Removal of Natural Steroid Hormones from Wastewater Using Membrane Contactor Processes[†]

JOSHUA L. CARTINELLA,[‡]
TZAHI Y. CATH,*[,§] MICHAEL T. FLYNN,[||]
GLENN C. MILLER,[⊥]
KENNETH W. HUNTER, JR.,[#] AND
AMY E. CHILDRESS[‡]

Department of Civil and Environmental Engineering, University of Nevada, Reno, Reno, Nevada 89557, Division of Environmental Science and Engineering, Colorado School of Mines, Golden, Colorado 80401, NASA-Ames Research Center, M/SS: 239-11, Moffett Field, California 94035-1000, Department of Natural Resources and Environmental Science, University of Nevada, Reno, Reno, Nevada 89557, and Department of Microbiology and Immunology, University of Nevada, Reno, Reno, Nevada 89557

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 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) are being investigated for wastewater treatment in space. Retention of two natural steroid hormones, estrone and 17β-estradiol, by these two processes was evaluated in the current investigation. 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.

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, such as 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, small footprint, simple operation, durability, 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 nonvolatile) through a hydrophobic microporous membrane. Some benefits of MD include very high rejection of nonvolatile 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 membrane (*6*). DCMD is one configuration of MD in which both sides of the membrane are in contact with aqueous solutions (i.e., the feed and product water streams). In DCMD, water from the heated feed stream evaporates through the membrane 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. Cath et al. (*7*) reported 99.9% rejection of salt using DCMD and a relatively minimal effect of feed salt concentration on flux.

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 semipermeable 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*). Water will continue to diffuse through the membrane and dilute the DS as long as the osmotic pressure in the DS is higher than that in the feed stream. 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 (*4*). If appropriate membranes are used, FO can achieve high fluxes with relatively low driving forces while providing very high rejection of both dissolved and particulate matter.

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. EDCs interfere with endocrine function in one of two ways: by mimicking hormones and triggering unwanted responses or by blocking hormone receptors and preventing hormone responses (*9*). Despite being present at trace concentrations, natural steroid hormones such as estrone and 17β-estradiol have relative

[†] This article is part of the Emerging Contaminants Special Issue.

* Corresponding author phone: (303) 273-3402; e-mail: tcath@mines.edu.

[‡] Department of Civil and Environmental Engineering, University of Nevada, Reno.

[§] Division of Environmental Science and Engineering, Colorado School of Mines.

[||] NASA-Ames Research Center.

[⊥] Department of Natural Resources and Environmental Science, University of Nevada, Reno.

[#] Department of Microbiology and Immunology, University of Nevada, Reno.

10.1021/es060550i CCC: $33.50
Published on Web 11/08/2006

estrogenic potencies that are several orders of magnitude higher than nonsteroidal and synthetic endocrine disruptors found in wastewater effluents at higher concentrations (*10*).

RO and NF have recently been investigated for hormone removal capabilities (*11*−*15*). 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 (*11*−*13*, *16*). In the case of adsorption, it is important to note that the adsorbed hormones may slowly diffuse through the matrix of RO membranes and result in increased permeate hormone concentrations over time (*16*). Ionic (charge) interactions between the hormones and membrane are not expected because, based on their pK_a values, the hormones are un-dissociated (neutrally charged) in systems where the pH is below 10.4 (*11*). Results from 5-day filtration experiments indicate that estrone and estradiol rejections of 80−90% can be maintained by RO membranes while hormone rejection by NF membranes drops to as low as 30%, depending on the "looseness" of the membrane (*12*, *13*). It has also been demonstrated that colloidal fouling of RO membranes causes a decrease in estradiol rejection by preventing back diffusion to the bulk solution. By preventing back diffusion, hormone concentrations at the membrane surface increase which, in turn, causes increased hormone diffusion through the membrane (*9*). Further, the presence of organic matter in RO feed solutions has been shown to enhance hormone rejection because the hydrophobic hormones can interact with the organic matter. The hormones are then no longer available for adsorption to or transport through the membrane (*12*, *13*).

