ADSORPTION, DESORPTION, AND STEADY-STATE REMOVAL OF ESTROGENIC HORMONE 17BETA-ESTRADIOL BY NANOFILTRATION AND ULTRAFILTRATION MEMBRANES

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ADSORPTION, DESORPTION, AND STEADY-STATE REMOVAL OF ESTROGENIC HORMONE 17BETA-ESTRADIOL BY NANOFILTRATION AND ULTRAFILTRATION MEMBRANES

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LIST OF ABBREVIATIONS

E2	17β-estradiol
EDC	Endocrine disrupting compound
ELISA	Enzyme-linked immunosorbent assay
GC/MS	Gas chromatography / mass spectrometry
HPLC	High performance liquid chromatography
LMH	Liters per meter squared per hour
MF	Microfiltration
MWCO	Molecular weight cutoff
NF	Nanofiltration
NOM	Natural organic matter
RO	Reverse osmosis
SPE	Solid phase extraction
SRNOM	Suwannee river natural organic matter
STW	Sewage treatment works
UF	Ultrafiltration

SUMMARY

Nanofiltration (NF) and ultrafiltration (UF) membranes were tested in cross-flow configuration for removal of the natural estrogenic hormone 17β-estradiol (E2). The NF membranes, FilmTec NF270 and NF90 and Saehan NE-70 and NE-90, showed significant adsorption of E2 during the initial stage of filtration followed by relatively high steady-state rejection. The rejection ranged from 70% for the NF270 to greater than 97% for the NF90 and NE-90. UF membranes, such as Saehan UE2010 and Sterlitech GH, showed relatively low rejection (0-20 %) at steady-state, but did show significant adsorption during the initial time period. In both NF and UF, adsorbed hormone was released into the permeate stream when the feed solution was replaced with pure water. The rate of desorption was approximately the same as that of adsorption. Similar results were observed at both high concentrations (100 μg/L), and at lower, environmentally-relevant concentrations (100 ng/L). Fouling of membranes by natural organic matter improved rejection, as did operation at higher permeate flux and higher pH. These results indicate that the high initial rejection of hormones due to adsorption on membranes may not accurately reflect true rejection of hormones by these membranes at steady state.

CHAPTER 1: INTRODUCTION

Endocrine disrupting compounds, EDCs, are a class of trace contaminants receiving increased attention in recent years. EDCs include hormones, such as the one considered in this research, as well as many other natural and synthetic chemicals capable of interfering with the endocrine system. The increased attention given to EDCs is due to several factors. First, improvements in analytical techniques have led to the detection of these compounds in places where their existence was once only speculated. For example, concentrations of estrogenic hormones between 0.1 and 10 ng/L have been frequently reported in sewage treatment works (STW) effluents and streams receiving these effluents (Desbrow et al., 1998; Ternes, 2001; Ternes et al., 1999; Huang and Sedlak, 2001; Shen et al., 2001; Kolpin et al., 2002). Measuring such low concentrations in complex matrices is typically a time-consuming, multi-step process. Samples must be concentrated, then cleaned up and/or derivatized before analysis. Analysis can be done by chromatography/mass spectrometry techniques, such as GC/MS, or by immunoassays, such as ELISA. The reported detection limits of these techniques for EDCs can be as low as 0.1 ng/L. Another factor leading to increased concern over EDCs is the observation of endocrine disruption in aquatic organisms which live in bodies of water exposed to these compounds, such as streams receiving STW effluents. Laboratory and field studies have confirmed a strong correlation between the concentration of STW effluent and the degree of endocrine disruption in these animals (Rodgers-Gray et al., 2001; Desbrow et al, 1998). Hormone concentrations as low as 1 ng/L have been observed to cause vitellogenesis (production of an egg yolk protein) in male fish (Rodgers-Gray et al., 2001; Thorpe et al.,

2001). It is thought that hormones such as E2 are responsible for the high estrogenicity of STW waste (Desbrow et al., 1998). While some have speculated that human exposure to trace levels of EDCs may be related to declining male sperm counts and increased incidence rates for certain types of cancer, there is not yet sufficient evidence to support this hypothesis (Solomon and Schettler, 2000). For this reason, the US EPA declined to include EDCs in its most recent Drinking Water Contaminant Candidate List (USEPA, 2005). Nonetheless, the issue presents a concern for the water industry, particularly systems with a high degree of water recycling. As available freshwater resources become scarce and demand for high quality drinking water increases, more utilities will be forced to consider indirect reuse of wastewater as a potable water source. With reuse comes public concern over the quality of water, including the potential presence of trace organics like EDCs (Higgins et al., 2002).

