) for the purpose. However, in many cases PTA needs off gas treatment before releasing to the atmosphere. Thus, PTA is not very effective at higher VOC concentrations and recovery of VOC is difficult due to the requirement of high air-to-water ratio. Large size of PTA also makes it unacceptable in populated areas. A part of the VOCs is air stripped during aerobic biodegradation process [3]. In addition to these conventional technologies, there has been active research on membrane processes, such as membrane pervaporation, membrane distillation and membrane air-stripping (MAS), for the removal/separation/concentration of organics from aqueous solution [4–14].

Separation of VOCs from liquid streams by MAS is being considered as an alternative that may help

The objective of the present study, was to evaluate the simultaneous removal of an aromatic and a halogenated aliphatic compound at parts per million (ppm) concentration levels. Chloroform, toluene and their mixture were used as model VOCs. This paper presents, the effect of the presence of toluene alone and in mixture with chloroform in aqueous feed on the mass transport of VOCs through the microporous polypropylene hollow fiber membranes during MAS. This paper also provides the results from the adsorption tests on toluene and chloroform on the polymer surfaces as well as experimentally determined values for Henry's law constant (HLC) of the VOCs.

Mass transfer fundamentals for the transport of VOCs in MAS systems have been reviewed in detail by Mahmud et al. [2,5]. VOCs are transferred from water to air through intimate contact of the two phases at the mouth of the air-filled pores. The driving force for the mass transfer is the difference in concentration between the two phases.

aqueous solution across the liquid boundary layer to the membrane surface. Second, it diffuses through the air-filled pores. This diffusion step does not exist in packed-tower air stripping. Third, it diffuses through the air boundary layer outside the membrane into the stripping air. Thus, the overall mass transfer resistance is the combined effect of these three separate mass transfer resistances. As mass transfer resistances are considered to be proportional to the inverse of the corresponding mass transfer coefficients, the overall liquid-phase based mass transfer resistance ($1/K_L$) can be expressed as follows:

where K_L is the overall liquid-phase based mass transfer coefficient (m/s), k_L the local liquid-phase mass transfer coefficient (m/s), k_a the local air-phase mass transfer coefficient (m/s), k_m the membrane mass transfer coefficient (m/s), H the dimensionless HLC, i.e. a ratio of the mass concentrations.

The local liquid-phase mass transfer coefficient, k_L , can be predicted based on the following correlation developed by Kreith and Black [15] for cross-flow in closely packed tube bank heat exchangers

where Re is the Reynolds number ($d_o u^w / \nu$), Sh the Sherwood number ($k_L d_o / D_w$), Sc the Schmidt number (ν / D_w), d_o the outer diameter of the hollow fiber (m), u^w is aqueous solution velocity on the shell side of the fibers as given by Eq. (7) (m/s); ν the kinematic viscosity of water (m^2/s), D_w the diffusion coefficient of compound in water (m^2/s).

The air phase mass transfer coefficient, k_a can be estimated by using a correlation for laminar flow in a cylindrical tube [16–18]. In this work, the following equation, derived from Lvque’s [16] correlation, is used by incorporating HLC, as the boundary layer is gaseous

$$\frac{1}{k_a H} = \frac{0.617}{H} \left(\frac{L d_i}{u^a D_c^2} \right)^{0.33} \quad (3)$$

where u^a is the air velocity inside the hollow fiber (m/s), d_i the inner diameter of the hollow fiber (m), L the length of fiber (m), D_c continuum (ordinary) diffusion coefficient of compound in air (m^2/s).

Membrane mass transfer coefficient, k_m can be predicted using the equations developed by Mahmud et al. [5], Qi and Cussler [19] or Kreulen et al. [20]. In this work, the equation developed by Mahmud et al. [5] has been used as the pores appeared to be partially air filled and partially water filled [5,21]

$$\frac{1}{k_m H} = x \frac{\delta \tau}{D_{\text{eff}} \varepsilon H} + (1 - x) \frac{\delta \tau}{D_w \varepsilon} \quad (4)$$

where x is the fraction of the pore filled with air, $(1-x)$ the fraction of the pore filled with water, δ the pore length (m), D_{eff} the effective diffusion coefficient of compound in air (m^2/s), τ the pore tortuosity (dimensionless), ε the fiber porosity (dimensionless).

