

MEMBRANE CONTACTOR PROCESSES FOR REMOVAL OF NATURAL HORMONES FROM WASTEWATER

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ABSTRACT: Growing demands for potable water have strained water resources and increased interest in wastewater reclamation for potable reuse. This interest has brought increased attention to endocrine-disrupting chemicals (EDCs) as emerging water contaminants. The effect of EDCs, and in particular natural steroid hormones, on humans is of heightened interest when considering potable reuse of wastewater in particular in the study of wastewater reuse in advanced life support systems (e.g., space missions) because they are excreted in urine and have high endocrine-disrupting potencies.

Direct contact membrane distillation (DCMD) and forward osmosis (FO) have been investigated for wastewater treatment in space. Retention of two natural steroid hormones, estrone and 17 β -estradiol, by the two processes was investigated. DCMD provided greater than 99.5% hormone rejection; DCMD also provided constant flux, greater than 99.9% urea and ammonia rejection, and high water recovery. FO provided from 77 to 99% hormone rejection depending on experiment duration and feed solution chemistry.

KEY TERMS: membrane contactors; membrane distillation; forward osmosis; life support systems.

INTRODUCTION

The concept of direct potable reuse of wastewater is being evaluated and studied around the world as water resources are being overly utilized and water demand is continuously increasing. In extreme cases, like in long-term human missions in space, a continuous and self-sufficient supply of fresh water for consumption, hygiene, and maintenance is required. The three main sources of wastewater that can be reclaimed and reused in advanced life support systems are hygiene wastewater, urine, and humidity condensate.

Membrane processes, and especially reverse osmosis (RO) processes, are appropriate for wastewater treatment in space because they have the advantages of high rejection, durability, small footprint, simple operation, and minimal resupply of consumable materials for continuous operation. However, RO membranes can be very sensitive to fouling by dissolved matter, particulate matter, salt precipitates, and microorganisms [1]. For this reason, RO systems, and especially those used for wastewater treatment, require pretreatment of the feed stream to reduce the potential for membrane fouling and to ensure acceptable performance [2, 3]. Recent studies have shown that membrane contactor processes, and in particular direct contact membrane distillation (DCMD) and forward osmosis (FO), can be very efficient as pretreatment processes for RO or nanofiltration (NF) [4, 5] and as the main treatment processes themselves [6].

Membrane distillation (MD) is a separation process in which mass transfer is carried out by evaporation of a volatile solute or a volatile solvent (when the solute is non-volatile) through a hydrophobic microporous membrane. Some of the benefits of MD include very high rejection of non-

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volatile compounds; lower operating temperatures than conventional distillation; lower operating pressures than RO and other pressure-driven processes; and reduced chemical interaction between the feed solution and the inert membrane [6]. In DCMD, water from the heated feed stream evaporates through the membrane pores into the cooler permeate stream (potable water) where it condenses and becomes part of the permeate stream. DCMD is well-suited for desalination applications in which water is the desired permeating/diffusing component [7].

FO is a membrane contactor process that uses osmotic pressure difference ($\Delta\pi$) across the membrane, rather than hydraulic pressure difference (as in RO), as the driving force for transport of water through a semi-permeable membrane. The FO process results in concentration of a feed stream and dilution of a highly concentrated stream (referred to as an osmotic agent or draw solution (DS)) [8]. Unlike DCMD, flux during FO is highly affected by the composition of both streams on either side of the membrane. In wastewater treatment, FO can be utilized as an advanced pretreatment process before RO or NF. FO has several advantages, including: relatively low fouling potential, low energy consumption, simplicity, and reliability [5]. If appropriate membranes are used, FO can achieve high fluxes with relatively low driving forces while providing effective rejection of both salts and organics.

When evaluating DCMD and FO as treatment processes for wastewater generated during long-term space missions, where crew members will consume water that is continuously recycled, it is important to ensure that trace contaminants, and particularly endocrine-disrupting chemicals (EDCs), are removed from the treated water. RO and NF have recently been investigated for hormone removal capabilities [9-14]. Size exclusion and adsorption to the membrane surface/matrix (via hydrogen bonding and hydrophobic interaction) are proposed as the primary mechanisms for hormone rejection by RO and NF membranes [9, 15, 12, 13]. New findings indicate that electrostatic repulsion and increased adsorption capacity due to membrane fouling can further enhance the rejection of organic solute even by NF and ultra-low-pressure RO membranes [14].