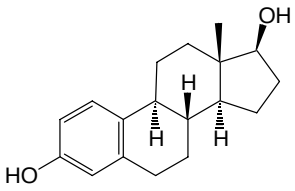
Hormones were selected for this research because of their high frequency of detection and high potency relative to other EDCs. While other EDCs such as nonylphenol and bisphenol A are found at higher concentrations, hormones have a much higher endocrine disrupting potency and are thought to be the primary cause of the estrogenicity observed in STW effluents (Desbrow et al., 1998; Thorpe et al., 2003; Harris et al., 2001; Sohoni et al., 2001). Hormones detected in wastewater and surface water include those naturally excreted by humans and other animals, as well as synthetic hormones such as 17α-ethinylestradiol, the active ingredient of the oral contraceptive pill.

The amount of hormones naturally excreted by humans varies widely. On average, women excrete about 14 µg/day of 17β-estradiol, but pregnant women can excrete more than ten times this amount (D'Ascenzo et al., 2002). Hormones are excreted as inactive

sulfate or glucuronate conjugates in urine, but bacteria present in sewers and treatment plants can easily cleave these conjugates, releasing the active estrogenic hormone (D'Ascenzo et al., 2002; Belfroid et al., 1999; Di Corcia et al., 2003).

The focus of this research is the natural hormone 17β-estradiol, or E2. The chemical structure of E2 is that of a steroid, as shown in Table 1, and it is the most potent human estrogen, or female sex hormone. Other estrogens, including estrone, have a similar molecular weight and hydrophobicity (Nghiem et al., 2004b), and their removal is expected to be comparable to that of E2.

TABLE 1. Physicochemical Properties of 17β-estradiol

Name	**Structure**	**Molecular Weight**	**L (Length)**
17β-estradiol (E2)		272.4 g/mol	1.285 nm
Function	**δ_P, polarity**	**pK_a**	**Charge at pH 7**
Natural Estrogenic Hormone	4.1 $(J/cm^3)^{1/2}$	10.4	Neutral
Log K_{ow}	**Henry's Law Constant**	**Dipole Moment**	**H_2O Solubility**
4.01	3.64×10^{-11} atm m^3/mol	0.798 debye	3.6 mg/L

L, log K_{ow} (logarithm of octanol-water partition coefficient), δ_P from Agenson et al., 2003; pK_a (negative logarithm of the acid dissociation constant) from Nghiem et al., 2004a; Henry's Law Constant, Dipole Moment, Solubility from Kimura et al., 2004

Hormones and other EDCs are removed by conventional treatment techniques with varying degrees of success. Removal of E2 in activated sludge processes can range

from 70% to 92% (Johnson and Sumpter, 2001; Ternes et al., 1999; Huang and Sedlak, 2001). However, hormone concentrations in effluents are often higher than those which have been demonstrated to induce feminization of male fish. The processes governing removal in activated sludge are similar to those thought to govern the ultimate fate of these contaminants, namely adsorption and biodegradation (Johnson and Sumpter, 2001; Hanselman et al., 2003; Lai et al., 2000; Jurgens et al., 2002). However, the rate of biodegradation in a typical activated sludge treatment plant may not be fast enough for adequate removal. Additionally, if the compounds adsorb to natural organic matter or particulate material not removed by the treatment process, they will likely pass through the plant.

In recent years, the use of membrane technologies for drinking water and wastewater treatment has become much more common, and this trend is expected to continue. For many systems, the cost of membrane technologies has become competitive with that of conventional treatment. Membranes are capable of removing a wide variety of contaminants, depending on membrane type and operating conditions. Those membranes with large pore sizes, such as microfiltration (MF) and ultrafiltration (UF) membranes, are typically expected to remove colloids and some organic molecules. Membranes with smaller pore sizes, such as nanofiltration (NF) and those with no pores, such as reverse osmosis (RO) membranes, are typically expected to remove smaller solutes, for example small organic molecules and divalent ions (removal of hardness) for NF and monovalent ions (desalination) for RO.

However, consideration of only the presence and size of membrane pores is sometimes not enough to explain observed membrane performance. For example, MF

and UF membranes can remove particles smaller than their pores when fouling reduces the effective pore size or when small particles adsorb to the membrane surface or to larger particles. Large molecules can pass through RO and NF membranes by partitioning into the solid membrane phase and diffusing across the membrane. Charge effects are also extremely important; membranes can reject molecules smaller than their pore size due to repulsive forces between negatively-charged ions and negatively-charged membrane surfaces.

Throughout this report, the conventional definition for membrane rejection has been used: rejection equals one minus the ratio of the permeate to the feed concentration (Taylor and Wiesner, 1999).

$$R = 1 - \frac{C_{Permeate}}{C_{Feed}}$$

The terms “retention” and “removal” are also sometimes used, and typically defined the same. Rejection can be time dependent because of adsorption and desorption processes, as will be shown in the results which follow. Based on the criteria mentioned above, NF membranes are likely to have good rejection of E2, and were the primary focus of this research.

