



Multipass membrane air-stripping (MAS) for removing volatile organic compounds (VOCs) from surfactant micellar solutions

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ABSTRACT

Air-stripping is one of the most effective technologies for removing volatile organic compounds (VOCs) from surfactant solutions, although the presence of surfactant poses some unique challenges. This study evaluated the effect of a mixed surfactant system on the apparent Henry's law constant of tetrachloroethylene (PCE) and the efficiency of PCE removal from surfactant solutions using a lab-scale hollow fiber membrane contactor. Results show that the presence of surfactant significantly reduced the apparent Henry's law constant of PCE, and the reduction was proportional to the total surfactant concentration. PCE removal efficiency by membrane air-stripping (MAS) decreased as the surfactant system transitioned from solubilization to supersolubilization. Besides significantly reducing the apparent volatility of VOCs, the presence of surfactant brings additional mass transfer resistance in air-stripping, which makes it difficult to achieve high levels of contaminant removal, even at very high air/liquid (A/L) ratios. In contrast, multipass/multistage MAS operated at low A/L ratios could achieve near 100% contaminant removal because of less mass transfer limitation during each stripping pass/stage. Experimental results, together with model calculations demonstrate multipass (and multistage) air-stripping as a cost-effective alternative for removing VOCs from surfactant micellar solutions compared to the options of using large air strippers or operating at high A/L ratios.

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1. Introduction

Chlorinated solvents, particularly chlorinated ethylenes such as trichloroethylene (TCE) and tetrachloroethylene (PCE), occur widely in contaminated groundwater aquifers in the United States and may pose a long term risk [1–7]. Because of their low water solubilities and relatively high densities (relative to water), chlorinated solvents are often trapped in the subsurface soils and aquifer materials and form dense non-aqueous phase liquids (DNAPLs). Traditional pump-and-treat remediation is inefficient at cleaning up these poorly water-soluble contaminants. Over the past two decades, surfactant enhanced aquifer remediation (SEAR) has emerged as a cost effective technology for cleaning up subsurface sites contaminated with NAPLs [8–10]. To minimize downward migration of contaminants during SEAR, DNAPLs are typically removed via the enhanced solubilization mechanism in which their apparent solubilities are increased by several orders of magnitude in surfactant micellar solutions [11]. Supersolubilization and gradient systems have been recently introduced to further improve

the efficiency of SEAR for DNAPL remediation [12–16]. A supersolubilization surfactant system is one that has ultralow interfacial tension (IFT) with the organic liquid and a high solubilization capacity without forming middle-phase microemulsion [13,14]. Being more efficient at solubilizing organic contaminants, such systems can significantly reduce the amount of surfactant required and the time of the remediation process compared to the traditional solubilization approach. A gradient approach in SEAR essentially employs surfactant solubilization to remove the more “mobile” fraction of DNAPL at the beginning of the remediation and then switches to more effective supersolubilization systems to remove the residual DNAPL [13,15]. In the supersolubilization/gradient approach, it is believed that by beginning the surfactant flush at higher IFT and gradually lowering the IFT (achieved via increasing the salt concentration) in three or four stages the solubilization enhancement can be maximized while the vertical migration of the DNAPL can be minimized [15].

One major economic consideration in the surfactant-based remediation technology is separation of organic compounds from surfactant solutions, which is necessary to reuse the surfactant solution and to lessen the demand on waste disposal in implementing SEAR [17–19]. Over the years, many contaminant-surfactant separation methods have been developed, such as air-stripping

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[20–23], vacuum stripping [24], pervaporation [25,26], solvent extraction [20,27–30], ion exchange [31], activated carbon adsorption [17,32], reverse micellar extraction [33], precipitation [34,35], and phase behavior manipulation [36]. The advantages and limitations of these technologies have been discussed in a recent review [37]. Among these technologies, air-stripping is the most widely used method for separation of volatile organic compounds (VOCs) from surfactant solutions.

Contaminant separation from surfactant solution by air-stripping is based on the principle that volatile compounds readily partition into the gaseous phase and can be carried away by the gas flow. Contaminant-free air is contacted with surfactant solutions in packed towers [16,20,21,23,24,38,39] or sieve-trays [22,32,40] to promote partitioning by creating a large air–water interfacial area, which facilitates the mass transfer of organic compounds from the solution to the air phase. Air-stripping based on hollow fiber membranes, in which the air–liquid interface is established in pores ranging from 30 to 50 nm that are typically present in microporous polypropylene/polyethylene hollow fibers, has also been developed [21,23,30,41]. Foaming is a major problem in packed tower and tray air strippers [20,22], while the use of hollow fiber membrane effectively eliminates this problem, except at very high liquid loading rates [23,41].

Surfactant molecules have an amphiphilic structure with a hydrophilic head and a hydrophobic tail, causing them to accumulate at interfaces and lower the interfacial tension. When their concentration reaches the critical micelle concentration (CMC), a portion of the surfactant molecules form micelles, which are spheres of surfactant molecules with a hydrophilic exterior and a hydrophobic core. The surfactant molecules that are not present as micelles exist primarily as unassociated molecules or ions in solution, which are known as monomers. As the total concentration of surfactant is increased beyond the CMC, the added surfactant goes to increase the micelle concentration with the monomer concentration unaffected. Depending on the surfactant, electrolyte concentration and other variables, the equilibrium time between monomers and micelles is usually around 10^{-8} – 10^{-3} s and the life time of micelles is in the range of 10^{-3} –1 s [42].