The estimation of the experimental overall mass transfer coefficient for the batch MAS system has been reviewed by Mahmud et al. [2]. According to this review, the change of organic concentration of the solution in a completely mixed reservoir of a batch MAS system with time, can be described by the following linear relationship [12]:

$$\ln \left(\frac{C_0}{C_t} \right) = kt \quad (5)$$

where C_0 is the VOC concentration in the reservoir at time 0 (ppm), C_t the VOC concentration in the reservoir at time t (ppm), k the rate constant (min^{-1}). A value of the rate constant, k is obtained, using Eq. (5), as the slope of the plot of $\ln(C_0/C_t)$ versus t . Substituting the value of k in the following equation will provide the overall liquid-phase based mass transfer coefficient, K_L , for the system when air and liquid solution streams are on the lumen and shell side, respectively [2]

$$K_L = \frac{u^w}{aL} (1-R)^{-1} \ln \left\{ \left[\frac{Q_w}{(Q_w - V_w k)} \right] (1-R) + R \right\} \quad (6)$$

where L is the effective length of the fiber (m), a the surface to volume ratio (m^2/m^3), R the stripping factor, $Q_w/(Q_a H)$, V_w the volume of the solution in the reservoir (m^3), Q_w the solution flow rate (m^3/s), Q_a the air flow rate (m^3/s).

The values for the parameters in Eq. (6) are available numerically from the experiments. The only exception is R , as it depends on H , which was obtained experimentally at $23.0 \pm 0.2^\circ\text{C}$. The water velocity outside the hollow fiber, u^w for the present study was estimated using the following equation [5]:

$$u^w = \frac{(Q_w/2\pi h)(1/(r_{\text{out}} - r_{\text{in}})) \ln(r_{\text{out}}/r_{\text{in}})}{\text{void fraction}} \quad (7)$$

where h is the length of each compartment, half of L (m), r_{in} the outer radius of the center tube (m), r_{out} the inner radius of the membrane module (m).

3. Experimental

Materials for this study were of analytical grade and were used without further modification. Chloroform and toluene with purity of 99.8% (BDH Inc., Toronto, ON, Canada) were used to prepare the feed solutions and the standards for the gas chromatographs. The diffusion coefficients of the compounds used in this study are given in Table 1.

3.1. Analytical equipments

Three types of analyzers were used to analyze the samples: (a) a total organic carbon (TOC) analyzer (Model TOC-5050, Shimadzu Corporation, Kyoto, Japan) equipped with an auto-sampler (Model ASI-5000, Shimadzu Corporation, Kyoto, Japan) was used to quantify the VOC concentration in the samples collected from experiments involving aqueous solutions

Table 1
Physicochemical properties of compounds used in this study

Compound	Temperature (°C)	$D_c \times 10^5$ (m^2/s)	$D_{\text{Kn}} \times 10^4$ (m^2/s)	$D_w \times 10^9$ (m^2/s)
Chloroform	23	0.923 ^a	2.29 ^b	0.893 ^c
Toluene	23	0.816 ^a	2.61 ^b	0.855 ^d

^a D_c , continuum diffusion coefficient of the component in air phase, calculated using the correlation given by Fuller et al. [22].

^b D_{Kn} , Knudsen diffusion coefficient, calculated using the correlation given by Cussler [23].

^c Diffusion coefficient of chloroform in water, calculated using the correlation given by Wilke and Chang [24], multiplied with a factor of 0.9 to match the observed deviation by Smith et al. [25] and Roberts and Dändliker [26].