The overall objective of this research was to quantify E2 adsorption, desorption, and steady-state removal efficiency for selected NF and UF membranes. These parameters were compared at high concentrations, where relatively simple analytical techniques such as HPLC are possible, and at low concentrations similar to those found in treatment plants. The effects of membrane fouling by natural organic matter, changes in permeate flux, and changes in feed water pH on hormone rejection and adsorption were also assessed.

CHAPTER 2: LITERATURE REVIEW

Recent studies have provided some insight into the removal of hormones and other trace organic contaminants by membranes. The mechanisms governing rejection are not yet well defined, and may vary considerably from case to case. It has become clear that adsorption of hormones to membranes has a large effect on initial rejection. However, a better understanding of the dominant bonding mechanisms for this adsorption and a predictive, dynamic model for hormone removal are still needed. To simplify experiments, conditions for most studies differ from those encountered in treatment situations. Accurate measurement of trace organic contaminants in complex matrices can be expensive and time-consuming. Additionally, characterizing both steady-state and dynamic conditions over a wide variety of treatment conditions (e.g. pH, flux, temperature, membrane type, etc.) and combinations of these conditions could become a nearly infinite task. The number of published studies on removal of hormones by membranes is still rather small, and while considerable research has been done on the removal of other trace organic contaminants by membranes, concentrations at which these chemicals become a concern is often orders of magnitude higher than that of hormones. Results of previous studies helped to guide this research, and that which follows is a summary of some of the major findings.

While steady-state rejection of hormones has been correlated with molecular weight (Kimura et al., 2004; Agenson et al., 2003; Kimura et al., 2003), initial rejection is greatly influenced by adsorption. Nghiem et al. (2002) suggested that this adsorption may be due to hydrogen bonding because membranes with high hydrophilicity also had high adsorption. Others have suggested that this adsorption is due to the high hydrophobicity

of hormones (Yoon et al., 2004). Regardless of the mechanism involved, it is apparent that adsorptive effects must be considered when assessing removal of hormones by membranes.

Several studies have addressed the question of whether hormone removal observed at elevated concentrations accurately represents removal at extremely low concentrations typical of treatment plants. Schäfer et al. (2003) did not observe any variation in retention over a concentration range of 1-1,000 ng/L. However, retention was only considered during the initial phase of filtration, rather than at steady-state conditions. Van der Bruggen et al. (1998) reached the same conclusion when assessing removal of pesticides, but only measured a very narrow and high concentration range (0.3 mg/L – 2.5 mg/L) and did not consider adsorption. Yoon et al. (2004) observed a similar percentage adsorbed during batch adsorption experiments over a range of 6.8-1360 ng/L. None of these studies considered effects of concentration on steady-state rejection, or the time required to reach steady-state. However, in a study by Kimura et al. (2003) using a cross-flow membrane apparatus and sampling after 24 hr operation, a lower percentage rejection was observed for several pharmaceutically-active compounds (PhACs) when experiments were conducted at low concentrations. Based on these results, it appears that concentration effects may be more noticeable when conducting experiments over long time frames, or when considering the rate of adsorption and desorption rather than just equilibrium values.

While most experiments have been conducted in relatively clean water, the presence of competing organics or colloidal material may affect hormone removal by membranes. Hormone molecules adsorbing to larger particles in the water or pore

blockage of membrane by a foulant could increase hormone removal. On the other hand, competition for adsorptive sites could decrease hormone removal, at least during the early phases of filtration when adsorption is the dominant mechanism of removal. The potential for competitive adsorption with other organics was also assessed by Chang et al. (2003). The authors observed less adsorption of estrone (E1), an estrogenic hormone similar to E2, to MF membranes when the hormone was in a matrix of surface water or secondary effluent than in buffer solution alone. Similarly, Yoon et al. (2004) observed decreased adsorption of E2 to NF and UF membranes when the hormone solution contained Suwannee River Natural Organic Matter (SRNOM). Agenson et al. (2003) did not observe any effect on E2 rejection by NF membranes when varying the concentration of landfill leachate. However, aside from stating that the leachate was filtered, the solution was not well characterized, and it is possible that the concentration of leachate was too low to affect membrane performance. Ng et al. (2004) fouled RO membranes with colloidal silica particles and observed a decreased rejection of E2 with the fouled membranes. This phenomenon was explained by the fact that the cake layer created on the membrane surface during fouling prevents back-diffusion of hormone and thereby increases concentration polarization. Because foulants are typically present in treatment applications, a better understanding of their effects on removal of trace organics is essential.

