REPORT

Title: Hollow fiber membrane air stripping for the removal of carbonate species in produced water from hydraulic fracturing

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Abstract:

Approximately 5.66 million m^3 of wastewater per year is produced by hydraulic fracking; the "flowback" water constitutes about 10-30% of the water used in the fracking process. The ideal situation would be to treat and reuse the flowback water to reduce disposal costs and the demand for fresh water, but such treatment is difficult due to high saline content and presence of oils and other organics. In their pilot study, Miller et al. addressed the use of ultrafiltration (UF) and reverse osmosis (RO) membranes modified with a polydopamine coating to treat produced water from the Barnett shale gas basin in Texas. This research examined the use of a hollow fiber (HF) air stripping membrane unit for CO_2 removal as an intermediate step in this treatment train to improve the desalination performance of reserve osmosis. The overall goal of the research was to evaluate removal of volatile contaminants in the HF membrane air stripper as a function of synthetic water composition. The research utilized the Liqui-Cel® Membrane Contactor as it has proven success for air stripping of volatiles and its baffled design prevents fiber bypassing and promotes enhanced liquid film mass transfer coefficients. An experimental system was designed and tested for both CO_2 and other volatile compounds and a model that more accurately captures the removal of volatile compounds from water in the Liqui-Cel Membrane Contactor was developed.

Problem and Research Objectives

The popularity of hydraulic fracturing, or fracking, over the past decade has increased the production of natural gas in North America and, consequentially, the need for improved technologies to treat the accompanying flowback water.[1] Fracking requires large volumes of water putting a strain on local freshwater demands and disposal practices. Approximately 5.66 million m^3 of wastewater per year is produced by fracking;[2] this "flowback" water constitutes approximately 10-30% of the water used in the fracking process.[1]

Disposing of the produced water can cost up to $4 per barrel including costs for transportation and injection wells.[1] Therefore, it is ideal to reuse the flowback water to reduce disposal costs and the demand for fresh water. However, challenges to produced water treatment occur due to the high saline content and presence of oils and other organics. According to Thiel et al., produced water samples from the Permian shale basin contained up to 183,000 mg/L of total dissolved solids (TDS), while Miller et al. reported produced water characteristics from the Barnett shale basin of up to 99,000 mg/L TDS.[2,1]

The rise of membrane technology for purification of flowback waters is attributed to their small energy footprint, high efficiency, and ability to be moved from one drill site to the next.[1] Recent advances in membrane research for flowback water treatment include the use of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Alzahrani et al. reviewed the different types of membrane technologies to conclude that current practices have "high potential" for meeting the needs of the petroleum industry while future goals can target a standard reference for produced water characterization, treatment of produced water at its source by integrated membrane technologies to aim for "zero liquid discharge," and the recovery of by-products from produced water.[3] The biggest drawback to membrane technologies is their tendency to foul due to the constituents in the water being treated.

In their pilot study, Miller et al. addressed the use of ultrafiltration (UF) and reverse osmosis (RO) membranes modified with a polydopamine coating to treat produced water from the Barnett shale gas basin in Texas.[1] The polydopamine coating was used as a surface modification for the membranes to reduce the effects of fouling. The polyacrylonite hollow fiber UF membranes were further modified by grafting poly(ethylene glycol) to the polydopamine coating. The UF membranes removed organic material, specifically emulsified oils, from the flowback water while RO membranes desalinated the UF permeate. The surface modifications successfully decreased the resistance to mass transport in the UF membranes. The polydopamine coating did not affect the water flux or the transmembrane pressure of the modified RO membrane compared with the unmodified RO membrane; the surface modification did, however, increase the salt rejection of the modified RO membrane. In that study, the TDS in the RO feed ranged from $2x10^{-4}$ to $6.5x10^{-4}$ mg/L, which represented the salt concentration of the waters.