^d Diffusion coefficient of toluene in water, calculated using the correlation given by Wilke and Chang [24].

of a single VOC. The total carbon (TC) values were directly converted to chloroform or toluene concentrations by multiplying TC values by a factor of 9.9483 or 1.10, respectively. (b) A gas chromatograph (Purge & Trap) GC(P&T), referred to as GC(P&T) hereafter, included a gas chromatograph (Varian—Vista Series 6000, Varian Instrument Group, Walnut Creek Division, Walnut Creek, CA) that had a flame ionization detector (FID), a packed column (Carbopack B 60/80 Mesh, 1% SP-1000, 8 ft by 1/8 in. SS, Supelco Canada Ltd., Oakville, ON) and to which a liquid purge and trap sample concentrator (Tekmar- LSC -2, Tekmar Company, Cincinnati, OH) and an integrator (Waters 820 Chromatography Data Station, Water Chromatography Division, Millipore Corporation, Milford, MA) were attached. (c) A gas chromatograph (HP 6890 series GC System, Hewlett-Packard, Wilmington, DE), referred to as gas chromatograph (HP 6890 series) (GC6890) hereafter, had a FID, a capillary column (SPB-5, 30 m $\times$ 0.53 mm, 1.5 μ m film, Supelco Canada Ltd., Oakville, ON) and was connected to an integrator (HPGC Chem Station, Hewlett-Packard, Wilmington, DE). For analysis by GC6890, the VOCs were extracted in *n*-pentane before injection into the GC column.

3.2. Removal of VOCs from aqueous solution by MAS

The MAS experimental setup included a reservoir (volume = $6.675 \times 10^{-3} \text{ m}^3$), a hollow fiber membrane module, an aqueous solution feed circulation line and an air-stripping line. The shell side of membranes was kept in contact with the aqueous phase for 48 h prior to the start of the tests to reach a steady wet state. The detailed description of the setup and the method of testing are given elsewhere [5]. A Liqui-Cel[®] Extra- Flow 2.5 in. $\times$ 8 in. laboratory-scale membrane contactor (Separation Products Division, Hoechst Celanese Corporation, Charlotte, NC, USA), made of polypropylene microporous hollow fibers (Celgard, Hoechst Celanese Corporation, Charlotte, NC, USA) was used.

The samples were collected from the reservoir for analysis every 10 min in the beginning of each run but the interval was increased at later stages. Stripping airflow rates were varied from 3.33×10^{-5} to $8.33 \times 10^{-5} \text{ m}^3/\text{s}$, while the liquid flow rate was kept

constant at $3.33 \times 10^{-5} \text{ m}^3/\text{s}$. Initial chloroform and toluene concentrations in the feed solutions were 680 ± 30 and $170 \pm 30 \text{ ppm}$, respectively when MAS tests were conducted with a solution of single VOC. The temperature of the solution as well as the air was kept at $23.0 \pm 0.2^\circ\text{C}$. The pressure drops for the air side and solution side were 1.2–3.0 and 10.0 kPa, respectively. The total duration of a typical test was 160 min.

A TOC analyzer was used to quantify the VOC concentration in the samples collected from MAS tests involving aqueous solutions of a single VOC. Periodically, samples were also analyzed using both TOC analyzer and GC(P&T) or GC6890 to identify any compounds other than chloroform or toluene in the solution and to know their contribution to the TC values. It was observed from the GC analysis that the peak related to organic impurities in samples containing chloroform as single solute, remained unchanged from the beginning to the end of a run. No other compounds were detected in the aqueous solutions of toluene single solute tests. The samples collected from the tests with binary mixtures of VOCs were analyzed by GC6890 only.

3.3. Determination of Henry's law constants

Although HLCs can be determined by many experimental methods [27–31], the method proposed by Munz and Roberts [28] was used in this study. According to this method, *H* is determined directly by the measurement of the liquid-phase concentration of a VOC that is in equilibrium with the air phase in a closed system. Gas tight syringes (Hamilton Co., Reno, NV) adapted with “Luer Lock” plugs were used for this experiment. The plugs were prepared by bending “Luer needles”. The 10 ml of stock solution was transferred into a syringe. The solution was left in the syringe for 1 h before determining its concentration, which was recorded as measured initial concentration, C_1 . Then, the solution volume in the syringe was reduced to 5 ml. Subsequently, 5 ml of air was introduced into the syringe. A 24 h period was allowed to reach the equilibrium. During this period, the syringes were shaken four times, for 2 min at each time. The liquid-phase VOC concentration was measured after the 24 h equilibration period and was recorded as the equilibrium concentration, C^* .

