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VOC removal from contaminated groundwater through membrane pervaporation. (II): 1,1,1-trichloroethane-SDS surfactant solution system

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Abstract: The conventional “pump-and-treat” technology for subsurface remediation of groundwater contaminated with volatile organic compounds (VOCs) such as 1,1,1-trichloroethane (TCA), a common chlorinated organic solvent, has limitation of prohibitively long treatment time due to extremely low water solubility of the VOCs. Surfactant-based soil remediation has emerged as the effective technology that substantially reduces the treatment time. In order to make the whole process economical, the surfactant used in soil washing has to be recovered and reused. This study examined the recovery of anionic surfactant, sodium dodecyl sulfate (SDS), from soil remediation fluids containing TCA, using a bench-scale membrane pervaporation unit. The effects of high TCA concentration, surfactant dosage, and flow rate on permeation flux and selectivity (α value) of the process were evaluated. In general, higher surfactant concentration yielded lower TCA flux and constant water flux, resulting in declining α values; higher flow rate of TCA feed stream results in higher VOC flux and selectivity, an indication of the effect of concentration polarization; higher TCA feed concentration produces higher TCA permeation across the membrane, however, the selectivity was virtually unchanged unless the total TCA concentration exceeded 2000 ppm.

Keywords: pervaporation; VOCs; SDS surfactant; groundwater remediation; 1,1,1-trichloroethane

Introduction

The conventional method for subsurface remediation of groundwater contamination with VOCs is the so-called “pump-and-treat” technology. The limitation of this approach is the prohibitively long treatment time for remediating the groundwater contaminated with common chlorinated solvents that have densities greater than that of water (classified as DNAPLs—dense non-aqueous phase liquids). This is largely due to the very low water solubility and low biodegradability of this class of solvents and the tendency of the solvents settling in the bottom of an aquifer and becoming a long-term source of pollution. An estimation of the remediation time for a VOC-contaminated groundwater site using “pump-and-treat” technology is said to be in several hundreds of years (USEPA, 1996). In an effort to directly address the long treatment time, researchers have been investigating the addition of chemical agents to enhance the solubility of VOCs in contaminated groundwater (Knox, 1992). The surfactant-based “pump-and-treat” approach has been proven an effective remediation technology that shortened the treatment of VOC-contaminated groundwater to a practical extent (Harwell, 1992; West, 1992). However, in order to make the whole process economical, the surfactant has to be recovered and reused.

The word, “surfactant” is actually a contraction of the term surface-active agent. Surfactant molecules have opposing moieties at tails and heads of the molecules. For example, a SDS (sodium dodecyl sulfate) molecule has a hydrophilic head (often polar) and a hydrophobic tail (usually non-polar). Some surfactants carry charges such as SDS carrying negative charge (referred to as anionic surfactant). A unique property of surfactant molecules is their ability to form, above the threshold concentration in water or other solvents (a condition also known as critical micelle concentration or CMC for short), micelles, self-assembling aggregates of surfactant molecules with ordered structures. In water, SDS molecules form spherical micelles with the hydrophilic heads pointed to the aqueous phase and the hydrophobic tails oriented toward the core of the cluster (away from the aqueous phase), constituting a hydrophobic (water-hating) pseudo phase. The hydrophilic (water-loving) exterior makes the micelles highly soluble while the interior cores of the micelles serves as the “oil” sinks into which the VOC such as TCA molecules can partition (Shiau, 1995).

The solubility of TCA or other VOCs will be enhanced substantially by adding surfactants to the aqueous solution above CMC levels of the surfactants as the VOC molecules partition into the interiors of the

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surfactant micelles. As a result, the “apparent” solubility of TCA in surfactant-containing aqueous environment is much higher than its intrinsic solubility in water. In surfactant solutions above CMCs, introduction of additional surfactants will only increase micelle concentrations (number of micelles per unit volume), thus increasing their capabilities of “dissolving” more VOC molecules (Edwards, 1991; Rosen, 1989).