The gas–liquid partitioning behavior of volatile solutes obeys Henry's law, which states that the partial pressure of a component in the gas phase is proportional to its concentration in the liquid phase under equilibrium conditions. The dimensionless form of Henry's law constant (H) can be expressed as:

$$H = \frac{c_{\text{gas}}}{c_{\text{aq}}} \quad (1)$$

where c_{aq} and c_{gas} are moles of the compound per volume of solution and gas, respectively. Anderson [43] showed that the presence of surfactant substantially reduced the partitioning of VOCs from the solution into the vapor phase and proposed a three-phase model to describe the impact of surfactant on contaminant vapor partitioning. This model employs a linear solute–surfactant partition coefficient [43], but ignores the important fact that this is valid only when excess hydrocarbon exists [8]. Rouse et al. studied micellar solubilization of unsaturated hydrocarbons by semi-equilibrium dialysis and observed that the solute–surfactant partition coefficient might change by one order of magnitude as a function of the hydrocarbon concentration in micellar pseudo-phase or aqueous phase [44]. Here a contaminant distribution constant, k_p , as defined by Dunn et al. [45] and used in the vacuum stripping model developed by Oetman [46], is adopted:

$$k_p = \frac{c_s}{c_m c_w} = \frac{c_t - c_w}{c_m c_w} \quad (2)$$

where c_s is the concentration of micellar-solubilized organic solute, c_m is the concentration of surfactant in micellar form, c_w is the con-

centration of water-solubilized organic solute, and c_t is the total concentration of the organic solute solubilized in the surfactant solution ($c_t = c_m + c_w$). k_p describes the partitioning of the solute between the aqueous solution (as water-solubilized molecules) and the micelles, and accounts for changes in the total contaminant concentration in the surfactant solution. Only the water-solubilized fraction of contaminant can readily evaporate from the surfactant solution into the gaseous phase. Assuming the activity coefficient of water-solubilized contaminant in the surfactant solution is unity (i.e., 1), we can express the solute's apparent Henry's law constant (H^*) as:

$$H^* = \frac{H c_w}{c_t} = \frac{H}{1 + k_p c_m} \quad (3)$$

Membrane air-stripping (MAS) using microporous hollow fiber membrane contactors is a process with great potential for the removal and recovery of VOCs from water/wastewater. Hollow fiber membrane contactors provide a much larger surface area per volume between gas and liquid than packed towers, which facilitates solute inter-phase mass transfer. The main disadvantage is that the overall mass transfer coefficient for membrane-based stripping is usually lower than that for conventional processes due to the mass transfer resistance created by the membrane, but this is overcome by the higher effective surface-to-volume ratio of the hollow fiber configuration [47,48]. In principle, the membrane pores can be filled by water, gas, or both depending on the operating pressure, surface tension, and contact angle between the two phases [49], with significant reduction in the membrane mass transfer coefficient occurring as the membrane pores become water-filled [49,50]. Models have been developed to describe the mass transfer through hollow fiber membranes with pores that are completely air- or water-filled, and with partially wetted pores [50–52]. The operating principles, mass transfer processes, and applications of membrane-based air-stripping have been summarized in reviews by Mahmud et al. [47] and Gabelman and Hwang [53].

Mass transfer in MAS involves three sequential steps: the VOC molecules first diffuse from the bulk aqueous solution across the liquid boundary layer to the membrane surface; they then diffuse through the air- and/or water-filled pores, and finally through the air boundary layer outside the membrane pores into the stripping air. Three mass transfer resistances are typically considered in MAS: that in the liquid, that across the hollow fiber membranes, and that in the gas surrounding the fibers, and the overall liquid phase based mass transfer resistance ($1/K_L$) is often expressed as [47–49]:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_m H^*} + \frac{1}{k_g H^*} \quad (4)$$

where k_l is the local liquid phase mass transfer coefficient, k_m is the membrane mass transfer coefficient, and k_g is the gas phase mass transfer coefficient. Various empirical correlations exist for predicting k_l and k_g values in air-stripping, while k_m is often experimentally determined [48,49,51].

Based on the fundamental mass transfer processes in MAS, a mathematical model for VOC removal can be derived as [47–49]:

$$\frac{C_{L,\text{in}}}{C_{L,\text{out}}} = \frac{\exp[(K_L a L / u_L)(1 - (Q_L / Q_A)H^*)] - (Q_L / Q_A)H^*}{1 - (Q_L / Q_A)H^*} \quad (5)$$

where $C_{L,\text{in}}$ and $C_{L,\text{out}}$ are concentrations of the VOC and the inlet and outlet of the membrane contactor, respectively, a is the interfacial contact area per unit contactor volume, L is the effective column length, u_L is the linear velocity of the liquid flow in the hollow fibers, and Q_L and Q_A are the flow rates of the liquid and air, respectively.

Despite the successful application of air-stripping in field scale operations in treating surfactant solutions, the presence of surfactant at high concentrations brings some unique challenges. In particular, high levels of contaminant removal are difficult to

Table 1
Physical properties of PCE microemulsions with selected surfactant systems used in this study^a.

System	Temp. (°C)	Winsor type	PCE (mg/L)	Viscosity (cP)	Coalescence time (h)	IFT (dyn/cm)
5% C16-DPDS/3% SDHS/3% NaCl	23	I	70,000	N.D.	2	1.0
5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl ₂	23	I	84,000	1.8	4	0.5
5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl ₂	7	I	70,000	3.5	12	N.D.

Note: N.D—not determined.

