Removal of Hormones by Nanofiltration: Effects of Hormone Concentration and Natural Organic Matter Fouling on Removal

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ABSTRACT

Selected nanofiltration (NF) and ultrafiltration (UF) membranes were tested for the removal of the natural hormone, 17β-estradiol (E2) using a lab-scale cross-flow filtration apparatus housing flat sheet membrane coupons. The primary focus of this study was to understand adsorption and desorption characteristics of E2 at different water quality and operating conditions. The NF membranes showed a significant level of adsorption of E2 during the initial stage of filtration. The adsorbed E2 was easily desorbed when the feed solution was replaced with Milli-Q water. UF membranes showed much lower rejection than NF membranes, but did show a significant level of adsorption during the initial time period. On-going and future research will explore whether the results obtained at a high feed concentration are applicable to lower feed concentrations typical of those found in water treatment plants. The effect of natural organic matter (NOM) fouling of the membranes will also be considered.

INTRODUCTION

Endocrine disrupting compounds (EDCs) are trace contaminants emerging as a concern for the water industry, especially for utilities with a high degree of water recycling. EDCs are chemicals, both natural and synthetic, which have the potential for disrupting the endocrine systems of humans and animals. Hormones, such as the steroid estrogens considered in this research, are typically found at lower concentrations than some other EDCs such as pesticides[1]. However, even at low concentrations these hormones have an extremely high endocrine disrupting potency. Among various hormones, E2 is the most potent steroid estrogen. It is naturally excreted by humans and animals and has been consistently detected in wastewater treatment effluent and surface water in the ng/L range[1, 2]. Some synthetic hormones such as ethinylestradiol, commonly used in birth control pills, have also been detected in wastewater effluent[2]. Hormone concentrations as low as 1 ng/L have been shown to affect fish in waters receiving sewage treatment plant effluent[3]. The effects on humans at such low concentrations are to date largely unknown.

Due to the incomplete removal of EDCs by conventional treatment processes[1], membrane technologies have been suggested as an alternative way to improve removal efficiencies. Previous research has demonstrated the effectiveness of nanofiltration (NF) membranes for removal of hormones. Adsorption of hormones to the membrane surface has been shown to be a major factor affecting removal[4]. Accordingly, the potential for desorption from membranes back into the treated water and subsequent recontamination has been cited as a concern[5]. However, the mechanisms dominating these adsorption and desorption processes are not yet well understood.

The objective of this research is to quantify the extent of E2 adsorption, desorption, and steady state removal efficiency for selected NF and UF membranes. These parameters will be compared at high concentrations, where relatively simple analytical techniques such as high performance liquid chromatography with fluorescence detection (HPLC with FLD) are possible[6], and at low concentrations similar to those found in real treatment plants, using solid phase extraction (SPE) and enzyme linked immunosorbent assay (ELISA)[1]. The effect of natural organic matter membrane fouling on hormone rejection and adsorption will also be assessed.

MATERIALS AND METHODS

Chemicals. E2 (Sigma, St Louis, MO) was prepared and kept refrigerated in a methanol stock solution. E2 is uncharged at neutral pH and has an estimated pK_a of 10.4[7]. It is relatively hydrophobic with a log K_{ow} of 4.01[7] and has a solubility in water of 13 mg/L at 20°C[7]. The molecular weight of E2 is 272.4 g/mol[7]. Suwannee River natural organic matter (International Humic Substances Society) was chosen as a representative NOM. All other chemicals were of reagent grade.

Membranes. The membranes used included two Saehan NF membranes (NE4040-90 and NE1812-70) (Saehan CSM, Seoul, Korea) and two FilmTec NF membranes (NF270 and NF90) (Dow Chemical, Midland, MI). All NF membranes were polyamide thin film composite. Ultrafiltration (UF) membranes from Saehan (UE4040-PF, polysulfone) and Sterlitech (GH type, thin film) (Sterlitech, Kent, WA) were also tested.