Surfactant-containing VOC solutions poses a particular challenge for post-pumping operations in groundwater remediation. Air stripping of VOC in order to recover the surfactant becomes impractical since the foam problem as a result of presence of surfactant would render the process ineffective, and the consequent removal of VOC from air using activated carbon involves costly regeneration processes. There have been several studies on the use of membrane pervaporation as a means of removing VOC and recycling surfactants (Jiang, 1997; Vane, 2000). Pervaporation of VOCs is based on the high vapor-liquid partition coefficient represented by Henry's Law constant (H_c) in aqueous environment:

$$H_c = \frac{C_v}{C_l}, \quad (1)$$

where C_v and C_l are the vapor and liquid phase concentrations, respectively, and the permeability of the VOC in the membrane matrix (ability to partition and diffuse).

Pervaporation is carried out by feeding a liquid mixture on one side of the non-porous membrane producing vapors permeate on the other side under vacuum (Cussler, 1997). The condensed vapor, often rich in preferentially permeating species (VOCs for our interests) is collected and the process continues. Pervaporation has found increasing acceptance for use in diverse areas of practical operations ranging from flavor and aroma recovery from food processing, to volatile organic compound (VOC) removal from soil remediation fluids (Jiang, 1997; Peng, 2003). The driving force for pervaporation is the difference in chemical potential (or partial vapor pressure as a first approximation) of each component across the membrane.

The performance of a pervaporation process is assessed by the flux of the permeating species and the selectivity of the species (Jiang, 1997):

$$J_i = k_i \rho_i (C_i^L - C_i^V), \quad (2)$$

where k_i , ρ_i , C_i^L , C_i^V are the overall mass transfer rate constant, molar density of feed, bulk liquid phase concentration (mole fraction), and bulk vapor phase concentration, respectively, for component i . Selectivity can be expressed in several ways. One common representation of selectivity, the separation factor, α , is analogous to the relative volatility of the component (i and j) of a binary liquid mixture:

$$\alpha_{ij} = \frac{(C_i/C_j)^V}{(C_i/C_j)^L}. \quad (3)$$

Sometimes, however, the enrichment factor, β_i , is used as an indication of the separation selectivity for component i :

$$\beta_i = \frac{(C_i)^V}{(C_i)^L}. \quad (4)$$

As the concentration of component i usually is very small, the concentration of component j in feed stream will be close to i . With dilute feed solution, there is usually no significant membrane swelling or interaction between components permeating through membrane. The separation factor will therefore be close to the value of the enrichment factor, β_i , for dilute solutions (Karlsson, 1996):

$$\alpha_{ij} \approx \beta_i. \quad (5)$$

It should be pointed out that permeation flux and selectivity are experimentally determined parameters, and Equations (1)–(4) are for data correlation purpose only because concentration polarization (discussed in the Results and Discussion section) often obscures computations of these parameters.

The objective of this study was to use a custom-made bench scale pervaporation unit using a polydimethylsiloxane (PDMS) membrane to remove/recover 1,1,1-trichloroethane (TCA) from surfactant solutions in order to recycle SDS and to examine the performance parameters of the pervaporation process under different operating conditions.

1 Experimental

1.1 Materials

1,1,1-trichloroethane (TCA): 99.5%, ACS reagent, Sigma-Aldrich Company, used as received; sodium dodecyl sulfate (SDS): 99% (GC); molecular formula: $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, $\text{CMC} = 8.2 \times 10^{-3} \text{ mol} = 2.36 \text{ g/L}$ at 25°C , Sigma Company in the USA, used as received; PDMS membrane: silicone rubber flat sheet with 0.0127 cm thickness from Specialty Manufacturing Inc, Saginaw, MI, USA; Methanol: HPLC grade, Fisher Scientific in the USA.