^a From Childs et al. [15].

achieve due to the significant reduction in the volatility of VOCs by micellar solubilization and the additional interfacial mass transfer resistance brought by the adsorbed surfactant film at gas–liquid interface. In this work, we systematically studied, for the first time, PCE removal from supersolubilization surfactant systems by MAS, and demonstrated that although a supersolubilization surfactant system could solubilized PCE more efficiently, the solubilized PCE was more difficult to remove with air-stripping. Previous researchers have focused on designing a single pass process in contaminant removal [16,20–24,32,38–41]. However, in supersolubilization surfactant systems, the reduced contaminant volatility and increased mass transfer resistance limit the contaminant removal using this approach. We propose multipass/multistage MAS as a more cost-effective alternative for removing VOCs from surfactant micellar solutions compared to a single pass process. Results reported here can help to better understand the partitioning behavior of organic molecules between air and surfactant solution and the mass transfer processes in air-stripping, and to design cost-effective treatment strategies in removing VOCs from surfactant solutions.

2. Materials and methods

2.1. Materials

The surfactant systems used in this study were candidates for a field demonstration of SEAR technology for remediation of PCE contamination [15]. They include both solubilization and supersolubilization systems, and the physical properties of PCE microemulsions with selected surfactant systems are shown in Table 1. These systems exhibited rapid coalescence, desirable IFTs with PCE, low microemulsion viscosities, and temperature independence of phase behavior, and no liquid crystal/gel formation at low temperature (7 °C), which make them ideal for applications in aquifer remediation [15]. DowFax 8390 was obtained from Dow Chemical (Midland, MI) as a liquid of 31–36% active, and the content of active ingredient was practically treated as 33.5%. The surfactant components are disodium hexadecyldiphenyloxide disulfonate and disodium dihexadecyldiphenyloxide disulfonate (C16-DPDS). It also contains a small percentage of sodium sulfate and sodium chloride. Aerosol MA 80-I was purchased from CYTEC (Willow Island, WV). It is composed of 80 ± 1% sodium dihexyl sulfosuccinate (SDHS) in a mixture of isopropanol (IPA, ~5%) and water. Brij 97 composed of polyoxyethylene (10) oleyl ether (POIE(10)) with ≤3% water was obtained from Croda (Edison, NJ). Reagent grade (>99%) PCE and sodium chloride, and 99.5+% IPA were purchased from Aldrich (Milwaukee, WI), anhydrous calcium chloride (>95%) was purchased from Fisher (Fair Lawn, NJ). All chemicals were used as received.

2.2. Batch partitioning

Batch PCE gas–liquid partitioning experiments were carried out in 40 mL I-Chem glass vials with Teflon-lined silicone septa and polypropylene closures. The average total volume of the vials was 43.03 ± 0.19 mL determined through gravimetric cali-

bration using DI water. The vials were added with 4.0 mL of 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solutions containing approximately 10,000–50,000 mg/L PCE. They were then stored head down to avoid vapor leak through caps in darkness for 3 days at room temperature of (23 ± 1 °C). After equilibration, the liquid phase was sampled with needle syringes. PCE vapor concentrations in the headspace of these vials were calculated from the liquid phase mass balances. Similar experiments were also conducted for a series of 5:3 C16-DPDS/SDHS mixed surfactant solutions (1.6–9.6 wt.%) containing 3% NaCl and 3% CaCl₂ saturated with PCE. All batch experiments were pentuplicated.

2.3. Hollow fiber membrane air-stripping

MAS experiments were conducted with a 2.5 in. × 8 in. Liqui-Cel extra-flow membrane contactor with X-30 hydrophobic hollow fiber membrane (Celgard, Charlotte, NC). The membrane has an effective pore size of 30 nm, and the surface area per volume of the contactor is 2930 m²/m³. Detailed characteristics of the contactor and the hollow fibers are listed in Table 2.

Fig. 1a shows the diagram for the MAS experimental setup. The surfactant solution was pumped through the fiber lumen (on the “tube side”) upward while the gas flowed downward outside of the fibers (on the “shell side”). A Beckman 110B solvent delivery module was used to deliver the surfactant solution, and grade D breathing air was supplied from a cylinder with flow rate controlled by a correlated flow meter with a high resolution valve (Cole-Parmer, Vernon Hills, IL). The exhaust air from the membrane contactor was connected to a column packed with powdered activated carbon to adsorb the PCE before being discharged to a fume hood. MAS at two solution flow rates, 3.5 and 9.0 mL/min (liquid loading rates: 4.17 × 10⁻⁸ and 1.07 × 10⁻⁷ m³/(m² s)), was studied, with the

Table 2
Characteristics of the hollow fiber membrane contactor used in this study.

Property	Specification ^a
Cartridge dimension	6.4 cm × 20.3 cm (2.5 in. × 8 in.)
Shell inside diameter	5.55 cm
Center tube outer diameter	2.22 cm
Shell side volume	330 mL
Lumen side volume	90 mL
Number of fibers	9950 ^b
Void fraction	0.654 ^c
Effective membrane surface	1.4 m ²
Effective surface to volume ratio	2930 m ² /m ³
Fiber potting material	Polyethylene
Housing material	Polypropylene
Fiber outer diameter	300 μm
Fiber inner diameter	240 μm
Fiber wall thickness	30 μm
Effective fiber length	15 cm ^b
Pore diameter	30 nm
Pore tortuosity	2.5 ^c
Porosity	40%
Maximum transmembrane differential pressure	414 kPa (60 psi)
Operating temperature range	1–60 °C

^a Supplied by the manufacturer.

^b Values reported in [64].

^c Value reported in [51].