Thus far, it has been demonstrated that RO and NF can be effective at hormone removal but the risk of hormone breakthrough requires further investigation [16]. Furthermore, while the data show promise for domestic wastewater treatment, the demands of closed life support systems have not been considered. In closed life support systems, where wastewater hormone concentrations could be significantly higher than domestic wastewater concentrations, 85-95% rejection would still produce water that has potentially adverse health effects. For this reason, it is important to investigate the capability of these membrane processes to reject trace levels of emerging contaminants such as estrone and estradiol.

The main objective of the project was to study the capability of FO and DCMD to reject EDCs, and specifically, the natural steroid hormones estrone and 17β -estradiol. The results of this study pertain directly to advanced life support scenarios, but also have further-reaching implications for domestic wastewater treatment.

MATERIALS AND METHODS

DCMD and FO Membranes

Hydrophobic microporous capillary membranes (MD020-CP-2N, Microdyn, Germany) were acquired for the DCMD experiments. Each Microdyn module contains 40 symmetric capillary membranes made of polypropylene with a nominal pore size of 0.2 μm and a total surface area of 0.1 m^2 . The Microdyn modules were chosen because previous studies [17] have shown them to provide a high rejection of urea, which, like estrone and estradiol, is a non-volatile organic compound. New Microdyn modules were used for each experiment.

Cellulose triacetate semi-permeable flat sheet membranes (CTA, Hydration Technologies Inc., Albany, OR) were used for the FO experiments. The CTA membrane is a unique membrane that was specifically developed for the FO process and has been found to have high water flux and high solute

rejection for various FO applications. [5, 8] The contact angle of the CTA membrane was measured to be 61° and the membrane was found to be negatively charged at the pH in which the system was operated. New CTA membranes were used for each experiment.

Solution Chemistries

Three synthetic wastewater solutions corresponding to the main sources of wastewater in closed life support systems were used in this study. Also, doubly deionized water (DDW) was used as a feed solution in some experiments for comparison purposes. The chemical compositions of the simulant solutions were adopted from Verostko et al. [18]. The hygiene wastewater contains an anionic surfactant (sodium cocoyl N-methyl taurate); the humidity condensate contains trace amounts of volatile organic acids; and the urine stream contains urea as the primary solute (5.2 g/L). All chemicals used for the simulated streams were certified ACS grade and were obtained from Fisher Scientific (Pittsburgh, PA).

DCMD and FO water flux and solute rejection (without hormones) were evaluated using the hygiene, humidity condensate, and urine components individually and in combination. DCMD and FO hormone removals were evaluated using select feed streams. DCMD was investigated as a treatment process for humidity condensate and urine because it has been shown to efficiently reject urea. Thus, the feed solution for the DCMD experiments was either a mixture of humidity condensate and urine or simply DDW. DCMD cannot treat waste streams having low surface tension; and therefore, DCMD was not investigated on hygiene wastewater. FO was investigated as a treatment process for hygiene wastewater and the feed solution was either hygiene wastewater or DDW. FO has very poor rejection of urea; and therefore, FO was not investigated on urine.

Because DCMD and FO were being considered for different feed streams, different hormones, bench-scale testing, and analytical techniques were used. For DCMD, non-radiolabeled hormones and enzyme immunoassay (EIA) kits were used. These kits have the advantage of being a non-radioactive method for detecting low concentrations of hormones and the disadvantage of requiring extensive preparations in order to minimize sample matrix interferences. Even so, this method is not recommended for use with surfactants because preliminary performance tests have demonstrated that sample containing surfactants interfere with the ability of the antibodies to bind to the hormones of interest. For FO, radiolabeled hormones and scintillation counting were used. This technique has the advantage of detecting extremely low concentrations of radiolabeled hormones without concern for sample matrix interferences. However, this technique requires the construction of several disposable FO systems and analytical instruments.

