



Evaluation of semi-volatile contaminant transport in a novel, gas-tight direct contact membrane distillation system



Kevin A. Salls^a, Danbi Won^b, Edward P. Kolodziej^{b,c}, Amy E. Childress^d, Sage R. Hiibel^{e,*}

^a Department of Civil and Environmental Engineering, University of Nevada, Reno, NV 89557, United States

^b Department of Civil and Environmental Engineering, University of Washington, Seattle, WA 98195, United States

^c School of Interdisciplinary Arts and Sciences, University of Washington, Tacoma, Tacoma, WA 98402, United States

^d Sonny Astani Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA 90089-2531, United States

^e Chemical and Materials Engineering Department, University of Nevada, Reno, NV 89557, United States

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ABSTRACT

A first-of-its-kind, gas-tight MD system was designed to provide insight into the dynamic transport of semi-volatile contaminants over time by closing the mass balance for each contaminant. Testing with non-volatile ions was used to confirm the integrity of the test system and sampling procedures. Non-volatile contaminants had consistently high rejection rates ($\geq 99\%$) for all analytes tested. For the most hydrophobic semi-volatile contaminants, sorption to the membrane and polymeric components within the system played a significant role in their fate. Less hydrophobic semi-volatile contaminants reached a pseudo-equilibrium governed largely by contaminant volatility, as predicted by Henry's Law. Rejection of semi-volatile nitrosamines varied from ~ 96 to 88% , demonstrating significant variation in behavior even within the same contaminant class. Results suggest that transport of semi-volatile contaminants in MD was consistent with a pseudo-equilibrium partitioning process and was highly correlated with contaminant volatility ($R^2 = 0.934$ for the combined data set). These results have implications for treatment of complex source waters where an understanding of the transport of volatile components is needed even if treatment objectives are focused on nonvolatile components.

1. Introduction

Membrane distillation (MD) is a separation technology that utilizes a hydrophobic, microporous membrane to produce high-quality water. The hydrophobic nature of the MD membranes results in a stable water-air interface at each pore entrance of the membrane that prevents liquid and non-volatile contaminant passage. In direct contact MD (DCMD), water flux is achieved by evaporation of a warm feed stream at the feed-side interface, followed by water vapor transport through the membrane pore space, with subsequent condensation in a cooler liquid distillate stream [1–4]. Vapor pressure difference between the two streams is the driving force for water transport in MD. MD offers several distinct advantages over pressure-driven processes, including 100% theoretical rejection of non-volatile contaminants [7], low or ambient hydraulic operating pressures, resistance to fouling [8], and decreased sensitivity to feed concentrations [8]. Additionally, the lower operating

temperatures required compared to traditional distillation offer the potential for the use of energy from low-grade waste heat [9] or renewable energy sources [10,11], which can improve the economics and potential applications of the technology [12].

Current MD applications include treatment of hypersaline brines and desalination [8,13–16], food industry separations such as dewatering fruit juices and whey protein [17], recovery of high-value metals from aqueous waste streams [18], treatment of hygiene water and human urine in long-term space missions [20,21], and recovery of ionic liquids used in lignocellulosic biomass pretreatment for biofuel production [19]. These applications uniformly focus on the separation of non-volatile components and consequently demonstrate rejection rates near 100%, as expected for MD [7]. Emerging applications for MD, including the treatment of process waters from various industries (e.g., petroleum and gas [22]), challenge MD technology with more complex source waters. These applications require an understanding of the

Abbreviations: C_d , distillate concentration; C_f , feed concentration; C_l , liquid-phase concentration; DCMD, direct contact membrane distillation; IC, ion chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; K_a , acid dissociation constant; K_H , Henry's constant; Log D, log of distribution coefficient; M_i , total initial mass; M_s , mass lost to sorption; MD, membrane distillation; MR, mass recovery; P, vapor pressure; PTFE, polytetrafluoroethylene; R, rejection; R_{eq} , equilibrium rejection; RO, reverse osmosis; V_f , feed volume; V_d , distillate volume

* Corresponding author at: Chemical and Materials Engineering Department, University of Nevada, Reno/MS 388, 1664 North Virginia Street, Reno, NV 89557, United States.