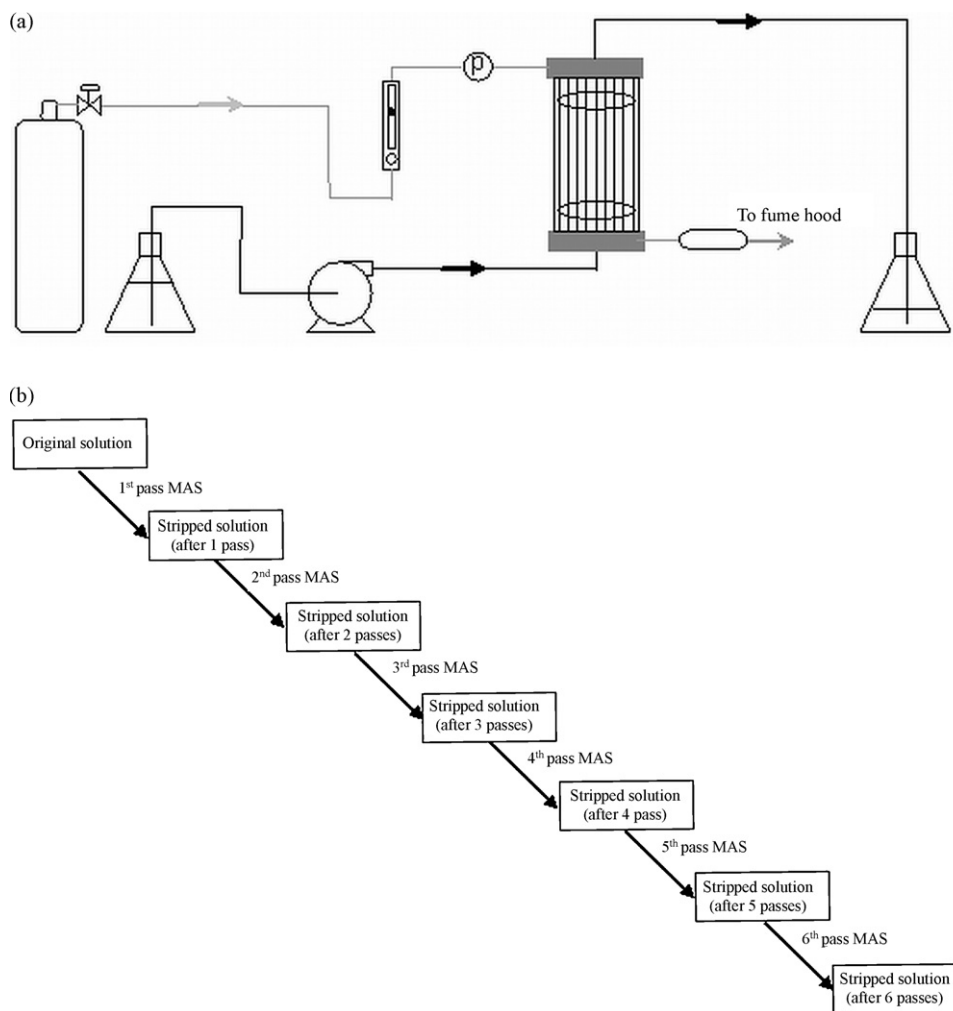


Fig. 1. Schematic illustrations for (a) experimental setup of air-stripping using a hollow fiber membrane contactor, and (b) multipass air-stripping procedures.

air flow rate varied to obtain different air/liquid (A/L) volumetric ratios. Samples of the stripped surfactant solution were collected for PCE analysis after more than 1.5 pore volume of surfactant solution had passed through the membrane contactor to ensure steady state had been reached. Multipass air-stripping was conducted by sequentially feeding the treated effluent through the membrane contactor while supplying clean air, as illustrated in Fig. 1b. All MAS results were based on measurements of at least triplicate samples of stripper effluent.

2.4. Sample analysis

All samples collected were stored in glass vials with no head space and analyzed within 5 h after collection. PCE was analyzed on a Shimadzu LC-10AD liquid chromatograph including SIL-10A auto-injector and SCL-10A controller. Separation of PCE from surfactant mixtures was achieved using an Alltech surfactant C8 column with 80% methanol/20% water as the mobile phase, and PCE was detected with a Waters 486 tunable absorbance detector at 225 nm.

3. Results and discussion

3.1. Batch equilibrium partitioning results

Fig. 2a shows the apparent Henry's law constants of PCE in 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution as a function of the

PCE concentration in the solution phase. It is observed that the apparent Henry's law constant did not change with the amount of PCE present in a given surfactant solution, which is consistent with the prediction of Eq. (3). The Henry's law constant (H) of PCE in water at 23 °C is approximately 0.717 [54], while the presence of 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ reduces its apparent Henry's law constant (H^*) to 0.054. This represents a greater than 99% reduction of the overall volatility of PCE in the surfactant solution. Fig. 2b shows PCE's apparent Henry's law constant as a function of the total surfactant concentration in 5:3 C16-DPDS/SDHS mixed surfactant system in the presence of 3% NaCl and 3% CaCl₂. The CMC of the mixed surfactant system in the presence of high electrolyte concentration (3% NaCl + 3% CaCl₂) is expected to be insignificant compared to the total surfactant concentration, thus the total surfactant concentration can be approximated as the micelle concentration. Based on the experimental results, the relationship between the apparent Henry's law constant of PCE and the total surfactant concentration can be expressed as:

$$H^* = \frac{0.717}{1 + 16.05c_{DA}} \quad (6)$$

where c_{DA} is the total wt.% concentration of 5:3 C16-DPDS/SDHS mixed surfactant system in the presence of 3% NaCl and 3% CaCl₂. The surfactant-concentration dependence of the apparent volatility is consistent with the prediction made by Kibbey et al. [22] and experimental observations by Lipe et al. [21].