To improve the desalination performance of reserve osmosis, different pretreatment options are available.[4] Jamaly et al. recommend the use of UF or NF as part of the pretreatment membrane train to extend the lifetime of RO membranes because the UF/NF membranes can handle a salinity range > 35,000 ppm.[4] Considering the pilot study in the Barnett shale gas region, an intermediate step between UF for organic removal and RO for desalination could be used to remove carbonate species from the produced water to prevent precipitation and scaling of the RO membrane. Thiel and Lienhard reported that the carbonate species in the produced water were the most likely to scale membranes based on their saturation index.[2] Therefore the overall goal of this research was to evaluate the addition of a membrane a hollow fiber air stripping membrane contactor as RO pretreatment to remove CO_2 from produced waters. Liqui-Cel® Membrane Contactor systems have been used to remove CO_2 from water prior to secondary treatment by RO or electrodeionization to decrease the scaling effect of the carbonate species. The objectives of this research were to 1) construct a micro-module system that could be used to test the performance of the membrane contactor over a range of background waters and operating

conditions; and, 2) to develop a model that could be used to predict performance in these systems.

Materials/Methodology

The research plan was divided into two phases consistent with the two objectives. In phase I, a model was developed that can be used to predict removal efficiencies of volatile contaminants in the current two-stage Liqui-Cel hollow fiber (HF) air stripping membrane contactor. Since most of the previous research conducted with this system employed an unbaffled membrane operated as a single-stage, countercurrent, air stripper with the liquid stream flowing through the lumen, modeling approaches developed based on this system were not appropriate for the current construction of HF membrane contactor. The redesigned Liqui-Cel® Extra-Flow module (Figure 1) from Membrana contains a shell-side baffle and a central tube feeder with air flow on the lumen-side. This design avoids the channeling seen in the previous, unbaffled model and increases the mass transfer coefficient compared to strictly parallel flow[7]. Thus, a two-stage efficiency model was developed as part of this research.

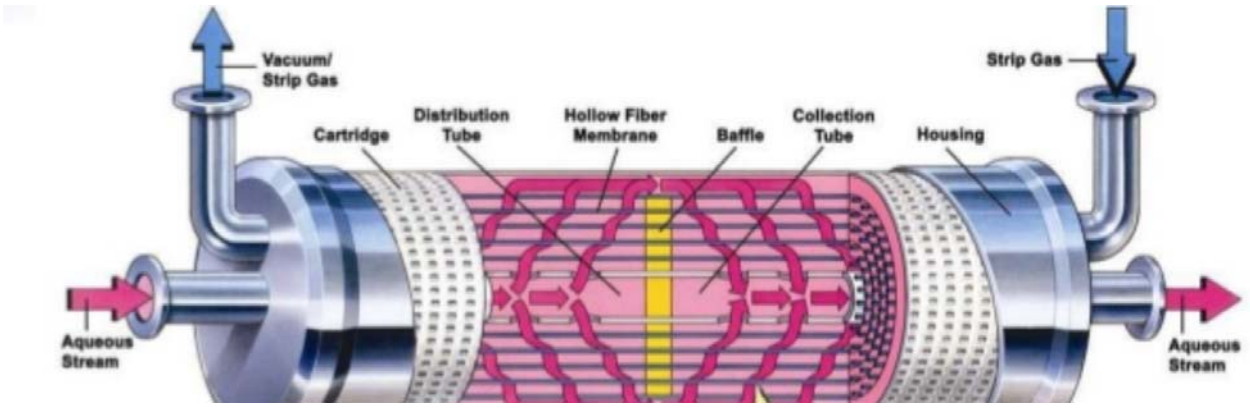

Figure 1. Liqui-Cel® Extra flow design (Drawing from Liqui-Cel® Membrane Contactors, Membrana).

