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Triple-bore hollow fiber membrane contactor for liquid desiccant based air dehumidification

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Abstract

Dehumidification is responsible for a large part of the energy consumption in cooling systems in high humidity environments worldwide. Improving efficiency is therefore essential. Liquid desiccants offer a promising solution for dehumidification, as desired levels of humidity removal could be easily regulated. The use of membrane contactors in combination with liquid desiccant is attractive for dehumidification because they prevent direct contact between the humid air and the desiccant, removing both the potential for desiccant carryover to the air and the potential for contamination of the liquid desiccant by dust and other airborne materials, as well as minimizing corrosion. However, the expected additional mass transport barrier of the membrane surface can lower the expected desiccation rate per unit of desiccant surface area. In this context, hollow fiber membranes present an attractive option for membrane liquid desiccant contactors because of their high surface area per unit volume. We demonstrate in this work the performance of polyvinylidene fluoride (PVDF) based triple-bore hollow fiber
membranes as liquid desiccant contactors, which are permeable to water vapor but impermeable to liquid water, for dehumidification of hot and humid air.

**List of abbreviations and nomenclatures**

PVDF, Polyvinylidene fluoride; LDAC, Liquid desiccant air conditioner; NMP, N-methyl-2-pyrrolidinone; OD, Outer diameter; ID, Inner diameter; SEM, Scanning electron microscopy; LEP, Liquid entry point; RH, Relative humidity; CaCl$_2$, Calcium chloride; RPM, Rotations per minute; $K_m$, Membrane phase mass transfer coefficient; $K_g$, Gas phase mass transfer coefficient.

Keywords: Hollow fiber membrane, air dehumidification, membrane contactor, liquid desiccant

1 **Introduction**

1.1 **Background**

Cooling is a major consumer of energy worldwide. In the context of Middle East countries, like Saudi Arabia, energy demand for cooling comprises approximately 52% of the total demand in summer [1]. Dehumidification, the removal of water vapor from the air, is responsible for a significant part of the energy consumption for cooling processes in humid climates worldwide. The energy required for dehumidification leads to both higher costs of electricity and a large carbon footprint in areas where grid energy is supplied via fossil fuels. Estimates are that the energy efficiency of cooling equipment can be improved by up to 33% using innovative dehumidification technologies [2]. Desiccants are one of the good choices of dehumidification technology. They function by direct absorption of water vapor [3] or by indirect absorption using a membrane contactor containing a liquid desiccant [4-9]. Liquid desiccants in particular are becoming increasingly popular because of their operational flexibility [10]. A common type of liquid desiccant is a highly concentrated inorganic salt solution. Typical inorganic salts include lithium bromide, calcium chloride, magnesium chloride and lithium chloride. The driving force for transfer or condensation of water vapor into the desiccant solution is its lower vapor pressure, as compared to pure water. The vapor pressure of the desiccant solution can be reduced even more by decreasing the
temperature of the solution or by increasing the concentration of salt in the solution. The condensation of water vapor leads to an increase of the desiccant temperature, since latent heat of water condensation is released. The air is cooled as latent heat is transferred to the desiccant solution. The extent of energy/moisture removal from the air is governed by the concentration of the liquid desiccant and its temperature; a concentrated cool desiccant is a good dehumidifying solution [11, 12].

A liquid desiccant air conditioner (LDAC) is adapted specifically for latent cooling (humidity removal), making it one of the best available technologies for cooling in humid climates [10, 13, 14]. Another advantage of liquid desiccant based air conditioning is that it uses heat as its primary operating energy source. Because of this feature, the electrical demand is estimated as low as 25% that of vapor-compression air conditioning [10, 15]. In the context of renewable energy sources, liquid desiccants offer an advantage over solid desiccants when using solar energy for regeneration [16-26].

1.2 Membrane dehumidification

In spite of energy-related advantages, liquid desiccants have some drawbacks. Corrosion of metals resulting from the contact with salt-based liquid desiccants is one of them [10]. Therefore, the potential for droplet carryover from traditional packed-bed or falling film liquid desiccant systems has prevented widespread adoption in all but a few carefully maintained applications.

The use of membrane contactors in liquid desiccant based dehumidification systems has been evaluated by a number of authors [5, 27-32]. Membrane contactor based dehumidification is attractive because it separates the desiccant and air streams by use of a porous membrane surface, effectively eliminating any chance for droplet carryover of desiccant solution into the airstream. Moreover, the membrane interface allows for independent operation of liquid and gas phases, so that no liquid condensate is generated as the desiccant absorbs the moisture [30, 33, 34]. The membrane also protects the desiccant solution from contamination by some airborne particulates, which could degrade the purity of the solution over time and lead to system clogging. Potential
drawbacks to application of membranes in liquid desiccant cycles are the added mass transport resistance of the membrane and the cost.