E2 is negatively charged at pH values above its pK_a of 10.3. While this is higher than the pH typically encountered during membrane filtration, cleaning solutions used on membranes often have a high pH. Therefore, understanding pH effects is critical to predicting membrane performance. Schäfer et al. (2003) looked at NF and RO

membranes during the initial phase of filtration and observed decreased adsorption and retention of E1 above its pK_a value. This effect was apparent for relatively loose membranes, while relatively tight membranes showed high retention regardless of pH. Nghiem et al. (2004b) confirmed this result with E2 as well, and attributed decreased retention to charge repulsion between negatively-charged hormone molecule and negatively charged membrane surface. Kimura et al. (2003) observed the opposite effect for a range of compounds, that is, negatively-charged compounds had a higher rejection than neutral compounds. The discrepancy in these results may have something to do with the time at which samples were taken. While Schäfer (2003) and Nghiem (2004b) looked at initial rejection, which for hormones is largely due to adsorption, Kimura (2003) looked at the 24 hour rejection, when adsorption and desorption have likely reached equilibrium. While charge repulsion will limit the initial adsorption, it will also limit the steady-state passage of hormone through the membrane.

Variations in operating pressure or permeate flux can also influence hormone rejection. A model presented by Nghiem et al. (2004a) for removal of hormones by NF membranes suggests that increased flux will lead to greater retention. This effect is verified for inert organic tracers used to calibrate the model, but no data on the effect of changes in flux were presented for hormones. According to the model, the effect should be most noticeable at very low flux values. Chang et al. (2003) observed faster adsorption to an MF membrane at higher permeate flux. However, they observed even faster adsorption when shaking the membrane in a flask with no flux. Agenson et al. (2003) observed lower rejection at lower pressure for a range of compounds including E2 and

using NF membranes. The results were attributed to decreased volume flux and relatively constant solute flux and fitted to the Spiegler and Kedem model.

Chang et al. (2003) demonstrated that microfiltration hollow fiber membranes with a pore size much larger than E1 can show high initial retention due to adsorption. They also demonstrated that this adsorption was largely reversible: decreasing the concentration of hormone in the feed solution led to negative values of retention as hormone which had previously adsorbed was released into the permeate. They went on to perform batch adsorption tests and demonstrated a linear adsorption isotherm through a concentration range of 13-154 ng/L (e.g. mass of hormone adsorbed per mass of membrane was proportional to equilibrium hormone concentration). The linearity of this isotherm indicates that the membrane was well below its ultimate capacity for adsorption. Model and experimental data on the kinetics of adsorption showed that equilibrium was typically achieved within a few hours, and that the amount of time required to reach equilibrium was greater when there was more membrane surface area. Based on the fitting parameters obtained from their model, they suggested that adsorptive surface reaction, rather than diffusive transport to the membrane surface, limited the rate of adsorption.

CHAPTER 3: MATERIALS AND METHODS

Chemicals

E2 (Sigma, St Louis, MO) was prepared at concentrations of 70-140 mg/L and kept refrigerated in a methanol stock solution. Some physicochemical properties of E2 are shown in Table 1. Suwannee River natural organic matter (International Humic Substances Society) was chosen as a representative NOM. All other chemicals were reagent grade.

Membranes

Membranes used included two Saehan NF membranes (NE-90 and NE-70) (Saehan Industries, Seoul, Korea) and two FilmTec NF membranes (NF270 and NF90) (Dow Chemical, Midland, MI). All NF membranes were polyamide thin film composite. Zeta potential data provided in Appendix A indicate that all NF membranes had a negative surface charge in the pH range tested (pH 5.5 to 11). The contact angle between a sessile water drop and the membrane is sometimes used to characterize membrane hydrophobicity. Contact angle data, also provided in Appendix A, indicate that the FilmTec NF270 may be more hydrophobic than the other membranes tested, although other factors such as surface roughness will also affect contact angle. Flux (LMH, liters per meter squared per hour) and salt rejection data provided by the manufacturers for the NF membranes are provided in Table 2. (Flux is in LMH, or liters per meter squared per hour). Based on these flux values and observed rejection of E2, the Saehan NE-70 and NE-90 membranes and the FilmTec NF90 membrane were classified as “tight” NF

membranes for this research, while the FilmTec NF270 membrane was classified as a "loose" NF membrane.

Ultrafiltration (UF) membranes from Saehan (UE2010, polysulfone) and Sterlitech (GH type, thin film proprietary material) (Sterlitech, Kent, WA) were also tested. The Sterlitech membrane molecular weight cutoff (MWCO) was 1000 kDa. MWCO for the Saehan membrane was not provided.