Experimental Setup. A schematic of the experimental apparatus is shown in Figure 1. Experiments were conducted with an Osmonics SEPA II crossflow membrane cell (Osmonics, Minnetonka, MN). The active membrane area for this system was 140 cm^2. The feed spacer thickness was 1.65 mm and the channel width was 95 mm. The cross flow velocity at a typical concentrate flow rate of 3.75 L/min was 0.40 m/s. A flow meter installed in the concentrate line was used to measure the concentrate flow rate. Permeate flow was measured by a digital balance and stop watch. A Hydra-Cell diaphragm pump (Wanner, Minneapolis, MN) was used with a Sentry pulsation dampener (Blacoh, Riverside, CA). Water was recirculated from a 14 L stainless steel feed tank. To minimize adsorption to the system, the membrane cell, feed tank, tubing, and fittings were all made of 316 stainless steel.

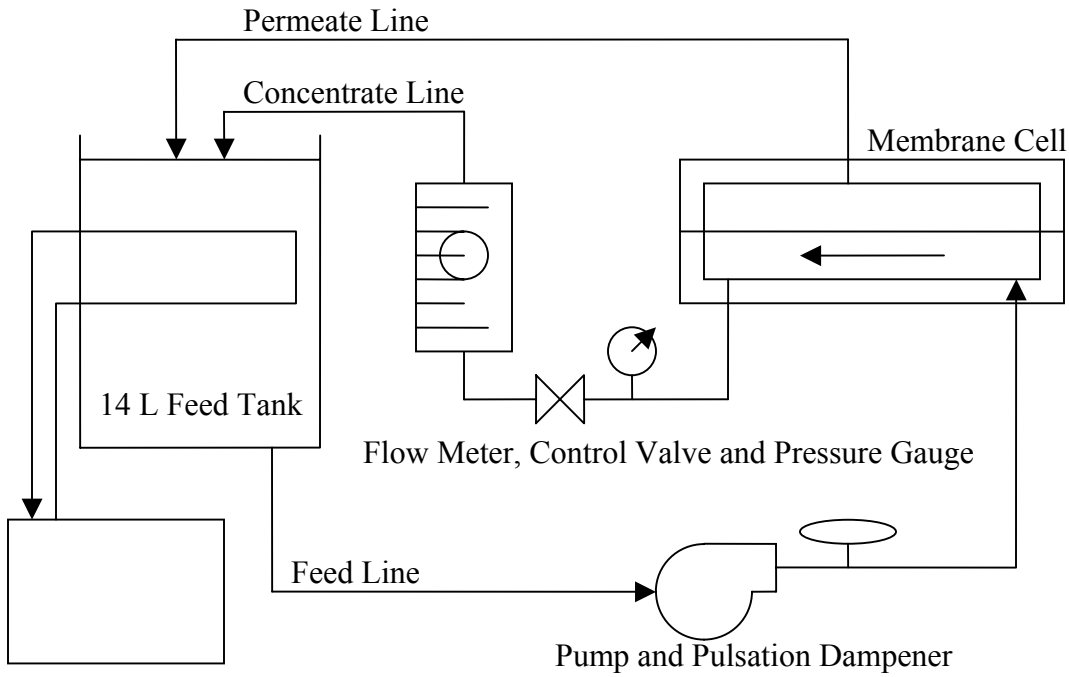

Figure 1. Experimental Apparatus

Experimental Procedure. Membranes were soaked in Milli-Q water (Millipore, Billerica, MA) for 24 hours before installation in the cell. After installation, membranes were compacted at 140 psi for 24 hours with 2000 mg/L $MgSO_4$ used as a feed solution. During compaction, membrane flux and salt rejection were measured and compared to manufacturer specifications as a quality control. If the membrane met the manufacturer specifications, the $MgSO_4$ solution was removed, the system rinsed, and the feed tank filled with the test solution. The baseline test solution contained 1 mM phosphate buffer, adjusted to pH 7 by NaOH and/or H_2SO_4, and 100 µg/L 17β-estradiol. Low-concentration experiments were conducted at a feed concentration of 100 ng/L 17β-estradiol. Temperature was maintained at 25^o C by a water bath with water recirculated through temperature control coils in the feed tank.