1.3 Hollow fiber membrane dehumidification

The use of hollow fibers with liquid desiccants for dehumidification applications is attractive because of the high surface area provided per unit volume [35]. In addition, the porosity of hollow fibers can offer faster, more efficient moisture transport if leakage can be prevented. Hollow fibers have been used successfully in liquid desiccant applications using a lithium chloride solution pumped through polyetherimide membranes [30].

In the present work we propose and test a new device for dehumidification based on a liquid desiccant solution pumped through polyvinylidene fluoride (PVDF) triple-bore hollow fibers under typical ambient summer air conditions in Jeddah, Saudi Arabia. We selected calcium chloride as the salt of choice in our experiments because it is a common salt in liquid desiccant applications and it is a lower-cost alternative compared to lithium chloride [10]. One of the short-term motivations is to integrate the dehumidification and cooling system in closed green houses, which could work with controlled humidity levels and low energy consumption in desert areas. We describe a new hollow fiber triple bore configurations, which has the advantages of high desiccant volume to surface ratios, high mechanical stability, and easy handling. Here we extensively demonstrate their performance in modular set-ups, which could be easily scaled up for dehumidification application.

2 Materials and methods

2.1 Polyvinylidene fluoride (PVDF) triple bore hollow fiber

2.1.1 Spinning solution

Polymer/dope solution with various concentrations ranging from 12 to 15 wt% of PVDF (purchased from Kynar®/ Arkema Inc., Dubai; Grade – HSV 900) were prepared by dissolving in N-methyl-2-pyrrolidinone (NMP, ≥99.5%, Merck). Powdered PVDF
was dried in oven overnight before using to prepare dope solution. Dried PVDF powder was added in small portions to NMP in order to avoid lump formation and stirred using overhead mechanical stirrer at 600 RPM for 24 h at 70°C. The prepared dope solution was charged into the feed reservoir of hollow fiber fabrication machine and degassed for 24 h to remove air entrapped within the dope solution.

2.1.2 PVDF hollow fiber fabrication

PVDF hollow fibers were fabricated by a non-solvent-induced phase-inversion process with a dry-wet spinning line (SepraTec Inc. Korea). The effect of dope concentration, flow rates of dope solution and bore liquid, air gap, and take-up speed were extensively studied. All hollow fibers for this study were prepared using water as bore liquid at 10 ml/min. Dope solution of 14wt% at 12.5 ml/min (or 20 RPM) was pumped using a gear pump through a specially designed triple-bore spinneret (Figure 1) (needle OD 0.6mm and orifice ID 2.4 mm) kept at 10 cm air gap before coagulating in the water bath. The formed hollow fibers were washed in hot water (50°C) for at least 10 hours and stored in RO water for three days (exchanging the water everyday) to remove any residual solvent.

![Image of triple-needle spinneret and its distribution with dimensions](image)

Figure 1. Image of triple-needle spinneret and its distribution with dimensions

2.2 Hollow fiber characterization

2.2.1 Scanning electron microscopy (SEM) analysis
SEM images to check the morphology of dry PVDF hollow fiber membranes were obtained using field emission scanning electron microscopes (FEI Quanta 200 or 600) at accelerating voltage of 5 kV. Fibers dried overnight were used for SEM analysis after being carefully fractured in liquid nitrogen. Hollow fiber membranes were sputter coated with platinum (~3nm-thick, Quorum Q150T ES) to make the polymer surface conductive for surface analysis.

2.2.2 Pore size distribution

Triple bore hollow fiber membrane pore size and the pore size distribution were estimated by using Porolux™ 1000 IB-FT instrument (Germany), at the pressure range up to 34.5 bar and using perfluoroether (Porefil) with a surface tension of 16 dynes cm\(^{-1}\) as the membrane pore filler. This analysis also measured liquid entry point (LEP), which is the minimum pressure required for liquid to pass through the membrane.