TABLE 2. Flux and Salt Rejection Data for NF Membranes

Membrane	Test Conditions	Flux (LMH)	Salt Rejection (%)
NE-70 (Saehan)	75 psi, 500 ppm NaCl	19.9	20.31
NE-70 (Saehan)	75 psi, 500 ppm MgSO4	18.9	98.54
NE-90 (Saehan)	75 psi, 2000 ppm NaCl	38.1	85-90
NE-90 (Saehan)	75 psi, 2000 ppm MgSO4	38.1	98.5
NF270 (FilmTec)	70 psi, 2000 ppm MgSO4	53.3	>97
NF270 (FilmTec)	70 psi, 500 ppm CaCl2	62.6	40-60
NF90 (FilmTec)	70 psi, 2000 ppm MgSO4	40.5	>97
NF90 (FilmTec)	70 psi, 2000 ppm NaCl	32	85-95

Experimental Setup

A schematic of the experimental apparatus is shown in Figure 1 and a photograph is shown in Figure 2. 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, as specified by the manufacturer. 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. At a permeate flux of 70 LMH (typical for NF270 membrane at 70 psi) the permeate flow rate was 0.0163 L/min and the membrane recovery, or ratio of permeate flow rate to feed flow rate, was less than 0.5%. This recovery is very low when

compared with the recovery of a commercial membrane module, typically 15 % or more. The amount of product water produced is very small, but because of this the concentration change across the membrane surface can be neglected. A Hydra-Cell diaphragm pump (Wanner #D03XASJSSSCA, Minneapolis, MN) was used with a Sentry pulsation dampener (Blacoh #TG12SST, 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. The concentrate pressure control valve supplied with the cell was replaced (Swagelok #SS-1RM4) to provide more precise control of pressure. The permeate carrier supplied with the system did not offer sufficient support for the membranes and was replaced with three permeate carriers cut from a commercial membrane module.