Hormones

Non-radiolabeled estrone was purchased from Acros Organics (New Brunswick, New Jersey) and non-radiolabeled 17 β -estradiol was purchased from Steraloids, Inc. (Newport, RI). Both are analytical grade chemicals. Radiolabeled hormones were purchased from GE Healthcare UK Limited (Buckinghamshire, UK). The {2,4,6,7-³H}-estrone has a specific activity of 96.0 Ci/mmol and a concentration of 1.0 mCi/mL in 95:5 toluene-to-ethanol solution; the {2,4,6,7-³H}-estradiol has a specific activity of 84.0 Ci/mmol and a concentration of 1.0 mCi/mL in 9:1 toluene-to-ethanol solution.

In the DCMD hormone experiments, feed solutions were spiked with both estrone and estradiol to produce initial concentrations of 1,000 ng/L for each compound. In the FO hormone experiments, feed solutions were spiked with 100 μ L of either radiolabeled estradiol solution or radiolabeled estrone solution, resulting in concentrations of 330 or 290 ng/L, respectively. Although the hormone concentrations used in these experiments are not representative of concentrations in normal wastewater effluents, it is possible to achieve concentrations as high as 7,000 ng/L in closed life support systems where wastewater is continuously being concentrated to produce potable water.

Experimental Setups and Procedures

A schematic of the bench-scale DCMD apparatus is shown in Figure 1. In the capillary membrane module, the feed solution flowed inside the bores and DDW was recirculated countercurrently on the shell side of the capillaries. The feed and permeate streams were recirculated each at a flow rate of 1.5 L/min. The temperatures of the feed and permeate streams were maintained at 40 ± 1 and $20 \pm 1^\circ\text{C}$, respectively.

During the DCMD experiments, the feed solution was concentrated from an initial volume of 8 L to a final volume of 2 L; each experiment was conducted for 30 to 40 hrs. The collecting flasks were exchanged every time 2 L of water had permeated from the feed side. Therefore, three permeate samples were collected for analysis during each experiment. Permeate samples 1, 2, and 3 corresponded to water recovery ranges of 0-25%, 25-50%, and 50-75%, respectively. Permeate samples were collected in this way to investigate the effects of water recovery on estrone and estradiol rejection. A feed sample was also collected at the end of each experiment.

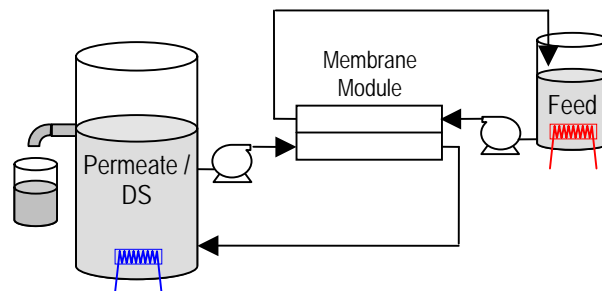


Figure 1. Schematic drawing of the DCMD and FO test unit.

The disposable FO bench-scale test units were very similar to the DCMD apparatus shown in Figure 1 with a few exceptions. A custom-made acrylic cell held the flat sheet CTA membrane. The cell was fabricated with symmetric channels on both sides of the membrane. The CTA membrane (0.008 m^2) was oriented with its active side facing the feed stream. The feed and DS streams flowed countercurrently to each other to maintain a constant osmotic pressure gradient.

During the FO experiments, an initial feed volume of 900 mL was concentrated down to 300 mL. Water permeating from the feed diluted 300 mL of DS from an initial concentration of 70 g/L to approximately 22 g/L NaCl. Each experiment was conducted for 9 to 10 hrs. 1 mL samples were taken in triplicate from both the feed and draw solution reservoirs approximately every 50 min throughout the duration of the experiments. To avoid radioactive contamination, new bench-scale units, CTA membranes, and acrylic membrane cells were used for each experiment.

Sample Analyses

Non-radiolabeled hormone concentrations were analyzed using enzyme immunoassay (EIA) kits for estrone (11-ESTROH-420, ALPCO Diagnostics, Salem, NH) and estradiol (582251, Cayman Chemical, Ann Arbor, MI). Information about the kits and their detection limits can be found in the Supporting Information section. Solid-phase extraction (SPE) was performed on all non-radiolabeled samples analyzed in this study to remove compounds that would interfere with the functionality of the EIA kits. Refer to the Supporting Information section for the SPE procedure. Based on results summarized in Table S1 of the Supporting Information section, an average extraction efficiency of 80% was used for rejection calculations.