2.3 Dehumidification experimental set-up

All of the dehumidification experiments were carried out in an enclosed environmental chamber wherein the humidity and temperature were maintained at 70 ± 5 % RH and 35 ± 2°C, respectively (Figure 2). Sensors for humidity and temperature (Testo 435 and 174 models) were used to continuously monitor and record the chamber environment. 43 wt% calcium chloride solution was used as the starting concentration feed for all the experiments. All the experiments were batch mode, the actual concentration of calcium chloride by weight decreased over time, as water vapor was condensed into the desiccant solution. This change in desiccant solution concentration over time influences the vapor pressure difference which has been considered during the calculation of the flux. The various experimental configurations studied are explained below -

(a) **Static experiment** (Figure 2a)– The desiccant solution (300ml) was placed in a glass beaker/container (ID-14.5cm) at the center of the chamber with the top open to the surrounding environment. The desiccant solution was either continuously stirred using a magnetic stirrer or allowed to remain stagnant. The whole unit was placed on
an electronic balance, connected to a computer to record the data at 10 min intervals. The static absorption rate (kg m\(^{-2}\) h\(^{-1}\)) of the CaCl\(_2\) desiccant was measured by recording the change in weight over time for a period of 5 hours.

(b) *Dynamic experiment with desiccant inside the chamber* (Figure 2b) – In this experimental set-up, the desiccant contained in an enclosed bottle was kept inside the environmental chamber. The desiccant temperature was warmed or cooled to that inside the chamber, as the walls of the bottle were in direct contact with the ambient chamber conditions. The desiccant solution was continuously pumped through the lumen of the triple-bore hollow fiber module.

(c) *Dynamic experiment with fan draft* (Figure 2c) - In this experimental set-up, a fan was introduced near the bottom of the fiber module such that the air draft from the fan could help in reducing the concentration polarization caused by a stagnant air layer at the membrane surface and also to maintain a uniform distribution of humidity within the chamber.

(d) *Dynamic experiment with cooled desiccant and fan draft* (Figure 2d) – A revised set-up based on condition (c) was applied, where the desiccant solution in this experimental set-up was externally cooled in a jacketed glass container (Figure 2d) to a set temperature and continuously pumped at a fixed flow rate through the lumen of the triple-bore hollow fiber module (length of exposed fiber for absorption – 15 to 70cm). The cold desiccant is expected to increase the absorption rate within the humid environment.

For all the dynamic experiments, 300 ml of desiccant solution (43 wt% CaCl\(_2\) dissolved in water) was used. Triple bore hollow fiber modules were prepared with a single hollow fiber such that only the ends are potted in 6mm polyethylene tubing with epoxy glue. These potted ends were connected to the pump desiccant solution through the lumen of the hollow fiber. The hollow fiber was held vertically in the middle of the environmental chamber by clamps to be in direct contact with the surrounding environment. These experiments were carried out for at least triplicates and 5 days continuously, with desiccant weight, humidity and temperature recorded every 10
minutes. Flux was calculated based on the amount (weight) of water vapor absorbed by the desiccant solution over time.
3 Results and discussion

3.1 Scanning electron microscopy (SEM) analysis

In order to fabricate mechanically stable triple bore hollow fiber, various polymer concentration and spinning parameters were investigated. Among them, 14wt% polymer dope solution with water as bore solution and air gap of 10 cm gave a stable nanoporous hollow fiber. The formed hollow fiber morphology was examined by SEM. Micrographs of the fiber cross-section, wall and surface, are as shown in Figure 3. The fibers have asymmetric pore distribution with macro voids extending from both inner and outer walls of the fiber.

<table>
<thead>
<tr>
<th></th>
<th>Full fiber</th>
<th>Outer wall</th>
<th>Center wall</th>
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<tr>
<td><strong>Cross section</strong></td>
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<td><img src="image2" alt="Cross section" /></td>
<td><img src="image3" alt="Cross section" /></td>
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<tr>
<td><strong>Surface</strong></td>
<td><img src="image4" alt="Surface" /></td>
<td><img src="image5" alt="Surface" /></td>
<td><img src="image6" alt="Surface" /></td>
</tr>
</tbody>
</table>

Figure 3. SEM images of PVDF triple-bore hollow fibers.
3.2 Pore size distribution and liquid entry point (LEP)

Pore diameter distributions of triple-bore hollow fiber membranes (measured by capillary flow porosimetry using Porefil as the wetting liquid) are shown in Figure 4. A narrow distribution of pore size was observed for the fabricated hollow fibers, with a mean pore size of 390 nm and a few smaller pores of 240 nm. The liquid entry point (LEP) value, determined on Porolux 1000, was 1.52 bar, which corresponds to a pore size of 420 nm. LEP values were measured with Porefil (perfluoroether) (surface tension 16 mN/m, according to the Porolux manual). Water has a surface tension of 72 mN/m at room temperature (63 mN/m, at 80 °C), much higher than Porefil. The LEP values (here measured using Porefil) are expected to be even higher if water were to be the “wetting” liquid. The LEP values in the case of these membranes are therefore much higher than the maximum inlet pressure of about 0.25 bar that was measured for flow rates of 5ml/min through the lumen of the triple-bore hollow fiber. Thus, there is no chance that the desiccant solution will pass through the pores. The dehumidification fluxes were obtained only from humidity transport through the membrane wall and into the recirculating desiccant solution.