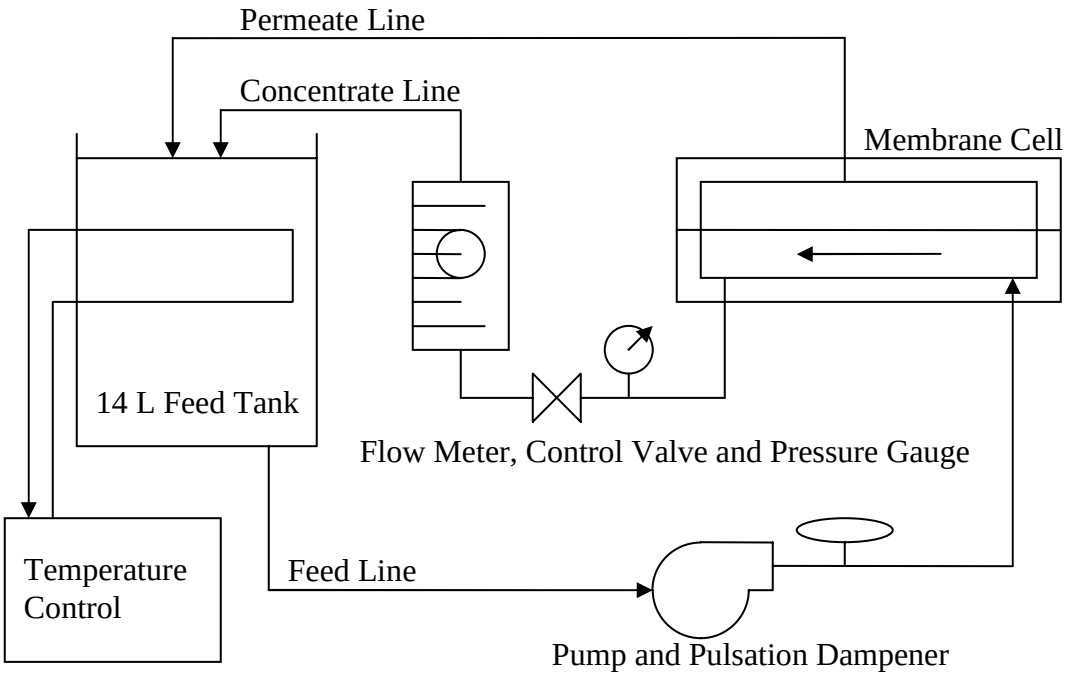


FIGURE 1. Diagram of Experimental Apparatus for Cross-flow Filtration

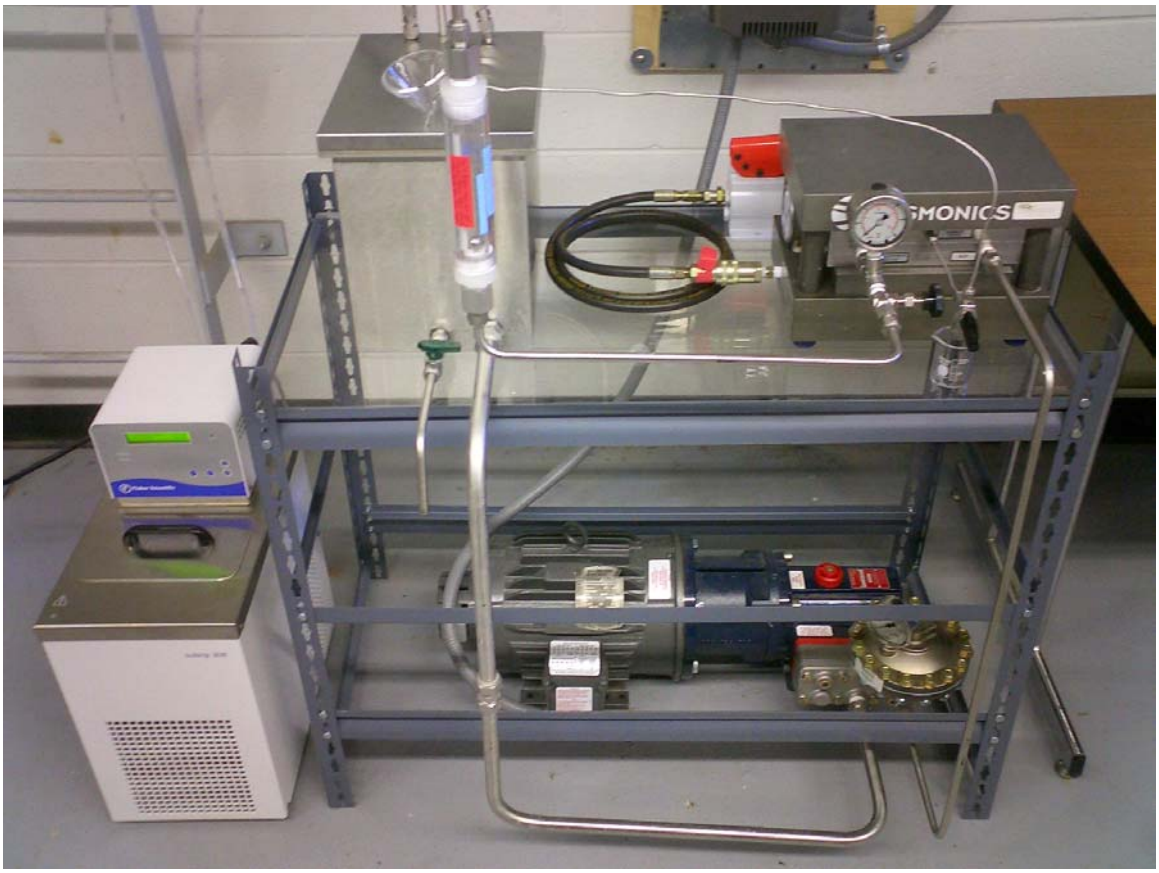


FIGURE 2. Photo of Experimental Apparatus for Cross-Flow Filtration

Experimental Procedure

Membranes were soaked in Milli-Q water (Millipore, Billerica, MA) for at least 24 hours before installation in the cell. After installation, NF membranes were compacted at 140 psi for 24 hours with 2000 mg/L $MgSO_4$ used as a feed solution. The $MgSO_4$ solution used for testing membrane salt rejection was stored at 4° C when not in use and a fresh solution was prepared every month. 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 until conductivity was less than 1 µS/cm, 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 100-500 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. $MgSO_4$ 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.

For the first phase 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 (E2). Permeate and feed samples were then taken at regular time intervals to determine adsorption to the membrane and steady-state rejection. The second phase of each experiment monitored desorption of E2 from the membrane, with the hormone feed solution replaced by Milli-Q water. Between the adsorption and desorption phases 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 (Appendix B). The waste from each experiment was oxidized by exposure to ozone for at least 5 minutes before disposal (Huber, 2003). Greater than 99% destruction of E2 was verified for this procedure.

For some experiments, membrane fouling was achieved with synthetic natural water. This solution consisted of 10 mg/L Suwannee River Natural Organic Matter

(SRNOM), 1 mM $CaCl_2$ (100 mg/L as $CaCO_3$ or 40 mg/L as Ca^{2+}), and 1 mM phosphate buffer adjusted to pH 7. 1 liter of 140 mg/L SRNOM stock solution was dissolved by mixing gently for at least 1 hr. 1 liter of 14 mM $CaCl_2$ stock solution was prepared in a separate beaker from the NOM, and the two stock solutions were added to the feed tank separately. Adding the two stock solutions separately eliminated visible flocculation and precipitation which caused near complete fouling of the membrane in an early trial run. Permeate flux was measured during a 24 hour fouling period and decreased approximately 25%.

Analytical Methods

To monitor the high concentration (100 µg/L E2) experiments, approximately 1 mL of sample was collected periodically and each sample took approximately 1 second to collect. These samples were analyzed by a 1100 Series HPLC (Agilent, Palo Alto, CA) equipped with a Zorbax 4.6 x 150 mm XDB-C8 column (Agilent, Palo Alto, CA) and fluorescence detector. An excitation wavelength of 280 nm and emission wavelength of 310 nm were selected for optimal detection of E2 (Yoon, 2003). The mobile phase was 35% H_2O and 65 % methanol at a flow rate of 1 mL/min. E2 eluted from the column at around 5.86 minutes. The method detection limit (MDL) was 0.7 µg/L (between 0.4 and 1.5 µg/L with 99% confidence) as determined by injecting 100 µL of a 5 µg/L standard seven times and calculating standard deviation and variance. For some HPLC samples near the detection limit, samples were analyzed twice and the average value reported.