1.2 Bench pervaporation unit

The schematic diagram of the bench scale pervaporation unit was illustrated in our previous paper (Peng, 2003). The feed stream was circulated by a liquid pump between a 0.02 m^3 stainless steel feed tank and the membrane cell in a loop via a stainless steel coil that was immersed in a thermostatic water bath. The TCA concentration in the feed tank was adjusted at the start of an experiment by adding an aliquot of water saturated with TCA. A magnetic stirrer was used for continuous uniform mixing in the feed tank and two rotometers (Gilmont Co., USA) were used to monitor/regulate a wide range of the flow rates. The feed stream was warmed up to a preset temperature by regulating the water bath temperature during circulation. The liquid temperature before and after the membrane cell and the permeate vapor temperature were monitored by the thermistor thermometers (Cole-Palmer Co., Vernon Hill, IL, USA). The vapor side of the membrane was operated under vacuum, and the permeate was collected in cold traps, immersed in Dewar flasks filled with liquid nitrogen. The permeate liquid collected over a specific time period is weighed and analyzed with a varian gas chromatography (GC) (Varian Co., USA) to evaluate permeation flux and selectivity.

The membrane cell is of rectangular shape so that the hydrodynamics within the cell can be well defined. The effective dimensions of the cell are 2.4 cm by 16.4 cm, yielding an effective area of 39.36 cm^2 . The thin pervaporation membrane was supported by a porous stainless steel sheet of 100-micron grade (316L SS, Mott Industrial Co., USA). The cell consists of a top and a bottom compartments sealed by a Viton O-ring. Feed streams enter the cell from one end of the cell and exit at the other, flowing in one direction.

1.3 Experimental conditions

The experiments conducted in this study were under the operating conditions compiled in Table 1. Our preliminary testing with the pervaporation unit ruled out the influence of permeate pressure (vacuum). We found that the process performance of the unit (permeation flux and selectivity) was not affected by the permeate pressure as long as the pressure was kept below 3 torr (about 400 Pa).

1.4 Experimental operation and analysis

Experiment setting and operation, GC analysis procedure were basically the same as our previous paper (Peng, 2003). As for the feed solutions containing surfactant, it was prepared 12 hours before the experiments so as to let the micelle solution reach equilibrium. As was in previous GC analysis by Varian 3500 equipped with FID detector, internal standard retention time was 14.5 minutes, and the TCA retention time was 17 minutes. Experiment errors were within 10% for duplicate analysis.

2 Results and discussion

2.1 Effect of surfactant concentration on pervaporation performance

The effect of surfactant concentration on pervaporation performance is evident in Fig.1 and 2. It can be seen that the water flux was relatively constant in the range of 0—8.8 CMC, but VOC flux showed a gradual decreasing starting from 2 CMC of SDS at 40°C . When SDS concentration reached about 2% (w/w) (about 8.8 CMC), TCA flux decreased to $21.23 \text{ g}/(\text{m}^2 \cdot \text{h})$ as compared with $45.93 \text{ g}/(\text{m}^2 \cdot \text{h})$ in an aqueous system without surfactant. Accordingly the separation factor showed a corresponding decrease,

Table 1 Operating parameters for all experiments

Operating parameters	Variation range
Feed concentration, mg/L	50—6100
Feed flow rate, L/min	1—5.4
Temperature, $^\circ\text{C}$	30—40
Permeate pressure, Pa	400
Surfactant concentration, %	0—2, equivalent to 0—8.8 CMC

from about 2800 to 1282. According to extracellular fraction data for VOCs (Vane, 2000), TCA had approximately 50% and 30% extracellular fractions in 4 and 8 CMC SDS solutions at 40°C, respectively. So the flux data in our experiment did not show as large a decrease of flux as was expected according to the data of equilibrium partitioning of TCA in surfactant solutions. The mechanism that might lead to this result lies in the reduced concentration polarization effect when the micelles could act as a source for depleted concentration boundary layer. This will be further studied in our future numerical study of concentration polarization by computational fluid dynamics (CFD) simulation approach.