Although, the syringes were gas tight, the possibility of losses of VOCs during this 24 h period should not be ignored [32,33]. To take into account any loss of VOCs from the syringe during this 24 h period, loss tests were conducted [21]. C_i was multiplied by the ratio of C_f/C_i to obtain the estimated initial concentration, C_o . Where, C_i and C_f are the initial concentration and the final concentration of loss test, respectively. This ratio accounts for the loss of VOCs in the syringe.

The mass balance of the VOC for the system could be expressed as follows:

$$C_o V_L = C^* V_L + X V_a \quad (8)$$

where C_o is the estimated initial concentration of the VOC in the liquid-phase (ppm), V_L the volume of the liquid (m^3), C^* the liquid-phase concentration that would be in equilibrium with the air phase concentration after 24 h (ppm), X the equilibrium mass concentration in the air phase (ppm), V_a the volume of the air (m^3).

Solving the above equation for X and substituting in the following Eq. (9), which is a dimensionless form of HLC based on mass concentrations, developed by Munz and Roberts [28] and Roberts and Levy [34] will yield Eq. (10)

$$H = \frac{X}{C^*} \quad (9)$$

$$H = \frac{(C_o - C^*) V_L}{C^* V_a} \quad (10)$$

As $V_L = V_a$, the above equation can be rewritten as:

$$H = \frac{C_o}{C^*} - 1 \quad (11)$$

Thus, only initial and equilibrium liquid-phase concentrations were needed for calculating H . The chloroform samples were analyzed by the TOC analyzer. The toluene samples were analyzed by the GC6890. Experiments for binary chloroform/toluene solutions were conducted by the same methods. The samples were analyzed via the GC6890 analyzer.

3.4. Adsorption tests

Adsorption tests were conducted to determine the amount of VOC adsorbed on the polymer surfaces that were in contact with the feed solution. The experimental steps are mentioned as follows:

- The total volume of the liquid in the system, which includes the reservoir, the pump, the rotameter, the shell side volume of module, connecting tubes and valves, was first determined to be $7.03 \times 10^{-3} m^3$.
- Module air inlet and outlet were sealed tight with glass plugs to avoid any air circulation.
- The system was filled with water, which was circulated in the system for some time.
- The circulation of water was stopped. Feed circulation line's inlet and outlet valves were closed, thus the pump, the rotameter, the module and the connecting tubes were isolated from the reservoir. Then, the water from the reservoir was partly drained.
- A VOC solution was prepared in a separate flask and was transferred to fill the reservoir (volume of the reservoir was $6.675 \times 10^{-3} m^3$). The solution was stirred with a magnetic stirrer. A sample was collected from the reservoir for analysis.
- The reservoir was connected to the system by opening the valves. The solution was circulated in the system for 60 min. The final sample was collected from the reservoir for analysis.

Samples were analyzed by a TOC analyzer when the adsorption tests were conducted for chloroform, while the GC6890 gas chromatograph was used when tests were conducted for toluene. Experiments were conducted at four different concentrations for each VOC at $23 \pm 0.2^\circ C$.

The mass of the VOCs adsorbed on the polymer surfaces were calculated via a mass balance

$$\text{mass of VOC adsorbed} = C_{ba} V_w - C_{aa} V_T \quad (12)$$

where C_{ba} is the concentration of the VOC in the reservoir before adsorption (ppm), C_{aa} the concentration of the VOC in the system after adsorption (ppm), V_T the total volume of solution in the system (m^3).