For low-concentration experiments, 100 mL samples were typically collected, and the time required to take each sample varied depending on the permeate flow rate. 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 during the NF low-concentration experiments. The replacement solution had a concentration of E2 similar to the estimated permeate concentration (5 ng/L for the Saehan NE-70 and NE-90 membranes, and 15 ng/L for the FilmTec NF270 membrane)

After collection, samples were concentrated by solid phase extraction (SPE) using 500 mg ENVI-18 SPE cartridges (Supelco, Bellefonte, PA). The cartridges were first conditioned with 9 mL methanol and 9 mL deionized water before sample extraction 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°C during blowdown to speed the drying process. Once dry, the samples were reconstituted in 100 µL methanol and 600 µL deionized water for the Saehan NE-70 and NE-90 membranes, and 200 µL methanol and 1200 µL deionized water for the FilmTec NF270 membrane. Extraction recovery was determined by analyzing duplicate standards of a known concentration prepared in the same matrix as the samples. For feed samples which would have had a concentration higher than the ELISA standard curve, only a portion of the total sample collected was analyzed, and the final result multiplied by an appropriate factor. For the Saehan NE-70 and NE-90 membranes, 0.5 mL of the total 6 mL SPE eluent was removed, dried and reconstituted like the other samples and the final concentration multiplied by a factor of 12. For the FilmTec NF270, 20 ml of feed solution was collected rather than 100 ml, and the final concentration multiplied by a factor of 5.

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 closely followed the procedure recommended by the manufacturer. Blanks, standards and samples were first added to a microplate tray. Then estradiol enzyme conjugate was added and the plate was allowed to incubate for 1 hr 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). Standards were prepared in a 1:6 (v/v) methanol and Milli-Q water mixture, the same ratio as the reconstituted SPE extracts. Five standards and one blank were prepared at concentrations of 0, 0.1, 0.2, 0.5, 1.0, and 2.0 ng/L. The detection limit was determined by analyzing 7 blank samples along with a typical standard curve. The ELISA detection limit of 0.3 µg/L is the concentration on the standard curve which is two standard deviations away from the mean blank signal. Detection limits and standard curves for standards prepared in pure Milli-Q water did not differ significantly from those for standards prepared in methanol/water mixture.

For the low-concentration experiment using the Saehan UF membrane, 500-mL samples were collected over a time period of approximately 4 minutes. These samples were concentrated by SPE following the procedure described above and analyzed by HPLC rather than ELISA. The SPE recovery for this method was determined to be between 92 and 96%. For all the samples that underwent preconcentration procedures, the measured concentration was divided by the appropriate concentration factor and reported, without being corrected by the extraction recovery (i.e., 100% recovery was assumed).

Modifications to Experimental Procedure

A permeate carrier mesh was provided by the membrane cell manufacturer for membrane support backing and as a means of channeling permeate flow out of the cell. By visual inspection of used membranes and the observation of increases in permeate flux during initial usage, it was determined that this permeate carrier did not provide adequate support for membranes. Membranes were visibly deformed in the area of the permeate collection channel, indicating that it had been pushed into the channel by the operating pressure of 70 psi. This permeate carrier was replaced with stronger permeate carriers cut from a commercial membrane module. Three of these stacked on top of each other provided sufficient support to prevent the membrane from being damaged by operating pressures up to 140 psi.

The membrane cell was also provided with a needle valve to control pressure in the cell. The valve provided was replaced with another valve that allowed for more accurate control of the operating pressure.

The diaphragm pump used in this research was selected for its ability to provide a consistent volumetric flow rate at a wide range of operating pressures. However, because the membrane cell and tubing were all constructed of rigid stainless steel, the system did not have the ability to absorb the strong pulsations produced by each stroke of the pump. The three diaphragms of the pump operated sequentially, making pulsations less severe than they would otherwise have been. However, the needle in the glycerin-filled pressure gauge vibrated severely at higher pressures, making accurate readings difficult. Additionally, these large variations in pressure may have affected membrane

performance. For this reason, a pulsation dampener (Blacoh #TG12SST, Riverside, CA) was installed at the pump outlet, and it effectively eliminated the noticeable pulsations.

Feed samples taken during the first 10 minutes of initial experiments had E2 concentrations that were much higher than later samples. It was determined that this was due to incomplete mixing in the tank after spiking the hormone stock solution. For later experiments, the tank was stirred for at least 30 seconds with a mechanical mixer immediately after spiking the hormone stock solution. Incomplete mixing was not observed after using this procedure. The initial feed samples that were inaccurate due to incomplete mixing were disregarded in subsequent analysis.