Radiolabeled hormones were analyzed using a liquid scintillation counter (Tri-Carb, Packard Instruments, Wellesley, MA). For analysis, 10 mL of scintillation cocktail (CytoScint ESTM, MP Biomedicals, Solon, OH) were added to each 1 mL of sample and samples were counted for 1 min. The detection limit of this method was 0.1 ng/L. A quenching test confirmed that constituents in the samples (e.g., soap and NaCl) had no effect on counting efficiency.

RESULTS AND DISCUSSION

Water Flux and Solute Rejection of the DCMD and FO Processes

Preliminary DCMD tests (Figure 2) demonstrated that under moderate operating conditions the capillary membrane was able to maintain a relatively steady flux over a long period of time while achieving high water recovery. Water recovery was calculated as a ratio of the cumulative permeate volume to the initial feed volume (10L). After approximately 50 hrs, 10 L of fresh feed solution was added to the feed reservoir. The flux declined after approximately 90% water recovery due to lower partial vapor pressure of water in the feed caused by increased solute concentration. Greater than 99.9% rejections of urea and ammonia were achieved by the DCMD process throughout the experiments.

Preliminary FO tests (Figure 3) were performed using three different feed solutions in batch mode. The initial DS concentration of 70 g/l NaCl was diluted to approximately 20 g/l NaCl as water diffused through the membrane to the DS. Flux was measured every 15 min. The data points are spread at higher DS concentrations because water is diffusing through the membrane at a higher rate — rapidly diluting the DS over the 15-min intervals.

Water flux levels and trends were similar for experiments with DDW feed solution and simulant wastewater containing the hygiene component only. However, the presence of urine and humidity condensate components resulted in a 20-30% flux loss throughout the DS range compared to the fluxes measured during experiments with feed containing hygiene component alone. This overall flux decline is due to the increase in osmotic pressure on the feed side of the membrane when humidity condensate and urine components are present in the feed stream. The result is a lower osmotic driving force across the FO membrane. It was anticipated and confirmed by the data in Figure 3 that hygiene wastewater would have very little effect on water flux because it does not contain salts and the surfactant that it does contain has low osmotic pressure. Yet, further investigations of scaling effects by surfactants at high concentrations are needed.

Rejection of estrone and estradiol by DCMD

Water flux and hormone rejection are illustrated in Figure 4 for the two feed solutions used during the DCMD hormone experiments. Overall, the capillary membrane rejected both hormones (estrone and estradiol) at or above 99.5% throughout the duration of the experiments. There was no apparent difference between estrone and estradiol rejection, and hormone rejection was not affected by water recovery. Furthermore, hormone rejection was not affected by the composition of the feed; rejections were similar for either DDW or simulant wastewater feed solutions. The high hormone rejection was expected based on the DCMD removal mechanism. DCMD is a thermally-driven process where constituents diffuse through the pores of the membrane according to their relative volatility. Estrone and estradiol were highly retained in the feed solution because they are non-volatile compounds with very low vapor pressures. These results are consistent with the DCMD performance experiments in which urea, another non-

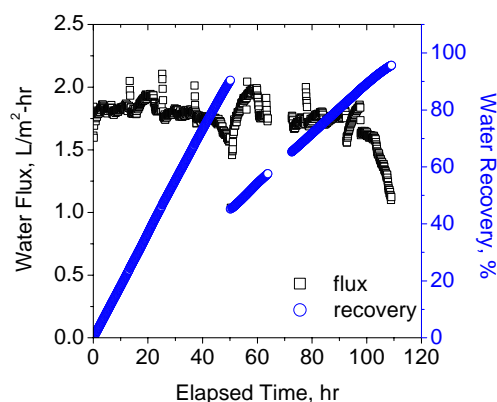


Figure 2. Water flux and recovery during a long-term semi-batch DCMD experiment with simulant wastewater as the feed solution.