4. Results and discussion

4.1. Results from adsorption tests

The results from the chloroform and toluene adsorption tests are shown in Fig. 1. It was found that the mass of chloroform and toluene adsorbed varied

Fig. 1. Adsorption of VOCs on membrane Matrix.

from 76 to 227 and 306 to 722 mg, respectively depending on the initial concentration of the solutions. It should be noted that the system tested consists of polypropylene hollow fibers with an effective surface area of 1.4 m², a module housing made of polypropylene and connecting tubes made of Teflon®. It was likely that VOCs would be sorbed on the surface of the housing and majority would be sorbed on the matrix of hollow fibers, which had a much larger surface area. Consequently, we have calculated the sorbed mass of VOCs per mass of hollow fibers. The masses of toluene adsorbed were much higher than those of chloroform at equivalent initial concentrations. This indicates that toluene has greater affinity for polypropylene/Teflon®. The amount of VOCs adsorbed was linearly related to the initial solution concentration. This indicates that if the adsorption is fully reversible and the adsorption and desorption processes are relatively fast, the VOC adsorbed at the start of a MAS test, when the concentration was higher, might be desorbed at later stages, as the concentration decreases.

4.2. Henry's law constant

The H was determined for chloroform in three series of experiments. Each series consisted of eight syringes. In each series, H was obtained for eight different chloroform concentrations. The average value of H was calculated for all the 24 samples from these three series. The results from HLC determination of chloroform are presented in Table 2. The final value of H for chloroform obtained from averaging all 24 samples at 23 °C with 95% confidence level (CI) is 0.1512 ± 0.0115 . All experimental data are presented in Fig. 2 as dimensionless HLC, H , versus initial chloroform concentration. The figure shows that the initial chloroform concentration in the concentration range studied, does not affect the value of the HLC. The results from H determination of toluene are also presented in Table 2. Unlike chloroform, one single toluene solution was used to fill all the syringes when H for toluene was determined. The average H value, obtained from averaging all 22 samples at 23 °C for toluene, with 95% CI is 0.2305 ± 0.0195 .

Table 2
Experimental values of Henry's law constant

Experiments	No. of points	Mean	C_v	95% CI
Chloroform as a single solute	24	0.1512	0.1795	0.1512 ± 0.0115
Toluene as a single solute	22	0.2305	0.1907	0.2305 ± 0.0195
Chloroform as chloroform/toluene mixture	8	0.1507	0.2388	0.1507 ± 0.0301
Toluene as chloroform/toluene mixture	8	0.2356	0.1996	0.2356 ± 0.0393

Fig. 2. Effect of initial chloroform concentration on its Henry's law constant.

The literature values of H obtained for chloroform and toluene at temperatures close to 23 °C are summarized in Table 3. Comparison was also made in Table 3 between H values, obtained in this study, and those estimated by using HLC versus temperature correlations. The agreement of data seems reasonable with the literature values and the estimated values. The results from the experiments conducted to determine HLC (HLC) for the mixture of chloroform and toluene are also presented in Table 2. The eight syringes were filled with the same solution. These results indicate that there was no significant effect of one compound on the other in respect of partitioning. The H for chloroform alone was 0.1512 ± 0.0115 compared to 0.1507 ± 0.0301 when measured from a binary aqueous solution of chloroform/toluene. The H for toluene was 0.2305 ± 0.0195 alone versus 0.2356 ± 0.0393 when measured from a binary aque-

ous solution of chloroform/toluene. Thus, the H of one VOC was not impacted by the presence of another VOC.

4.3. Removal of VOCs from aqueous solution

Experiments were conducted for MAS of VOCs from aqueous solutions under wet conditions as described in our earlier work [5,21]. The rate constants obtained for toluene removal by plotting the $\ln(C_0/C_t)$ versus time, were lower than those observed for chloroform. A typical example is presented in Fig. 3, which shows a significantly lower rate constant (slower removal) for the toluene test than that for the chloroform test under identical operating conditions. The diffusion coefficients for toluene in the air phase and in the water phase are lower than those of chloroform by 11.6 and 13.8%, respectively. Thus, the removal of toluene and the mass transfer coefficient should be slightly lower than that of chloroform and not the 50% observed in Figs. 4 and 5. The observed overall mass transfer coefficients, K_L , were calculated from the rate constants using Eq. (6) for chloroform and toluene and compared with the values predicted by using qs. (1–4 with $x = 0.75$ in Figs. 4 and 5, respectively.