E-mail address: shiibel@unr.edu (S.R. Hiibel).

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separation of volatile components in addition to quantifying non-volatile rejection. An understanding of the transport of volatile components present when treating complex source waters is needed even if treatment objectives are focused on nonvolatile contaminants.

It is generally assumed that volatile contaminants will be poorly rejected by MD, and may even be concentrated in the distillate stream relative to the feed stream if the contaminants have vapor pressures higher than that of water [23]. Some research has examined MD treatment of volatile and semi-volatile contaminants, including industrial chemicals (benzene, trichloroethylene) [24], methyl tert-butyl ethyl (MTBE), and ethyl acetate [24,25]. In a recent water reuse study of MD, the fate of a suite of trace organic contaminants was examined. It was found that rejection in MD is linked to contaminant volatility and hydrophobicity [23,26,27]. Wijekoon et al., [23] reported that all contaminants with $pK_H > 9$ had $> 95\%$ removal by MD, but that contaminants with higher volatility had lower rejection rates, ranging from 54 to 73%. Further interpretation of these results was somewhat complicated by mass loss and incomplete mass balances, likely due to evaporative and sorptive losses during testing.

In the current study, a novel, gas-tight, bench-scale DCMD system was designed and fabricated to examine the transport of a set of model contaminants with a range of volatility encompassing three orders of magnitude of Henry's constant (K_H). The main objective of this research was to quantify semi-volatile contaminant removal and to gain greater understanding of contaminant classes that can be removed by MD. The system was first tested with non-volatile contaminants to confirm the basic integrity of the gas-tight system and inline sampling procedures. Semi-volatile testing specifically addressed the hypothesis that MD removal performance is a pseudo-equilibrium process directly predictable by Henry's Law. To the best of the authors' knowledge, this is the first demonstration of a gas-tight DCMD system, which is critical to close the mass balance for semi-volatile contaminants.

2. Materials and methods

2.1. Gas-tight DCMD system

Preliminary experiments using a DCMD system with open feed and distillate containers and plastic tubing and fittings exhibited significant mass loss when volatile organic components were tested, likely due to evaporation to the atmosphere and sorption to system components. An innovative, gas-tight bench-scale system was designed (Fig. 1). To minimize evaporative losses, the traditional open feed and distillate reservoirs were replaced with flexible Kynar® gas sampling bags (Analytical Specialties Inc., Elbourn, IL, USA). To minimize sorptive mass loss, stainless steel tubing and fittings were used in place of plastic tubing and fittings throughout the system.

The Kynar® gas sampling bags enabled the system to be gas-tight while still flexible enough to eliminate headspace created by changes in feed and distillate volume during experimental tests. The feed-side reservoir bag was placed in a hot water bath (Precision, Thermo-Fisher Scientific, Waltham, MA, USA) and a pump was used to recirculate the feed solution at 1 L/min. The distillate-side reservoir bag was placed on a balance (FG-ISOKAM, A&D Weighing, San Jose, CA, USA) and its mass was monitored using LabView (Version 14.0.1.4008, National Instruments, Austin Texas, USA). Temperature probes (EI1024, LabJack, Lakewood, CO, USA) were placed at the inlets and outlets of the feed and distillate streams to the membrane module, with temperature data collected via LabView. Feed temperature was maintained at $50 \pm 3^\circ\text{C}$ using a water bath and distillate temperature was maintained at $25 \pm 3^\circ\text{C}$ using a high-efficiency heat exchanger (McMaster-Carr, Elmhurst, IL, USA) connected to a recirculating chiller (Isotemp 1013S, Fisher Scientific, Waltham, MA, USA). Two stainless steel sampling valves were installed immediately downstream of the membrane module to enable sampling of the feed and distillate solutions without interrupting operation. Experiments were performed for 48 or

56 h, depending on sample volumes required for analyses.