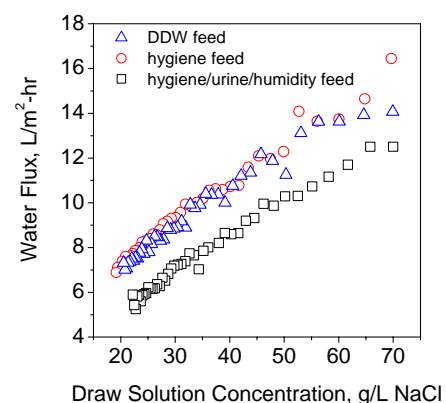


Figure 3. Water flux as a function of DS concentration during FO experiments with different feeds solutions.

volatile organic compound, was highly rejected at a wide range of water recoveries (feed concentrations). The ability to provide greater than 99.5% hormone rejection makes DCMD an ideal wastewater treatment process – especially in closed systems where trace contaminants (e.g., EDCs) will accumulate. In any closed system, removing hormones to low levels is important because of their potential to be harmful at trace concentrations of 1-10 ng/L [19].

Steady water flux was achieved during both experiments after the feed and permeate streams reached 40 and 20°C, respectively (Figure 4b). The steady flux is in accordance with the capillary membrane performance shown in Figure 2. Lower water flux was measured during the experiment in which simulant wastewater feed solution was used (Figure 4a). It was initially suspected that these results were due to the different chemistries of the two feed streams, and particularly, due to the decline in partial vapor pressure of water as a result of high solute concentration in the simulant wastewater. However, following the experiment with the simulant wastewater, the apparatus was cleaned and another experiment was performed on the same membrane using DDW feed solution. Results were similar at approximately 1.5 L/m²·hr. Thus, the flux discrepancy illustrated in Figure 4 is likely due to differences in membrane module manufacturing and not feed chemistry. In order to verify that the manufacturing differences did not result in low membrane integrity or functionality, urea rejection was measured on permeate samples collected during the hormone experiment with simulant wastewater feed solution. Greater than 99.9% rejection was achieved.

Rejection of estrone and estradiol by FO

To date, no publications could be found in the literature on hormone rejection by FO. Because FO and RO have similar transport and rejection mechanisms, [8] hormone rejection achieved during the FO experiments is compared to studies that investigated hormone rejection by RO. Results for hormone rejection as a function of water recovery during FO experiments are illustrated in Figure 5. Unlike DCMD experiments, where non-radiolabeled hormones were used, estrone and estradiol could not be spiked simultaneously into the same feed solution because radioactivity was used to indirectly measure hormone concentration. Therefore, three separate experiments were conducted; one using simulant hygiene wastewater feed solution spiked with estradiol, one using simulant hygiene wastewater feed solution spiked with estrone, and the other using DDW feed solution spiked with estrone only.

For the FO experiments involving simulant wastewater feed solutions, hormone rejection was greater than 99% until 20% recovery was reached. From 20 to 45% recovery, rejection declined steadily to 95-96%; from 45% recovery to

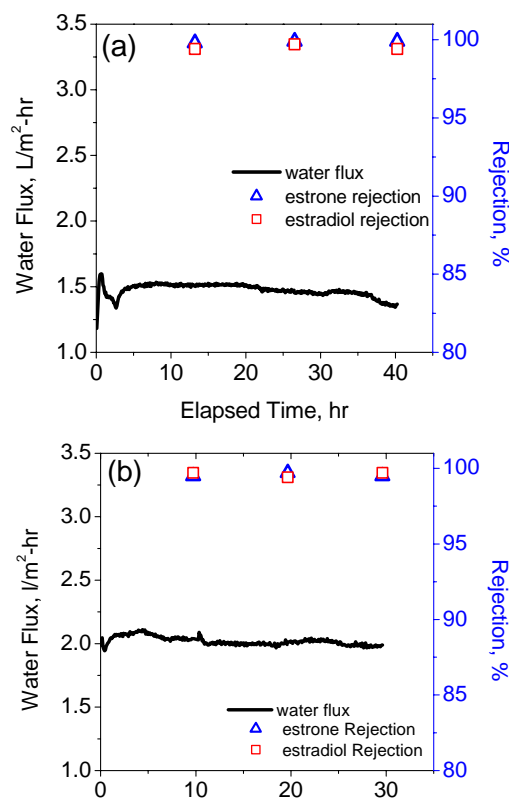


Figure 4. Water flux and estrone and estradiol rejection as a function of time during DCMD experiments. Feed solutions are either (a) wastewater simulant containing urine and humidity condensate or (b) DDW. Permeate samples were collected and analyzed for hormone rejection every time 2 L of water had permeated across the membrane.