The 1.7 x 5.5 MiniModule® PP X50 membrane contactor system from Membrana Contactors was used in this research and the experimental system developed for this research was constructed as part of this project (Figure 2). The module can accommodate a maximum flowrate of 2.5L/min, appropriate to handle a laboratory scale water flowrate of up to 0.8L/min. The hollow fiber membrane in this unit is hydrophobic polypropylene appropriate for CO_2 removal in a countercurrent flow setup with water on the shell side and either a vacuum or sweep gas on the tube side to remove CO_2 from the system. Air was used as the sweep gas in the

experimental tests in this research. The synthetic water was prepared with Millipore water with varying concentrations of sodium chloride added for ionic strength up to 0.5M. The solutions were placed in 3 L Tedlar bags to prevent volatilization and the pH was adjusted to 5. Carbonate was added to the solutions using sodium bicarbonate and the initial bicarbonate concentration tested was 100 ppm. At pH 5 (the pH expected from upstream membrane processes), it was assumed that all of the carbonate was present at H_2CO_3* ($H_2CO_3 + CO_{2(aq)}$). Samples of the CO_2 concentration in the feed were taken prior to the beginning of the experiments. The liquid flow rate was set to 20 mL/min and air flow rates were determined based on the desired stripping factors. Initial testing used stripping factors from 10 to 20. The air flow rate was calibrated at the beginning and end of each experimental run using a bubble flow calibration device. Samples were taken in headspace free 40 mL vials at 10 minute intervals. Samples were stored at 4 ◦C for 24 hours or less and measured on a Shimadzu L total organic carbon analyzer for inorganic carbon. Additional experiments for model validation were also conducted in a similar manner using chloroform as a pH independent model compound. Chloroform analysis was conducted using GC/MS analyses.

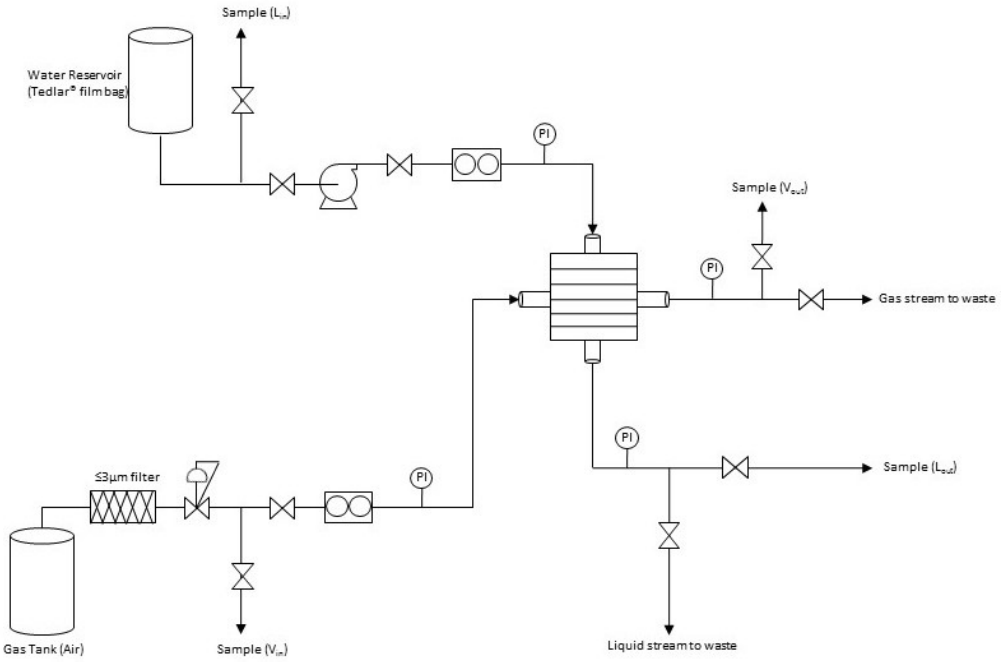

Figure 2. Process flow diagram for the continuous flow experimental setup with the MicroModule for THM air stripping.