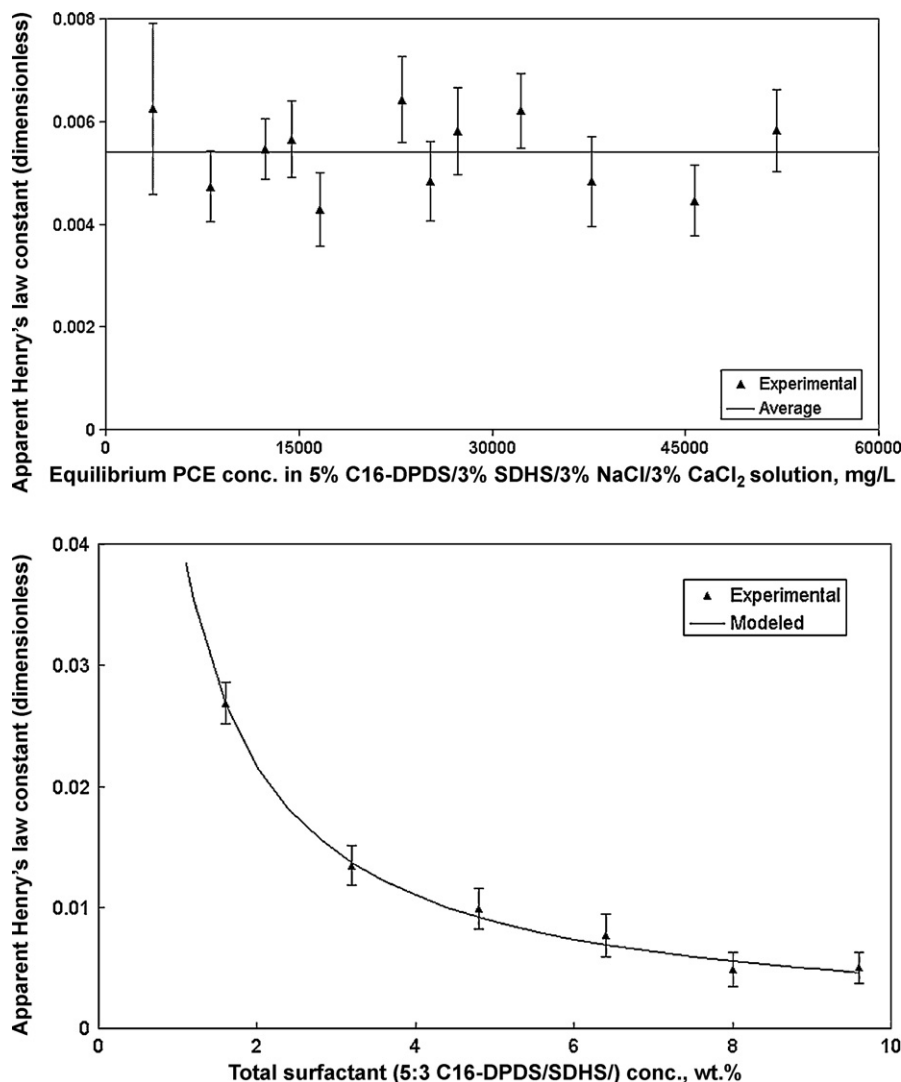


Fig. 2. The apparent Henry's law constant (H^*) of PCE as a function of (a) equilibrium aqueous PCE concentration in 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution; and (b) total surfactant (5:3 C16-DPDS/SDHS) concentration in the presence of 3% NaCl and 3% CaCl₂. Error bars represent 95% confidence intervals (CIs).

3.2. Hollow fiber membrane air-stripping results

In batch experiments, PCE had sufficient time to partition between water, micelles and gas, and the final PCE distribution was not limited by any mass transfer processes. In contrast, the actual contaminant removal efficiency is often affected by mass transfer in air-stripping process. Fig. 3a shows PCE removal from surfactant systems composed of 5% C16-DPDS/3% SDHS/3% NaCl/0–3% CaCl₂ by MAS at an A/L ratio of 517 and a liquid loading rate of $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$. With CaCl₂ concentration increases from 0% to 3%, the solubility of PCE increases significantly as the surfactant system is pushed from a solubilization system to a supersolubilization system (Table 1). It is observed that PCE removal by MAS decreased as the total electrolyte concentration increased, which indicates that contaminant solubilized in the more efficient supersolubilization surfactant system is also more difficult to be stripped off compared to a normal solubilization system. One of the possible explanations for this is the greater PCE affinity of the more “swollen” micelles (lower H^*) [12,14], which reduces partitioning of PCE from the solution to the gas phase.