![Figure 4. Pore size distribution of triple bore hollow fibers measured by using Porolux](image)

3.3 Static experiment
The static experiment (Figure 2a) was considered as the control. Static experiments were carried out for 5 hours. In order to consider a membrane contactor as feasible, the absorption rate must exceed the static absorption rate. Figure 5 shows the flux results normalized for vapor pressure difference for two static conditions. The first condition is an open, undisturbed container of desiccant solution. The second condition included a magnetic stirrer to continuously mix the desiccant solution, thus preventing concentration polarization within the solution. Average absorption was 0.02 g m$^{-2}$ h$^{-1}$ Pa$^{-1}$ in the undisturbed solution and 0.05 g m$^{-2}$ h$^{-1}$ Pa$^{-1}$ in the continuously stirred solution.

![Figure 5. Water vapor flux (vapor pressure-normalized) into open containers of undisturbed and continuously stirred desiccant solution (Static experiment, Set-up (a), Figure 2)](image)

3.4 Dynamic experiment: effect of CaCl$_2$ solution flow rate

Three different flow rates of CaCl$_2$ solution through the hollow fiber lumens were compared to evaluate potential changes in flux based on solution velocity, using set-up (b) in Figure 2. The flow rates evaluated were 1, 3, and 5 ml/min, with corresponding liquid velocities and residence times through the lumens as shown in Table 1. Liquid desiccant solution temperatures entering the fibers were approximately equal to the surrounding bulk air in the chamber (Figure 1S). The solution concentration was expected to decrease and the temperature to increase along the length of the hollow fiber as water vapor condensed and the heat of condensation was released into the solution. The bulk air around the hollow fiber was stagnant; no fan was used in these experiments.
The mass transfer resistance coefficient of the membrane phase ($\frac{1}{k_m}$) and gas ($\frac{1}{k_g}$) were not expected to change with varying solution velocities.

Table 1: Flow rates of liquid desiccant

<table>
<thead>
<tr>
<th>CaCl$_2$ solution flow rate (ml/min)</th>
<th>1</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$ solution velocity (m/s)</td>
<td>0.012</td>
<td>0.035</td>
<td>0.058</td>
</tr>
<tr>
<td>Length of hollow fiber (mm)</td>
<td>580</td>
<td>580</td>
<td>580</td>
</tr>
<tr>
<td>CaCl$_2$ solution residence time in fiber (s)</td>
<td>50</td>
<td>17</td>
<td>10</td>
</tr>
</tbody>
</table>

Results of the tests showed that the solution flow rate had no significant effect on vapor flux into the desiccant (Figure 6), as the flow rate does not substantially increase the vapor pressure difference between the liquid desiccant and humid air. Similar observation has been reported by Kneifel et al. [30] for lithium chloride as desiccant and PEI membranes coated with PDMS as hollow fiber contactor membrane system. However, differences in vapor pressure between the desiccant solution and the air is clearly affecting vapor flux (Figure 7). Variations in the vapor pressure difference are caused by changes in the temperature and humidity of the air around the membrane and changes in the concentration and temperature of the desiccant solution. Figure 7 clearly shows that a change in vapor pressure difference caused by desiccant and air physical properties increases vapor flux.
3.5 Effects of air flow at surface of hollow fiber on vapor flux

The flux through the membranes increased after addition of a fan to circulate the bulk air around the hollow fiber (Set-up (c), Figure 2). Circulation of air around the hollow fiber was expected to reduce the mass transfer resistance coefficient of the gas phase \((\frac{1}{k_g})\) caused by a layer of stagnant air adjacent to the membrane surface. After addition of the fan circulating air at a velocity of ~1.1 m/s, the dehumidification rate largely increased (Figure 8).