It was found that the observed values of K_L for toluene are far smaller than those predicted. It is stated above that, adsorption of toluene on the hydrophobic surface of the system including the membrane was higher than that of chloroform. When adsorbed onto

Table 3
Comparison of the H values for chloroform and toluene

Chloroform			Toluene		
Temperature (°C)	H	Reference	Temperature (°C)	H	Reference
23.0	0.1512 ± 0.0115	Present study	23.0	0.2305 ± 0.0195	Present study
22.0	0.1446	[27] ^a	22.7	0.2298	[27] ^a
24.9	0.1508	[27] ^a	23.0	0.2539	[27] ^a
19.9	0.153	[33] ^a	25.0	0.263	[35] ^a
29.8	0.185	[33] ^a	25.0	0.24	[31] ^a
20.0	0.224	[28] ^a	19.9	0.189	[33] ^a
23.0	0.2369	[35] ^b	29.8	0.375	[33] ^a
23.0	0.1593	[33] ^b	23.0	0.2372	[35] ^b
23.0	0.1486	[27] ^b	23.0	0.1973	[33] ^b
23.0	0.1475	[36] ^b	23.0	0.2417	[27] ^b

^a Experimental value.

^b Estimated using correlations.

Fig. 3. Comparison of rate constant of chloroform and toluene (air velocity = 0.13 m/s and solution velocity = 5.95×10^{-3} m/s).

Fig. 4. Comparisons between predicted and observed K_L for MAS of chloroform.

Fig. 5. Comparisons between predicted and observed K_L for MAS of toluene.

hollow fibers, toluene probably swelled the polymer matrix, resulting in the reduction of the pore size. Hence, the membrane transport resistance possibly increased. Wang and Cussler [37] reported that the results from their stripping experiments of toluene were not reliable. They have attributed it to the swelling effect of toluene on polypropylene hollow fibers. It was also reported that toluene increased the weight of polypropylene by 11% after a contact period of 10 days as a result of swelling [38]. The gradual desorption of the adsorbed toluene at the later stage of experiments likely contributed to the higher toluene concentration in the solution and had a negative impact on its apparent air-stripping rate.

The main factor behind this deviation was likely the reduction of the effective pore diameter, which was directly related to the adsorption/swelling by toluene of the membrane. On the other hand, this adsorption was dependent on the toluene concentration in the solution. For the batch system used in our study, the toluene concentration decreased with time. Thus, it is difficult to account for the changes of the pore shape and size over the period of the experiment to model it properly. It can be concluded that the interactions between the membrane and toluene in terms of adsorption/swelling played an important role during mass transport of toluene and should be taken into account during design of MAS process for such VOCs. Precise quantification of swelling effect by toluene is out of scope of this study. A further investigation regarding this phenomenon is needed.

4.4. Removal of mixtures of chloroform and toluene from aqueous solution

The partitioning of one VOC was not affected by the presence of another VOC. This indicates that if there was no influence of external factors, the mass transport of one VOC should not be affected by the presence of another VOC. Thus, the rate constants were calculated separately for chloroform and toluene by plotting the $\ln(C_0/C_t)$ versus time similarly as done for single solute. The rate constants for toluene were similar to those obtained from experiments with single toluene solute. But, the slopes observed for the removal of chloroform were much lower than those observed from experiments with single chloroform solute. A typical example is presented in Fig. 6, which shows a lower rate constant (slower removal) for the test with chloroform/toluene mixture than that for single chloroform test under identical operating conditions. K_L values were compared between single and mixed solute systems for chloroform and for toluene in Figs. 7 and 8, respectively. The decrease in K_L of chloroform in the presence of toluene might have been caused by the reduction of the pore size as a result of toluene adsorption/swelling. On the other hand, the slight increase in K_L values for toluene might have been caused by the competition between toluene and chloroform for adsorption sites, which inevitably reduces toluene adsorption/swelling and hence the degree of pore size reduction. This also might have reduced desorption of toluene at the later stages.