Thus far, it has been demonstrated that RO and NF are ineffective at long-term hormone removal, and the risk of hormone breakthrough requires further investigation (*17*). 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 those in domestic wastewater, 90% rejection would still produce water that has potentially adverse health effects. For this reason, it is important to investigate the capability of the membrane contactor processes to reject trace levels of emerging contaminants such as estrone and estradiol.

The main objective of this paper is to study, for the first time, the capability of FO and DCMD to reject EDCs, and, specifically, the natural steroid hormones estrone and 17*β*-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 *μ*m and a total surface area of 0.1 m^2. The Microdyn modules were chosen because previous studies (*18*) have shown them to provide high rejection of urea, which, like estrone and estradiol, is a nonvolatile organic compound. New Microdyn modules were used for each experiment.

Cellulose triacetate semipermeable 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 (*4*, *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 simulant wastewater components 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. (*19*) and are summarized in the Supporting Information (Table S1). The hygiene wastewater contained an anionic surfactant (sodium cocoyl *N*-methyl taurate); the humidity condensate contained trace amounts of volatile organic acids; and the urine stream contained urea as the primary solute (5.2 g/L). All chemicals used for the simulants 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 with 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 to minimize sample matrix interferences. Even so, this method is not recommended for use with surfactants because preliminary performance tests have demonstrated that samples 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-^{3}H}-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-^{3}H}-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 1000 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 and 290 ng/L, respectively. Although the hormone concentrations used in these experiments are not representative of concentrations in many wastewater effluents, it is possible to achieve concentrations as high as 7000 ng/L in closed life

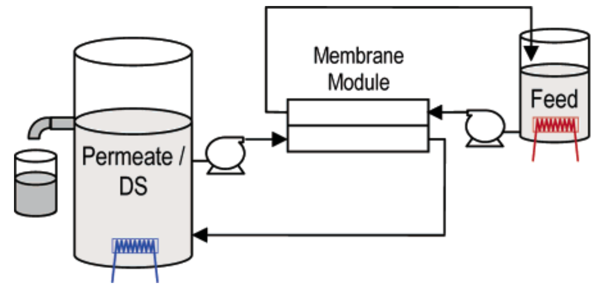

FIGURE 1. Schematic drawing of the DCMD and FO test unit.

support systems where wastewater is being continuously 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 ± 1 °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 30−40 h. 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.

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 9−10 h. Samples of 1 mL each 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. 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 for the SPE procedure. Based on results summarized in Table S2 of the Supporting Information, 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 ES, MP Biomedicals, Solon, OH) was 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.

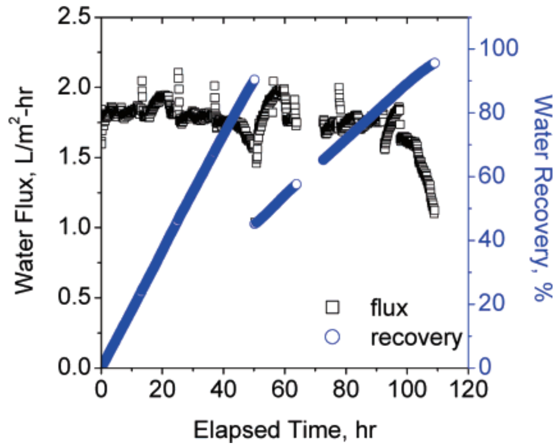

FIGURE 2. Water flux and recovery during a long-term semi-batch DCMD experiment with urine simulant as the feed solution. Temperature difference across the membrane is 20 °C and flowrates of both feed and permeate are 1.5 L/min.