A chiller was then added to cool the bulk desiccant before input into the hollow fiber lumen (Set-up (d), Figure 2). The chiller functioned to decrease the vapor pressure of the liquid desiccant, thereby increasing the driving force for dehumidification. Flux observed with air flow past the hollow fiber (~1.1 m/s) and chilled desiccant was 3-4 times higher than that observed in the experiments without the fan and chiller (Figure 8). The effect of the fan on dehumidification rate was much larger than the effect of the chiller when flux was normalized for vapor pressure [36]. Although the experimental conditions vary with that reported by K. Kneifel et al. [30] the average flux obtained is \(0.35 \pm 3 \text{ g m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}\), which is in the same range as that of fan on and chiller on the experiment reported in this paper (Figure 8).
3.6 Effects of hollow fiber length on vapor flux

The length of the hollow fiber is expected to have an effect on the vapor flux and the liquid pressure drop along the length of the membrane. As the hollow fibers become longer, the temperature of a cool input desiccant solution is expected to increase due to heat transfer from the ambient environment (assuming the desiccant comes in cooler than the ambient humid air temperature). The temperature will also increase due to the release of the heat of condensation from the water vapor as it condenses into the desiccant solution. In addition to the increase in temperature, the concentration of the solution is expected to decrease due to the addition of water. Both of these effects are expected to increase the solution vapor pressure, decrease the vapor pressure difference, and lower the vapor flux rates along the length of the fiber.

Varying lengths of hollow fibers from 150-660 mm were tested with the fan and chiller on. Table 2. Length of hollow fibers evaluated summarizes the experimental hollow fiber characteristics.
Experimental results showed no significant change in vapor flux related to length of hollow fiber from 150-660 mm (Figure 9 and Figure 10). The lack of a measurable change in flux is likely due to two factors:

- The solution residence time in the fibers may have been too short to notice a substantial change in concentration due to vapor flux from beginning to end and
- The sensible heat may have been lost through the membrane at such a high rate that there was no significant change in solution vapor pressure from the beginning to the end of the fibers. The heat transfer coefficient of hollow fibers is expected to increase as the diameter decreases [37].

![Figure 9. Vapor flux (vapor pressure-normalized) vs. hollow fiber length (Set-up (d), Figure 2)
3.7 Effects of hollow fiber length on pressure drop along the membrane

The expected pressure loss as desiccant solution is pumped through the fibers is an important variable related to pump selection and expected energy use. Total pressure drop along the length of the membrane is expected to increase as the fiber length increases. However, the pressure drop per unit length is expected to decrease with increasing fiber length due to two factors:

- Lower viscosity of the desiccant at the outlet end of longer fibers as a result of a higher temperature and a lower concentration (both caused by vapor condensation into the solution) and
- The friction losses experienced at the junction of the hollow fiber and the desiccant supply tubes are spread out over longer lengths (hollow fiber diameters were ~4 times smaller than the supply tube diameters in the experimental setup).
Figure 11 and Figure 12 document the pressure losses in the solution from entry to exit of the hollow fiber. As expected, the longer fiber has more total pressure drop from entry to exit and the pressure drop per unit length is less in the longer fiber compared to shorter fiber.
4 Conclusion – Outlook

The triple-bore hollow fibers used in this study were chosen for three reasons: high desiccant volume to surface ratios, high mechanical stability, and easy handling and potting. PVDF hollow fiber membranes were used successfully with CaCl₂ desiccant solution to dehumidify air without any liquid desiccant carryover to the surrounding environment.

Results showed no relation between vapor flux and the desiccant solution velocity within the range from 0.012-0.058 m/s. The use of a fan to mix the air at the surface of the hollow fiber reduced the mass and energy transport resistance coefficient in the gas phase, while increasing vapor flux. The vapor flux observed was approximately 4 times higher with airflow at the surface of the membrane than that observed with stagnant air. The vapor flux rate showed no obvious relationship to the length of the hollow fiber within the range of lengths from 150 to 660 mm, although a higher pressure at the inlet of the hollow fiber was required to maintain the flow rate as the fiber length increased. However, the pressure loss per unit length decreased with increasing fiber length.

The membranes tested in this study are further being tested in a bench scale greenhouse environment. Arrays of fibers will be tested to control temperature and humidity in order to maintain an environment that is optimal for plant growth. Integrated desiccant regeneration to its initial concentration and fresh water recovery based on membrane distillation processes (without any cross contamination) using solar energy is also under evaluation.

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References


**Highlights**

- New membrane-based modular device for dehumidification
- Triple bore hollow fiber membranes with optimized morphology for air dehumidification
- Testing and parametric analysis carried out

Graphical abstract