Principal Findings

Stage Efficiency Modeling

The Liqui-Cel® Extra Flow module can be considered a stage device due to the physical attributes of the baffle. If either side of the baffle acts as one separation stage, then a stage efficiency model can be implemented to model the performance. Seibert and Fair designed experiments to formulate a stage efficiency modeling using a liquid-liquid

extraction process[9]. The model is based on the Murphree efficiency of the system. Murphree efficiency typically describes the mass transfer efficiency at a particular stage in a separation process, where 100% efficiency is based on vapor and liquid phases leaving said stage in equilibrium in accordance with Henry's Law[8]. According to the model proposed by Seibert and Fair, the Murphree efficiency, E_m, can be calculated by:

$$E_m = \frac{\alpha}{1+\frac{\alpha}{2}} \tag{1}$$

where

$$\alpha = \frac{K_o A_i}{Q_t} \tag{2}$$

and

$$A_i = \frac{A_m}{1+N_{baffles}} \tag{3}$$

where K_o is the overall liquid film or shell-side mass transfer coefficient of a system (m/s), A_i is the contact area per stage (m^2), Q_t is the tube-side volumetric flow rate (m^2/s), A_m is the contact area per module (m^2), and $N_{baffles}$ is the number of baffles in the module[9]. The predicted overall efficiency of the module can then be calculated from the follow expression:

$$E_o = \frac{\ln[1+E_m(S-1)]}{\ln S} \tag{4}$$

where

$$S = \frac{HQ_G}{Q_L} \tag{5}$$

where S is the stripping factor, H is the Henry's law constant (L_L/L_G), Q_G is the gas phase volumetric flow rate (m^3/s), and Q_L is the liquid phase volumetric flow rate (m^3/s)[9]. The actual overall stage efficiency can be calculated using the Kremser equation:

$$N_{eq} = \frac{\ln\left[\left(\frac{C_0}{C}\right)\left(1-\frac{1}{S}\right)+\frac{1}{S}\right]}{\ln S} \tag{6}$$

where N_{eq} is the number of theoretical stages, C_0 is the initial concentration of contaminant to be removed, C is the final concentration of contaminant, and S is the stripping factor[8]. Dividing the number of theoretical stages by the number of physical stages in the module gives the actually efficiency of the separation process. The stage efficiency model was tested against several sets of data from the literature for volatile contaminants. Significant

variability between measured and predicted efficiencies was observed; however, most of the experimental data was either collected using the unbaffled module configuration or using experimental conditions that were not consistent with the model (e.g. liquid phase flow on the tube side, vacuum application to the gas phased). Thus, the need for collecting data with the current module configuration is necessary for model validation.

Preliminary Results from Hollow Fiber Membrane Contactor Experimental System

Experimental data from the HF micro-module system demonstrated that removal of both CO_2 and chloroform were possible. Steady-state was achieved within 10 minutes of operation. Since the Henry's Constants for these two compounds varies over an order of magnitude, the contactor has significant potential for stripping a range of volatile contaminants. Under the conditions of the experiments, removals of CO_2 ranged from 65 to 75 percent which suggests that CO_2 membrane stripping is feasible. No significant differences were observed over the range of ionic strengths tested (up to 0.5M).

Significance

The Liqui-Cel® Membrane Contactor system employed in this research has significant potential for removing dissolved gases from liquid streams. Removal efficiency appears to be independent of ionic strength which indicates that the process has potential for serving as an intermediate step for removing carbonate from water to prevent precipitation and scaling of the RO membrane. In particular, the contactor can provide an intermediate step between UF for organic removal and RO for desalination of produced water.

A Murphree stage efficiency model was developed based on previous research by Seibert[10]. The Murphree efficiency describes the efficiency of a single separation stage in the overall module based on how well mixed the vapor and liquid phases are before moving to the next stage. The overall efficiency of the module can be calculated from the Murphree efficiency. Thus, this stage efficiency model can be used to predict removals and develop design parameters once it is validated with a larger set of data from the experimental system.

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