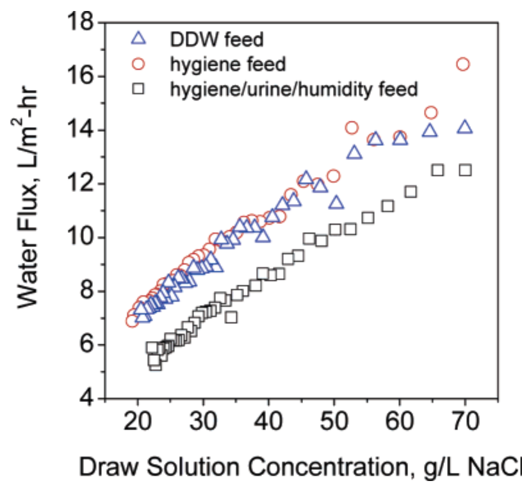

FIGURE 3. Water flux as a function of DS concentration during FO experiments. Feeds are DDW, wastewater containing only the hygiene component, or wastewater containing a mixture of hygiene, urine, and humidity condensate components.

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 (10 L). After approximately 50 h, 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 out at higher DS concentrations because water is diffusing

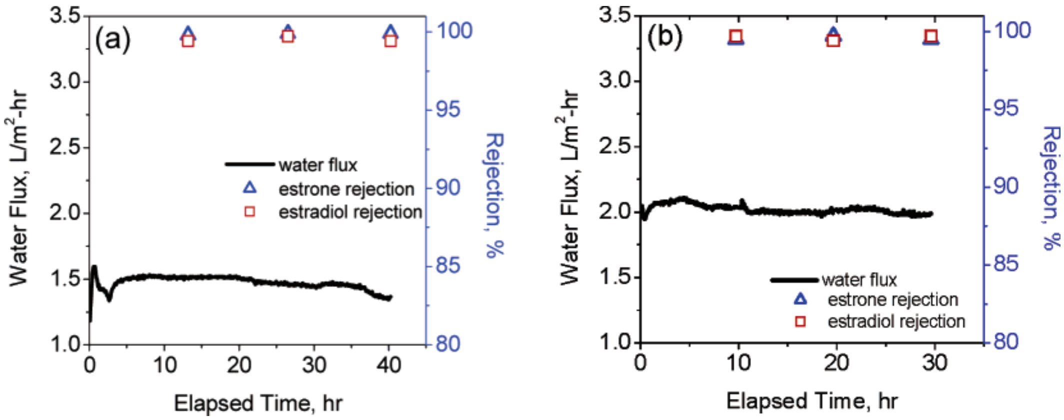

FIGURE 4. Water flux and estrone and estradiol rejection as a function of time during DCMD experiments. Feed solutions are either (a) wastewater stimulant containing urine and humidity condensate, or (b) DDW. Permeate samples were collected and analyzed for hormone rejection every time 2 L of water had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

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 in which 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 nonvolatile compounds with very low vapor pressures. These results are consistent with the DCMD performance experiments in which urea, another nonvolatile 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 (*20*).

Steady water flux was achieved during both experiments after the feed and permeate streams reached 40 and 20 °C, respectively (Figure 4). 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 originally thought 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/m^2·h. 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.

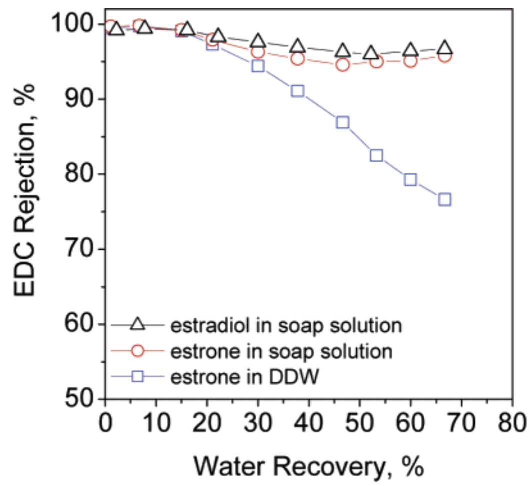

FIGURE 5. Hormone rejection as a function of the water recovery achieved during FO radiolabeled hormone experiments.

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 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. (*13*), 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 are consistent with the findings by Ng and Elimelech (*16*) where rejection decreased 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 (*16*).

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 (*12*, *13*, *21*) suggesting that RO and NF membranes provide increased hormone rejection when organic matter is present in the feed solution.