For the first step of each experiment the system was allowed to equilibrate at a set temperature, pressure, and flow rate for at least one hour before spiking with 17β-estradiol. Permeate and feed samples were then taken at regular intervals to determine adsorption to the membrane and steady state rejection. The second step of each experiment monitored desorption from the membrane, with the hormone feed solution replaced by Mill-Q water. Between the adsorption and desorption steps of each experiment the system was stopped for approximately thirty minutes. During this time, the feed tank and tubing were drained, rinsed and refilled with Milli-Q water. The pump was then started and the concentrate discarded for the first minute of operation to rinse the cell and concentrate tubing. The permeate tubing was not rinsed. A mass balance was performed to determine the total mass of E2 left in the liquid of permeate tubing

prior to the desorption run. It was determined that this mass was insignificant compared with the total mass desorbed.

Analytical Methods. Samples with relatively high concentrations of E2 were analyzed by a 1100 Series HPLC (Agilent, Palo Alto, CA) equipped with a Zorbax column (Agilent, Palo Alto, CA) (4.6 x 150 mm) and FLD. An excitation wavelength of 280 nm and emission wavelength of 310 nm were selected for optimal detection of E2[6]. The mobile phase was 35% H_2O and 65 % MeOH at a flow rate of 1 mL/min. E2 eluted from the column at 5.9 min. The method detection limit (MDL) was 0.7 µg/L, or between 0.4 and 1.5 with 99% confidence, as determined by injecting 100 µL of a 5 µg/L standard seven times and calculating standard deviation and variance.

For low concentration experiments, 100 mL samples were collected. To keep the feed concentration as constant as possible, a 100 mL replacement solution of E2 was added to the feed tank after each permeate sample was collected. The replacement solution had a concentration of E2 similar to the estimated permeate concentration. Samples were then concentrated by solid phase extraction (SPE). The 500 mg ENVI-18 SPE cartridges (Supelco, Bellefonte, PA) were first conditioned with 9 mL methanol and 9 mL deionized water. The samples were then extracted at a flow rate of approximately 5 mL/min. Hormones were eluted from the cartridges with 6 mL of methanol and blown down to dryness under a gentle stream of nitrogen gas. The samples were kept at 37^{o}C during blowdown to speed the drying process. Once dry, the samples were reconstituted in 100 µL methanol and 600 µL deionized water. Extraction recovery was determined by analyzing duplicate standards of a known concentration prepared in the same matrix as the samples.

The reconstituted sample extracts were then analyzed by enzyme-linked immunosorbent assay (ELISA) kits (Neogen, Lexington, KY). Samples were analyzed in either duplicate or triplicate on the ELISA kits and the average absorbance values were reported. The analysis essentially followed the procedure recommended by the manufacturer. To create a calibration curve, seven standards and one blank were prepared in the same matrix as samples, at concentrations from 0.05 to 5 µg/L. Estradiol enzyme conjugate was added to the blank, standards and samples. The plate was allowed to incubate for 1 hour before adding substrate. The substrate was allowed to develop for thirty minutes before stopping the reaction with 1 N HCl and reading the absorbance at 450 nm using an automated microplate reader (Bio-Tek, Winooski, VT).

$MgSO_4$ salt rejection was determined with an Accumet AR50 conductivity/pH meter using Accumet conductivity and temperature probes (Fisher, Pittsburgh, PA). Solution pH was measured by the same meter, using an Accumet pH probe.

RESULTS AND DISCUSSION

Preliminary results at high feed concentration indicated relatively low steady state rejection of E2 by UF membranes (data not shown). The Saehan UF membrane reached 90% passage of E2 after approximately ten minutes of operation. The Sterlitech GH membrane, a much tighter UF membrane, reached 90% passage of E2 after 4 hours of operation. The GH membrane did, however, show significant rejection due to adsorption during the initial period of time.

The NF membranes tested showed a much higher steady-state rejection of E2. With an E2 feed concentration of 100 µg/L, steady-state rejection ranged from 99% for Filmtec NF90 to 80% for Filmtec NF270. Both of the Saehan membranes showed steady state rejection greater than 90%. Desorption of hormones from the membranes to the permeate was observed when the feed solution was replaced with Mill-Q water (Figure 2). This observation suggests that hormones adsorbed during episodes of high concentration in the feed water might recontaminate the treated water at appreciable concentrations during episodes of lower feed concentration.