Fig. 6. The $\ln(C_0/C_t)$ vs. t plot for aqueous solutions involving chloroform as a single solute or as chloroform/toluene mixture (air velocity = 0.13 m/s and solution velocity = 5.95×10^{-3} m/s).

- [28] C. Munz, P.V. Roberts, Transfer of Volatile Organic Contaminants into a Gas Phase During Bubble Aeration, Technical Report No. 262, Department of Civil Engineering, Stanford University, Stanford, CA, USA, 1982.
- [29] N. Nirmalakhandan, R.A. Brennan, R.E. Speece, Predicting Henry's law constant and the effect of temperature on Henry's law constant, *Wat. Res.* 31 (6) (1997) 1471–1481.
- [30] R.A. Brennan, N. Nirmalakhandan, R.E. Speece, Comparison of predictive methods for Henry's Law coefficients of organic chemicals, *Water Res.* 32 (6) (1998) 1901–1911.
- [31] J. Altschuh, R. Brüggemann, H. Santl, G. Eichinger, O.G. Piringer, Henry's law constants for a diverse set of organic chemicals: experimental determination and comparison of estimation methods, *Chemosphere* 39 (11) (1999) 1871–1887.
- [32] P. Lamarche, Air Stripping Mass Transfer Correlations for Volatile Organics, M.A.Sc. Thesis, Department of Civil Engineering, The University of Ottawa, Ottawa, Ontario, Canada, 1986.
- [33] P. Lamarche, R.L. Droste, Air-stripping mass transfer correlations for volatile organics, *J. Am. Water Works Assoc.* 81 (1) (1989) 78–89.
- [34] P.V. Roberts, J.A. Levy, Energy requirements for air stripping trihalomethanes, *J. Am. Water Works Assoc.* 77 (4) (1985) 138–146.
- [35] J.E. Singley, A.L. Ervin, M.A. Mangone, J.M. Allan, H.H. Land, Trace Organics Removal By Air Stripping, *Am. Water Works Assoc.*, Rept. ESE No. 79-227-001, Denver, CO, USA, 1980.
- [36] M.C. Kavanaugh, R.R. Trussell, Design of aeration towers to strip volatile contaminants from drinking water, *J. Am. Water Works Assoc.* 72 (12) (1980) 684–692.
- [37] K.L. Wang, E.L. Cussler, Baffled membrane modules made with hollow fiber fabric, *J. Membr. Sci.* 85 (1993) 265–278.
- [38] J.I. Kroschwitz, Eds., *Encyclopedia of Polymer Science and Engineering*, 2nd Edition, Vol. 13, Wiley, New York, USA, 1985, pp. 464–530.
- [39] A. Gabelman, S. Hwang, Hollow fiber membrane contractors, *J. Membr. Sci.* 159 (1999) 61–106.
- [40] S.R. Wickramasinghe, M.J. Semmens, E.L. Cussler, Mass transfer in various hollow fiber geometries, *J. Membr. Sci.* 69 (1992) 235–250.
- [41] R. Prasad, K.K. Sirkar, Hollow-fiber solvent extraction: performance and design, *J. Membr. Sci.* 50 (1990) 153–175.
- [42] R. Prasad, K.K. Sirkar, Dispersion-free solvent extraction with microporous hollow-fiber modules, *AIChE J.* 34 (2) (1988) 177–187.
- [43] A.K. Zander, R. Qin, M.J. Semmens, Membrane/oil stripping of VOCs from water in hollow-fiber contactor, *J. Environ. Eng.* 115 (4) (1989) 768–784.
- [44] R.H. Norris, M.Y. Schenectady, D.D. Streid, Laminar-flow heat-transfer coefficients for ducts, *ASME Trans.* 62 (1940) 525–533.