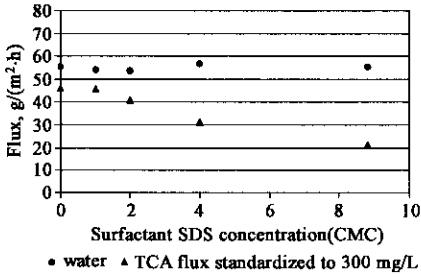


Fig.1 Effect of SDS concentration on flux at 40°C

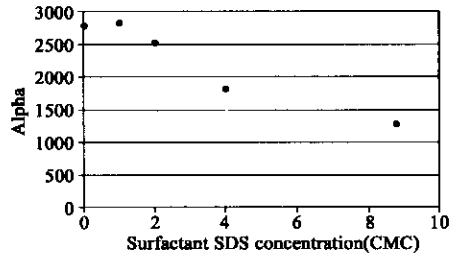


Fig.2 Effect of SDS concentration on separation factor at 40 °C

2.2 Effect of feed velocity on pervaporation performance—laminar flow

Typically, flow rates affect VOC removal rate and this trend was shown in the results of pervaporation experiments with surfactant solutions in Fig.3 and 4. When surfactant was present at 2% (w/w), similar influence of feed velocity on both VOC flux and separation factor were observed. The feed concentration in this set of experiments was around 600 ppm thus making the extra-micellar TCA concentration (defined as the concentration of TCA outside the micelles; 600 ppm is the total TCA concentration including extra-micellar and micellar concentrations) at the same level of a similar experiment describe in our previous paper (Peng, 2003). Both VOC flux and separation factor showed improvements as the flow rate increased. However, the effect observed here was not as dramatically as the one in a TCA-water system. VOC showed only about 2-fold increase when the flow rate was changed from 0.1 gallon/min to 0.3 gallon/min, and separation factor only showed 160% increase as compared to more than 2-fold increase in the absence of surfactant. This difference might come from the viscosity increase with the presence of 2% (w/w) surfactant. Another possible reason is that the presence of micelles in the concentration boundary layer provided an additional source for depleted VOCs near membrane surface, thus reducing feed side mass transfer resistance.

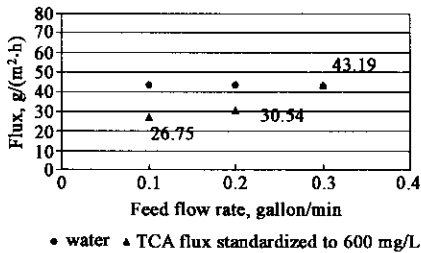


Fig.3 Effect of feed flow rate on TCA flux at 40°C and 2% (w/w) SDS

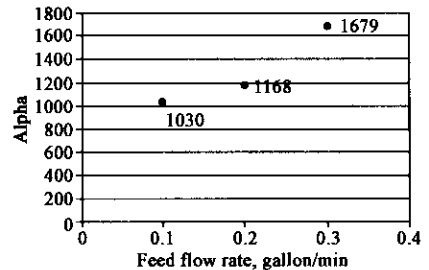


Fig.4 Effect of feed flow rate on separation factor at 40°C and 2% (w/w) SDS

2.3 Effect of feed velocity on pervaporation performance-turbulent flow

The effect of the turbulent flow on fluxes and α is illustrated in the plots below (Fig. 5 and 6). As with water-TCA system, the water flux was not affected by TCA feed flow rate. The TCA flux increased gradually all the way to as high as 332 g/(m²·h) when feed rate reached 1.4 gallon/min, corresponding to a superficial velocity of 1.84 m/s and a Reynolds number of 10324. The separation factor showed about

2.5-fold increase within this range. The presence of concentration polarization was evident even with turbulent flows.