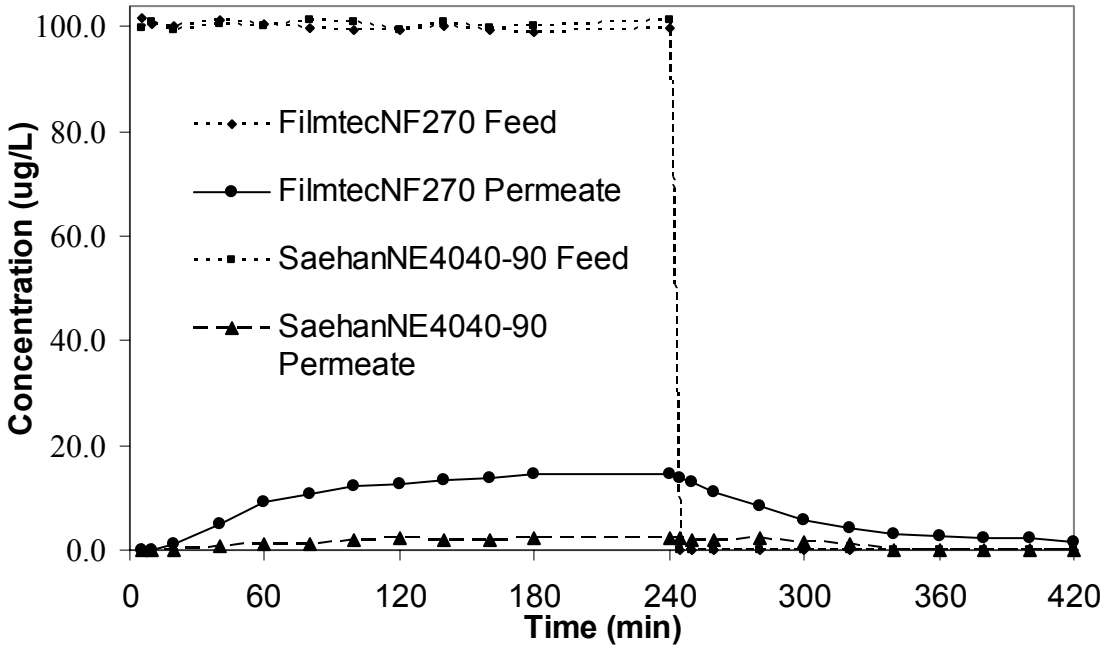

Figure 2. Adsorption and Desorption of E2 to and from NF Membranes

Ongoing and future research will examine whether the results obtained at high concentration (100 µg/L) are applicable to actual treatment systems where much lower concentrations are typical. Experiments will be conducted at a feed concentration of 100 ng/L and analysis performed by SPE and ELISA. Additionally, the effect of NOM fouling is being evaluated. The adsorptive interactions between the membrane and E2 may be significantly affected by NOM fouling, which is a common problem in real treatment systems. Finally, a mathematical model to describe the adsorption and desorption phenomena are being developed to gain a better understanding of the fundamental processes involved.

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REFERENCES

[1] Huang, C.-H., D. L. Sedlak. (2001). "Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry." *Environmental Toxicology and Chemistry*. 20(1): 133-139.

[2] Desbrow, C., E. J. Routledge, et al. (1998). "Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening." *Environmental Science and Technology*. 32(11): 1549-1558.

[3] Jobling, S., M. Nolan, et al. (1998). "Widespread sexual disruption in wild fish." *Environmental Science and Technology*. 32(17): 2498-2506.

[4] Schafer, A. I., L. D. Nghiem, et al. (2003). "Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis." *Environmental Science and Technology*. 37(1): 182-188.

[5] Nghiem, L. D., A. I. Schafer, et al. (2003). "Membrane filtration in water recycling: Removal of natural hormones." *Water Science and Technology: Water Supply*. 3(3): 155-160.

[6] Yoon, Y., P. Westerhoff, et al. (2003). "HPLC-fluorescence detection and adsorption of bisphenol A, 17β-estradiol, and 17α-ethynyl estradiol on powdered activated carbon." *Water Research*. 37(14): 3530-3537.

[7] Nghiem, L. D., J. McCutcheon, et al. (2004). "The role of endocrine disrupters in water recycling: Risk or mania?" *Water Science and Technology*. 50(2): 215-220.