As reported in the Material and Methods section, the FO CTA membrane is relatively hydrophilic (contact angle of approximately 61°). At the pH of the feed solutions used in the FO experiments (pH 6.5), the FO CTA membrane has a negative charge (*22*) and the hormones are un-dissociated (uncharged). The surfactant used in the hygiene component of the simulant wastewater is anionic. Given these properties, it is likely that at pH 6.5, individual surfactant molecules adsorb to the membrane due to hydrophobic interactions between the surfactant tail and the membrane surface (Figure 6a) (*22*, *23*). Individual surfactant molecules are likely because the surfactant in the hygiene wastewater is below its critical micelle concentration (CMC). During the radiolabeled hormone experiments, it is possible that the CMC of the surfactant was surpassed because the feed was concentrated throughout the experiments. In this case, micelles may have formed in the bulk aqueous solution (Figure 6b) but would not likely have adsorbed to the membrane due to electrostatic repulsion. However, the hydrophobic hormones may have bound to the micelles by hydrophobic attraction. Therefore, anionic surfactants may facilitate increased FO hormone rejection by two proposed mechanisms. In the first mechanism (Figure 6a), the anionic surfactant adsorbs to the membrane surface via hydrophobic interaction and increases the resistance to hormone transport by hindering hormone adsorption to the membrane. In the second mechanism (Figure 6b), the hormones are made less available for adsorption to the membrane because they are adsorbed to the hydrocarbon chains of the micelles in the bulk feed solution.

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 (*12*, *13*). 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 (*24*)) because it has been shown that RO rejection of estrone is not significantly affected by varying the feed hormone concentration (*9*).

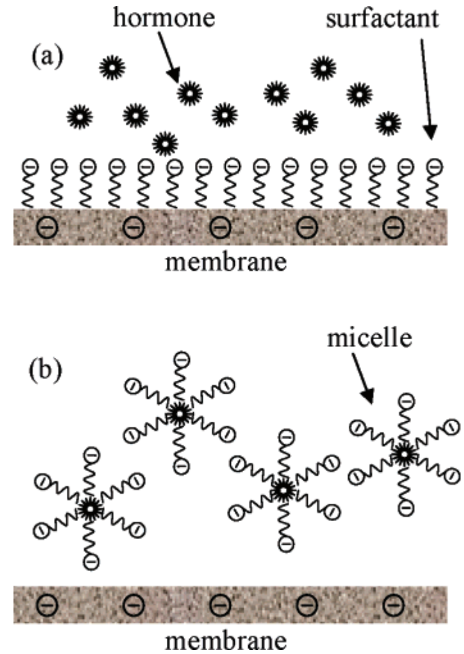

FIGURE 6. Schematic drawing of the proposed mechanisms by which anionic surfactants may facilitate increased FO hormone rejection (a) below and (b) above the CMC.

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 nonvolatile 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%.

Acknowledgments

We acknowledge the support of the National Aeronautics and Space Administration (NASA), Award No. NNA04-CL12A and the Office of Naval Research (ONR), Award No. N00014-04-1-0812.

Supporting Information Available

Information and data on SPE, EIA analysis information, and chemical pretreatment effects on EDC removal. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; p 564.

(2) Kim, S. L.; Chen, J. P.; Ting, Y. P. Study on feed pretreatment for membrane filtration of secondary effluent. *Sep. Purif. Technol.* **2002**, *29* (2), 171−179.

(3) Van Hoof, S. C. J. M.; Hashim, A.; Kordes, A. J. The effect of ultrafiltration as pretreatment to reverse osmosis in wastewater reuse and seawater desalination applications. *Desalination* **1999**, *124* (1−3), 231−242.

(4) Cath, T. Y.; Gormly, S.; Beaudry, E. G.; Flynn, M. T.; Adams, V. D.; Childress, A. E. Membrane contactor processes for wastewater reclamation in space: Part I. Direct osmosis concentration as pretreatment for reverse osmosis. *J. Membr. Sci.* **2005**, *257* (1−2), 85−98.