It is also well known that the presence of surfactant micelles affects solute mass transfer rates, and thus contaminant removal, during air-stripping. The dynamic equilibrium between the water-

solubilized and micellar-solubilized VOC molecules is expected to reduce their diffusion coefficient in the surfactant micellar solution (k_l). Furthermore, significant reduction in the VOC's mass transfer coefficient across the membrane (k_m) is expected with increased liquid filling of the membrane pores caused by the surfactant, which modifies the solution's surface tension and contact angle on the membrane. On the molecular level, the presence of surfactant molecules at a gas–liquid interface affects the mass transfer rate of a solute from the liquid to the gas by altering the interfacial region and providing additional resistance to diffusion through formation of a “condensed” layer of adsorbed surfactant [55,56]. Numerous studies have shown that the presence of adsorbed surfactant film at the interfaces retards the diffusion across interface in gas–liquid [57–60] and liquid–liquid systems [61–63]. Quantifying the individual mass transfer coefficients (i.e., k_l , k_m , and k_g) is beyond the scope of this study. Also, the true interfacial contact area (a) in the MAS system is unknown. Therefore, we use $K_L a$ as a lumped parameter to describe the overall mass transfer based on liquid side. By assuming that the apparent Henry's law constants (H^*) were approximately the same (the individual H^* values for these systems were not measured), we estimate that the $K_L a$ values of PCE were 2.88×10^{-3} , 2.52×10^{-3} , 2.05×10^{-3} , and $1.92 \times 10^{-3} \text{ 1/s}$ in MAS, as the CaCl₂ content in the 5% Dow/3% AMA/3% NaCl surfactant system increased

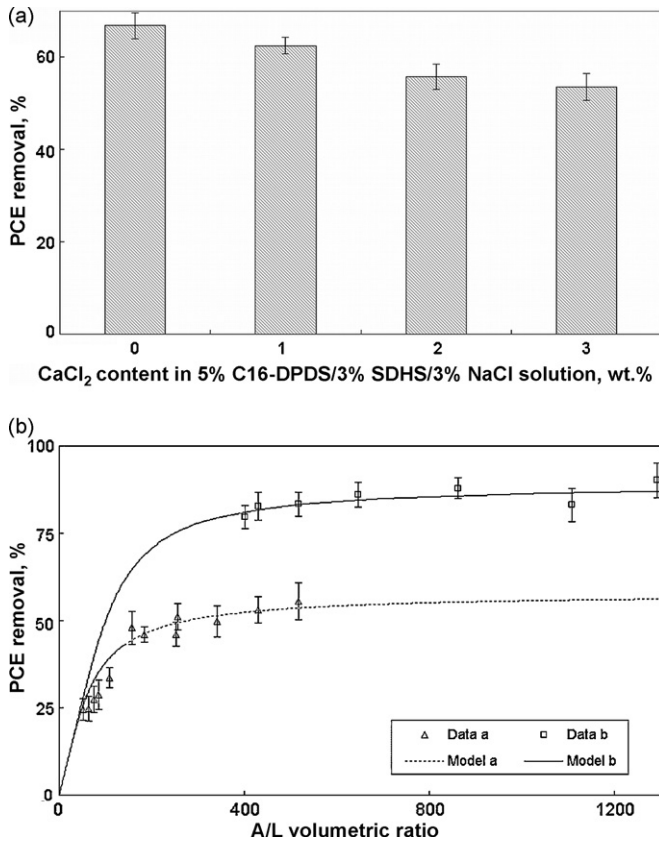


Fig. 3. PCE removal from surfactant solutions by single pass MAS: (a) PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/0–3% CaCl₂ solutions at an A/L ratio of 517 (at $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$ liquid loading); and (b) PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution as a function of A/L ratio, where the liquid loading rates were 1.07×10^{-7} and $4.17 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ for groups a and b (both experimental data and model predictions), respectively. Error bars represent 95% CIs.

from 0% to 1%, 2%, and 3%, respectively. The lower rates of mass transfer at higher electrolyte concentrations can be explained by the formation of more “condensed” interfacial surfactant films at higher electrolyte concentrations [55].

Fig. 3b shows removal of PCE from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution as a function of A/L ratio in MAS at liquid loading rates of 1.07×10^{-7} and $4.17 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$. As expected, PCE removal increased gradually with A/L ratio, while the rate of increase declined at high A/L ratios. As A/L ratio increases, the interfacial region deviates farther away from local equilibrium and the PCE removal starts to be affected more by the mass transfer across the membrane (k_m) and probably also the mass transfer in bulk surfactant solution (k_l). At a given A/L ratio, PCE removal from the surfactant solution increased when the liquid loading rate was reduced from 1.07×10^{-7} to $4.17 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$, due to the longer residence times (and thus less mass transfer limitation) of liquid and air in the membrane contactor. In surfactant micellar solutions, the volatility of the solute is significantly reduced. To achieve high levels of contaminant removal, air-stripping may need to be operated at much higher A/L ratios compared to the system without the presence of surfactant. Meanwhile, the volumetric air removal efficiency (i.e., the amount of contaminant removed from the solution per unit volume of air passed through the membrane contactor) goes down as the A/L ratio increases. Furthermore, the hollow fiber membrane is limited to a certain transmembrane differential pressure (414 kPa in this case), which sets an upper limit on A/L ratio that can be practically used in MAS.