A hydrophobic, microporous polytetrafluoroethylene (PTFE) membrane (QM022, Clarcor, Inc. Franklin, TN, USA) consisting of a single PTFE active layer with a nominal pore size of 0.18 μm , porosity of 80.1%, and thickness of 67 μm [28] was used. Membrane coupons were placed in the membrane module with gaskets forming flow channels that measured $155 \times 92 \times 3$ mm on each side. The effective membrane surface area was 143 cm^2 . Plastic cross-mesh spacers were installed in each flow channel to support the membrane and ensure well-mixed flow.

2.2. Experimental protocol

2.2.1. Non-volatile ions

A combined salt solution was used to evaluate non-volatile ion rejection. ACS-grade sodium fluoride (NaF), calcium sulfate (CaSO_4), and potassium chloride (KCl) were added to 4 L of ultrapure feed water and mixed well prior to equilibration for 24 h at 4°C to ensure complete dissolution. The 4 L of salt solution were transferred to the feed-side reservoir and mixed with an additional 14 L of ultrapure water to achieve an initial target anion concentration of 20 mg/L; the respective cation concentrations varied according to the salts used. Anions were analyzed by ion chromatography (IC) using EPA Method 300.1 [29]. Cations were analyzed by inductively coupled plasma – mass spectrometry (ICP-MS) using EPA Method 200.8 [30].

Similarly, an aqueous solution of metal ions was used to evaluate metal ion rejection. ACS-grade arsenic pentoxide (As_2O_5), zinc sulfate (ZnSO_4), chromium trichloride (CrCl_3), and copper chloride (CuCl_2) were added to 4 L of ultrapure water and equilibrated with mixing (24 h) at 4°C . The 4 L of metal ion solution was transferred to the feed-side reservoir and diluted with an additional 14 L of ultrapure water to achieve an initial target metal ion concentration of 20 mg/L. Feed and distillate samples for metal ion analysis were collected in 250-mL acid-washed polyethylene containers. Metal ions were analyzed by ICP-MS using EPA Method 200.8 [30].

Boron and bromide rejection were evaluated in two additional experiments. For each, either ACS-grade sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) or sodium bromide (NaBr) was added to 4 L of ultrapure water and mixed well prior to equilibration for 24 h at 4°C to ensure complete dissolution. The 4 L of boron (or bromide) solution were transferred to the feed-side reservoir and mixed with an additional 14 L of ultrapure water to achieve an initial target concentration of 20 mg/L. Feed and distillate samples for analysis were collected every 8 h in 500-mL acid-washed polyethylene containers. Anions were analyzed by ICP-MS using EPA Method 300.0 [29].

2.2.2. Nitrosamines

The EPA 8270 Appendix XI Nitrosamine mix (Supelco, Bellefonte, PA.), containing seven semi-volatile and two non-volatile nitrosamines, was used for testing. Physicochemical parameters of interest for each nitrosamine are reported in Table 1.

A 1-mL ampule of the stock mixture, which contained 2 mg of each nitrosamine prepared in dichloromethane, which is poorly miscible in water, was added to 15 mL of methanol and d sonicated for 5 min. The dichloromethane-methanol mixture was then added to 3.984 L of ultrapure water in an amber glass bottle and agitated prior to equilibration for 24 h at 4°C to ensure complete dissolution. The 4 L of nitrosamine solution were transferred to the feed-side reservoir and mixed with an additional 14 L of ultrapure water to achieve initial target concentrations of 20 mg/L.

Feed and distillate samples for nitrosamine analysis were collected in 1-L amber glass bottles with sodium azide (1 g) and sodium thiosulfate (80 mg) preservation. Nitrosamines were solid-phase extracted (activated charcoal SPE, Restek 521 cartridges) and analyzed by gas chromatography-tandem mass spectrometry (Varian 4000 Ion Trap GC-MS/MS; positive chemical ionization with methanol,

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