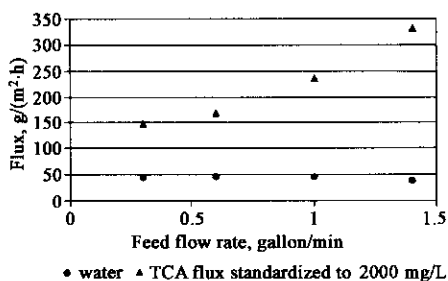


Fig.5 Effect of feed flow rate on flux at 30°C and 2% (w/w) SDS

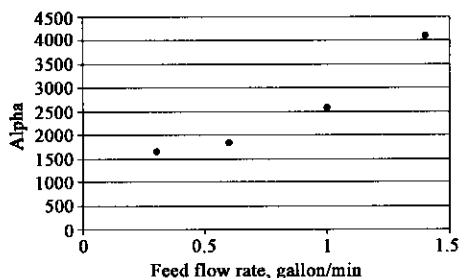


Fig.6 Effect of feed flow rate on separation factor at 30°C and 2% (w/w) SDS

2.4 Effect of high VOC concentration on pervaporation performance in surfactant solutions

The effect of high TCA concentration on TCA flux and selectivity in surfactant solutions are illustrated in Fig.7 and 8. Good linear relationship between TCA flux and feed concentration was observed. Unlike dilute systems, separation factors showed a little increase with high-concentrated TCA surfactant solutions here. The separation factor showed about 50% increase when the total TCA concentration in surfactant solution was 6000 ppm as compared to 666 ppm. The increase for TCA flux at high concentration was most evident after 2000 ppm. At the same time, water flux shows little change by keeping around 40 g/(m²·h). This trend for selectivity was not the same as literature (Jiang, 1997) where water flux was found increasing, which contributed to the reported decreasing of the separation factor. In this experiment, however, water flux remained constant. This indicates that PDMS membranes can be used in high VOC concentrations with no significant interaction between water and membrane systems during operations. The possible explanation for increased the separation factor under high feed concentration conditions is that availability of TCA from TCA in the micelles near the membrane reduced the effect of concentration polarization substantially. Membrane swelling, if any, could also bring the increasing effect for TCA flux. As similar effect was not observed in water flux, nevertheless, it should not be very substantial. As the concentration of TCA was much higher than that of water in the permeate after the feed concentration was above 2000 ppm, the hydrophobic environment within the membrane matrix could hinder water permeation in addition to interfering effect from large amount of TCA molecules present in the matrix.

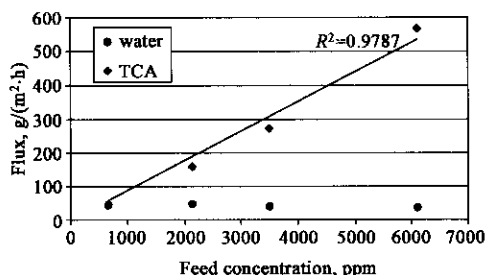


Fig.7 Effect of high TCA concentration on flux at 30°C and 2% (w/w) SDS

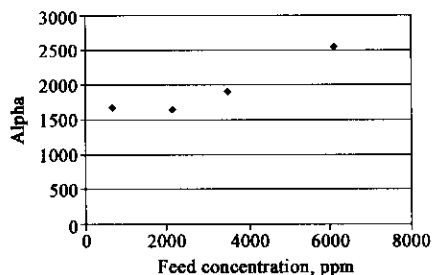


Fig.8 Effect of high TCA concentration on separation factor at 30°C, 2% (w/w) SDS and feed flow rate of 0.3 gpm

3 Conclusions

Detailed in this paper are the 1,1,1-trichloroethane (TCA) removal characteristics from surfactant solutions using a bench scale pervaporation unit. The effects of surfactant concentration, high TCA concentration, and flow rate (flow velocity) on permeation flux and selectivity were evaluated. It is obvious that partitioning of TCA molecules into surfactant micelles reduced the available TCA for permeation, thus

reducing the driving force for TCA permeation across the membrane. The decline in TCA flux across the membrane translates into a decrease in selectivity while the water flux remains unchanged. The effect of flow rate was somewhat predictable: the increase in the flow rate yielded an increase in TCA flux. The concentration polarization was evident in the data in the form of the linearity between flow rate and TCA flux as the diffusion of sparsely soluble TCA molecules in water (a polar solvent) is slower than that in the PDMS membrane matrix (a hydrophobic non-polar polymer). Also the water flux under different flow rates showed no sign of changing one way or the other. This is because the TCA surfactant solution, even when it was high as compared with its normal solubility, was still made up of almost all water and the water permeation in the membrane was a slow diffusion process not subject to the influence by the flow dynamics in the system. The adverse effect of concentration polarization was most apparent by examining experiment result under turbulent regime. The results also suggested that increase in TCA feed concentration above 2000 ppm resulted in higher separation factor because of possible reduced concentration polarization effect and the hindrance effect for water permeation.

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