3.3. Multipass air-stripping results

Even if the constraint of the membrane structure was not considered and the A/L ratio could go to infinity, inter-phase mass transfer rate still restricts the removal achievable by air-stripping. Model calculations suggest that the practical upper limit of PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ system is close to 56% at liquid loading of $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$, and 87% at $4.17 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ with the lab-scale membrane contactor. Therefore, high contaminant removal efficiencies (e.g., >90%) from the surfactant solution cannot be achieved by simply increasing the A/L ratio in MAS. Treatment of the surfactant solution by multipass air-stripping can circumvent this limitation. Fig. 4a shows results of PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/0–3% CaCl₂ surfactant systems by multipass MAS. As expected, the PCE removal efficiency decreased (remaining PCE concentration increased) as the surfactant system transitioned from solubilization to supersolubilization with increasing electrolyte concentration. In addition, the remaining PCE concentration in the surfactant solutions decreased exponentially as the number of treatment passes increased. The overall PCE removal achieved over four passes for the surfactant systems ranged from 95.5% to 98.8% for the surfactant systems studied. Fig. 4b shows results of PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ surfactant solution at different A/L ratios by multipass MAS. PCE removal efficiency increased with A/L ratio for a given stripping pass. Over five passes, an A/L ratio of 329 only achieved a slightly lower final PCE concentration (better PCE removal—97.3% vs. 96.3%) compared to at an A/L ratio of 171. At an A/L ratio of 329, removal of PCE from 38,150 mg/L down to <1800 mg/L from 5% C16-DPDS/3%

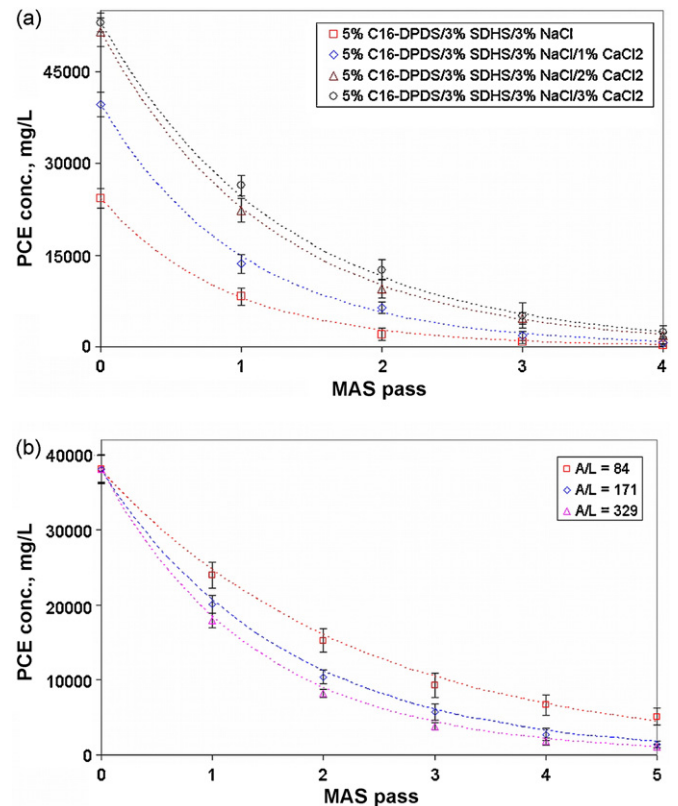


Fig. 4. PCE removal from surfactant solutions by multipass MAS at a constant liquid loading rate of $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$: (a) PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/0–3% CaCl₂ solutions at an A/L ratio of 517; (b) PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution at selected A/L ratios. Error bars represent 95% CIs.

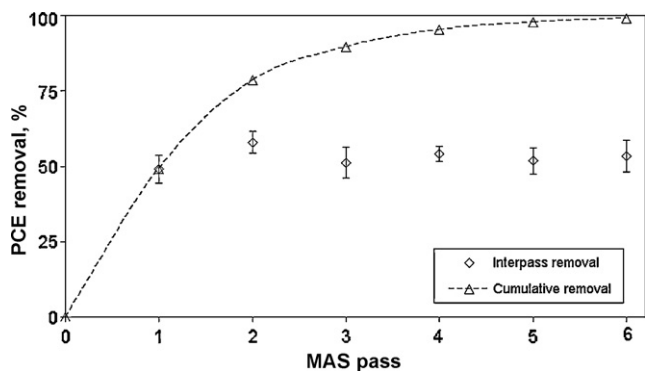


Fig. 5. PCE removal from 3% POIE(10)/3% IPA solution by multipass MAS at a liquid loading rate of $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$ and an A/L ratio of 461. Error bars represent 95% CIs.

SDHS/3% NaCl/3% CaCl₂ solution required 1316 volumes of air for each volume of surfactant solution (over four passes), while only 855 volumes of air were needed at an A/L ratio of 171 (over five passes). Obviously, operating at a low A/L ratio over multiple passes can significantly reduce the volume of contaminated air that needs to be subsequently treated for large scale operations.

Fig. 5 shows the results of PCE removal from a surfactant system composed of 3% POIE(10)/3% IPA by multipass MAS. PCE removal efficiency remained approximately constant at 53% over six passes of air-stripping at a constant liquid loading rate of $1.07 \times 10^{-7} \text{ m}^3/(\text{m}^2 \text{ s})$ and an A/L ratio of 461. This is consistent with the observations made with the 5% C16-DPDS/3% SDHS surfactant systems. Over the six passes of air-stripping, the cumulative removal of PCE was as high as 98.9%, with PCE concentration reduced from 99,350 to 1070 mg/L. These results, together with those of the 5% C16-DPDS/3% SDHS surfactant systems, clearly demonstrate the effectiveness of multipass MAS at VOC removal from surfactant solutions.