(5) York, R. J.; Thiel, R. S.; Beaudry, E. G. *Full-scale experience of direct osmosis concentration applied to leachate management*; Sardinia '99 Seventh International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Sardinia, Italy, 4−8 October 1999.

(6) Lawson, K. W.; Lloyd, D. R. Review: membrane distillation. *J. Membr. Sci.* **1997**, *124* (1), 1−25.

(7) Cath, T. Y.; Adams, V. D.; Childress, A. E. Experimental study of desalination using direct contact membrane distillation: A new approach to flux enhancement. *J. Membr. Sci.* **2004**, *228* (1), 5−16.

(8) Cath, T. Y.; Childress, A. E.; Elimelech, M. Forward osmosis: Principles, applications, and recent developments. *J. Membr. Sci.* **2006**, *281* (1), 70−87.

(9) Schäfer, A. I.; Nghiem, L. D.; Waite, T. D. Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environ. Sci. Technol.* **2003**, *37* (1), 182−188.

(10) U.S. EPA. *Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis*; EPA/630/R-96/012; Washington, DC, 1997; p 120.

(11) Nghiem, L. D.; Schäfer, A. I.; Elimelech, M. Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms. *Environ. Sci. Technol.* **2004**, *38* (6), 1888−1896.

(12) Nghiem, L. D.; Schäfer, A. I.; Waite, T. D. Adsorptive interactions between membranes and trace contaminants. *Desalination* **2002**, *147* (1−3), 269−274.

(13) Nghiem, L. D.; Manis, A.; Soldenhoff, K.; Schäfer, A. I. Estrogenic hormone removal from wastewater using NF/RO membranes. *J. Membr. Sci.* **2004**, *242* (1−2), 37−45.

(14) Kimura, K.; Amy, G.; Drewes, J. E.; Heberer, T.; Kim, T.-U.; Watanabe, Y. Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *J. Membr. Sci.* **2003**, *227* (1−2), 113−121.

(15) Kimura, K.; Toshima, S.; Amy, G.; Watanabe, Y. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *J. Membr. Sci.* **2004**, *245* (1−2), 71−78.

(16) Ng, H. Y.; Elimelech, M. Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis. *J. Membr. Sci.* **2004**, *244* (1−2), 215−226.

(17) Nghiem, L. D.; McCutcheon, J.; Schäfer, A. I.; Elimelech, M. The role of endocrine disrupters in water recycling: Risk or mania? *Water Sci. Technol.* **2004**, *50* (2), 215−220.

(18) Cath, T. Y.; Adams, V. D.; Childress, A. E.; Gormly, S. J.; Flynn, M. T. *Progress in the development of direct osmotic concentration wastewater recovery process for advanced life support systems*; Presented at The 35th International Conference on Environmental Systems (ICES), Rome, Italy, 11−14 July 2005.

(19) Verostko, C. E.; Carrier, C.; Finger, B. W. *Ersatz wastewater formulations for testing water recovery systems*; Presented at The 34th International Conference on Environmental Systems, Colorado Springs, CO, July 19−22, 2004.

(20) Routledge, E. J.; Sheahan, D.; Desbrow, C.; Brighty, G. C.; Waldock, M.; Sumpter, J. P. Identification of estrogenic chemicals in STW effluent. 2. In vivo responses in trout and roach. *Environ. Sci. Technol.* **1998**, *32* (11), 1559−1565.

(21) Pronk, W.; Palmquist, H.; Biebow, M.; Boller, M. Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine. *Water Res.* **2006**, *40* (7), 1405−1412.

(22) Childress, A. E.; Elimelech, M. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **1996**, *119* (2), 253−268.

(23) Childress, A. E.; Elimelech, M. Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics. *Environ. Sci. Technol.* **2000**, *34* (17), 3710−3716.

(24) Johnson, A. C.; Belfroid, A.; Corcia, A. D. Estimating steroid estrogen inputs into activated sludge treatment works and observations on their removal from the effluent. *Sci. Total Environ.* **2000**, *256* (2−3), 163−173.

Received for review March 8, 2006. Revised manuscript received September 21, 2006. Accepted September 25, 2006.

ES060550I