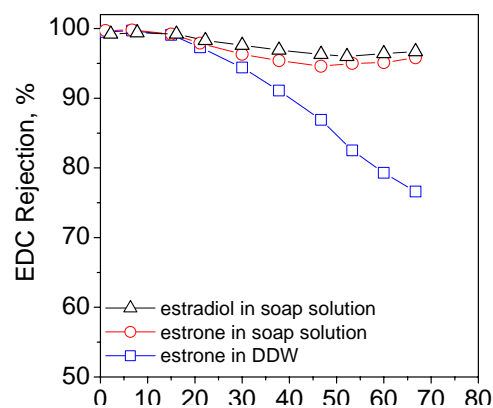


Figure 5. Hormone rejection as a function of the water recovery achieved during FO radiolabeled hormone experiments.

the end of the experiments (70% recovery), hormone rejection increased steadily to 96-97%. Less than a 1.5% difference in estrone and estradiol rejection was observed throughout the duration of these experiments. The small difference in rejection between estrone and estradiol is consistent with findings by Nghiem et al. [12], who reported no significant difference (< 3% difference) between estradiol and estrone rejection by RO.

During the experiment in which DDW was used as feed solution, estrone rejection was greater than 99% until 20% recovery was reached. At this point, however, rejection began to decline linearly; decreasing to 77% by the time 70% water recovery was reached. The hormone rejections observed during this experiment is consistent with the findings by Ng and Elimelech [15] where rejection decreases linearly due to the gradual diffusion of hormones through the membrane matrix. However, it should be noted that a greater decline in rejection (approximately 20%) was observed during the FO DDW experiment than the decline in rejection (approximately 10%) reported by Ng and Elimelech for RO [15].

The results from the FO hormone experiments suggest that the surfactant in the hygiene component used in the simulant wastewater enhances hormone rejection. These results are also consistent with reports [9, 12, 20] suggesting that RO and NF membranes provide increased hormone rejection when organic matter is present in the feed solution. Results from Xu et al [14] demonstrated that membrane fouling can substantially increase the rejection of organic pollutants. Thus, it is most likely that the fouling layer formed on the membrane during experiments with surfactants, enhanced the rejection of estrone and 17 β -estradiol.

It was anticipated that FO would have lower hormone rejection than DCMD because unlike DCMD, solutes cross the FO membrane via diffusive transport. Although FO is not a pressure-driven membrane process, its removal mechanisms are very similar to those of RO. Therefore, it was expected that FO would have hormone rejections similar to those found in the literature for hormone removal by RO [9, 12]. Further, it is not anticipated that the rejection of estrone and estradiol by FO would be much different if feed concentrations were on the order of 50 ng/L (a more representative feed concentration [21]) because it has been shown that RO rejection of estrone is not significantly affected by varying the feed hormone concentration.

In conclusion, experiments revealed that DCMD consistently rejects both estrone and estradiol at or above 99.5%, independent of feed composition. The high hormone rejection is consistent with the high rejections of organic and inorganic non-volatile chemicals achievable with MD. The ability to provide greater than 99.5% hormone rejection while operating over a wide range of water recovery makes DCMD an ideal water treatment process. Nevertheless, during real-urine treatment at high water recovery, membrane scaling may develop and reduce process performance. This topic needs to be further investigated and tested in longer term experiments.

FO experiments demonstrated that FO rejects estrone and estradiol similarly, and hormone rejection is affected by feed composition. Surfactants in the feed solution improve the ability of FO to retain hormones; resulting in hormone rejections at or above 95%. With DDW feed solution, hormone rejection was found to decrease steadily to approximately 77%.

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