3.4. Multipass/multistage MAS as a cost-effective alternative

Two other options are available to achieve high levels of contaminant removal in MAS, besides the multipass strategy. These include: (1) reducing the liquid loading rate, which decreases the system throughput; and (2) increasing the effective column length (and the total membrane surface area as well), which results in a larger air stripper. As demonstrated in Fig. 6a, the liquid loading rate has to be reduced to $1.35 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ or the length of the hollow fibers has to be increased to 1.27 m to remove 90% of PCE from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution at an A/L ratio of 200. Alternatively, using a multipass approach, 90% PCE removal can be achieved by MAS at A/L ratio of 100 over four passes or at A/L ratio of 150 over three passes at $6.67 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ liquid loading for a column with 0.15 m long hollow fibers, as shown in Fig. 6b. It should be noted that multipass/multistage air-stripping reduces the net liquid throughput per membrane contactor. Although having a series of membrane contactors operated in multistage configuration essentially increases the total surface area of the contacting media (i.e., total column length), the overall contaminant removal is better than that of a single long column because of the greater contaminant concentration gradient between the surfactant solution and the clean air encountered at the head of each stripping pass/stage.

Compared to a single pass process operated at high A/L ratios, multipass/multistage air-stripping at a much lower A/L ratio has a higher volumetric air removal efficiency. By operating at relatively low A/L ratios, lower air pressure is necessary, which means lower

pressure head on the hollow fiber membranes and lower energy consumption for the air blower. For SEAR application, it may require large membrane surface areas or high A/L ratios in order to adequately clean contaminants from the surfactant solution. This can lead to large strippers that are expensive and difficult to service or large volumes of air carrying contaminants at low concentrations, which needs to be treated before being discharged. Multipass MAS at low A/L ratios can remove VOCs more efficiently because the operation conditions are subjected to less mass transfer limitation, thereby reducing the total surface area of the membrane required and the volume of air carrying the contaminants. In large scale implementation, multiple membrane contactors can be arranged in series instead of using only one contactor with multiple passes. Such multistage configuration can also allow the relatively “clean” air from the strippers at the late stages to be reused in the earlier stages. This will result in more effective utilization of the air and blower power consumption since a single air stream passes through every stripper before exiting the treatment train. Furthermore, the VOCs are more concentrated in the smaller volume of exhaust air stream.

The self-contained hollow fiber membrane contactors have high surface-to-volume ratios and are capable of high performance. The modular nature of hollow fiber membrane contactors allows rapid installation, easy integration and maintenance, and portability. It also drastically reduces scale-up problems [47]. They can be easily operated in multistage configurations, and addition or subtraction of stages to increase or decrease the overall removal efficiency can be made easily. As a result, multipass/multistage MAS can be a viable and cost-effective strategy in removing VOCs from surfactant solutions.

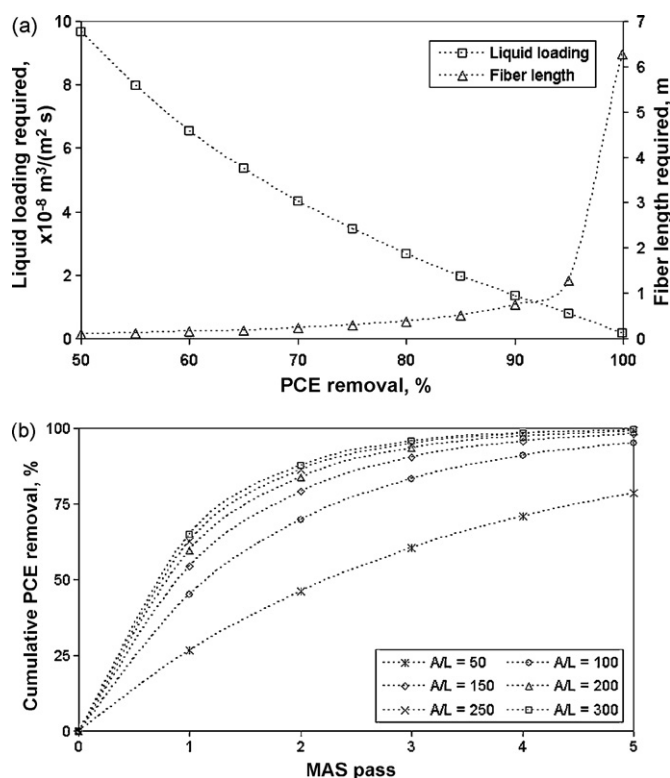


Fig. 6. Model predictions of PCE removal for single pass and multipass MAS: (a) liquid loading rate required (for 0.15 m fiber length) and the fiber length required (at $6.67 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ liquid loading rate) to achieve different levels of PCE removal from 5% C16-DPDS/3% SDHS/3% NaCl/3% CaCl₂ solution in single pass MAS operated at a constant A/L ratio of 200; and (b) cumulative PCE removal from the same surfactant solution as a function of A/L ratio in multipass MAS (at $6.67 \times 10^{-8} \text{ m}^3/(\text{m}^2 \text{ s})$ liquid loading rate with 0.15 m fiber length).

4. Conclusion

Experimental results show that the apparent Henry's law constant of PCE was greatly decreased in the presence of surfactant micelles, and the reduction was approximately proportional to the surfactant concentration. Results also indicate that although a supersolubilization surfactant system solubilized PCE more efficiently, the solubilized PCE was more difficult to remove. Due to reduced contaminant volatility and increased mass transfer limitation in supersolubilization surfactant systems, high efficiencies of contaminant removal are difficult in a single pass air-stripping process while multipass/multistage MAS can be a more cost-effective alternative. Furthermore, multipass/multistage MAS is able to achieve high overall contaminant removal efficiency without requiring large air strippers or producing large volumes of contaminated air that needs to be further treated. The advantages of a multipass/multistage process, coupled with the modular nature of hollow fiber membrane contactors, make multipass/multistage MAS a promising strategy for removing VOCs from surfactant micellar solutions and for regenerating the solutions for reuse. Future studies should explore scale-up and economic evaluations to further optimize this approach.

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