During some of the initial experiments, the concentration of E2 in the feed solution was significantly different than the target feed concentration. The initial spiking procedure involved adding a small volume of methanol-based E2 stock solution to the tank with a plastic-tipped micropipette. The methanol stock solution stuck to the micropipette tip, making accurate measurement difficult. In later experiments, a 10 ml glass pipette was used for spiking the methanol-based E2 stock solution and preparing standards. This method improved the accuracy of results considerably.

While there was significant variation in replicate data sets obtained under the same experimental conditions for the membranes (Appendices D, E, and F), much of this variation may be due to physical variations among membrane coupons tested. In the future, repeated experiments should be conducted on the same membrane coupon. Different membrane coupons, even when cut from the same roll, may show different levels of rejection and adsorption. Each membrane was tested for $MgSO_4$ salt rejection

and flux before beginning hormone experiments to ensure that manufacturer specifications were met.

Verification of Experimental Procedures

The gradually decreasing permeate concentration observed during the second (desorption) phase of each experiment was assumed to be a result of hormone desorption from the membrane. However, a small volume of permeate was always left above the membrane in the permeate carrier and permeate tubing at the end of the first (adsorption) phase of each experiment. Rinsing this E2 from the system with pure Milli-Q water would also result in a gradual decrease in permeate concentration. A mass balance, presented in Appendix B, was performed to determine whether E2 remaining above the membrane in the permeate carrier and permeate tubing was significant when compared with total mass desorbed. It was determined that this mass was less than 1% of total mass desorbed, and was assumed to be insignificant.

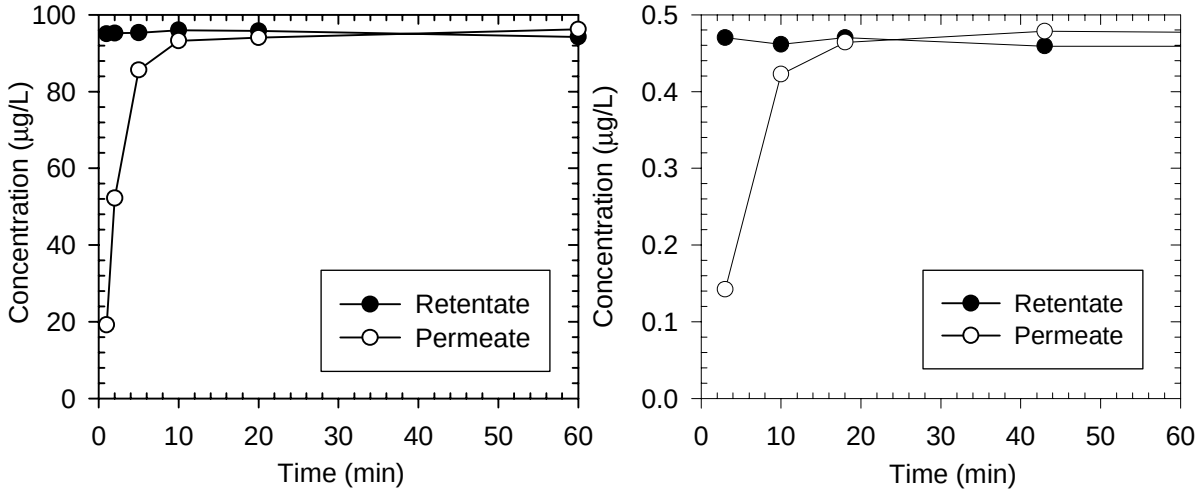
Even if there was no adsorption to the membrane, a chemical which was spiked into the feed tank would not instantaneously appear at the permeate sampling point. Some time would be needed for the feed tank to become completely mixed and for a non-adsorbing chemical to pass across the membrane and reach the permeate sampling point. For this reason, a tracer test was performed using NaCl as a non-adsorbing tracer, following a spiking and sampling procedure similar to that used for the hormone experiments on the NF270 membrane. The results, presented in Appendix C, indicate that for a non-adsorbing tracer, permeate samples taken approximately 5 minutes after spiking the feed tank were already at or near the steady-state concentration. Because 5 minutes

was the first sample taken for most of the hormone experiments, it was assumed that the initial low concentrations observed were due to adsorption and not incomplete mixing in the system. Although samples were taken at less than 5 minutes for the Saehan UE2010 membrane, the observed flux of this UF membrane is more than 5 times as high as the NF270. Therefore the time required for a non-adsorbing tracer to pass through the system should be much less than 5 minutes.

CHAPTER 4: RESULTS AND DISCUSSION

UF Membrane - Saehan UE2010

The Saehan UE2010 membrane (Figure 3) showed an initial high rejection, or low permeate concentration, due to adsorption of the hormone to the membrane. However, after 20 minutes of operation, the adsorptive capacity of the membrane was exceeded, and the membrane did not show any significant rejection. This result seems reasonable, as the size of an E2 molecule is much smaller than the typical pore size of an ultrafiltration membrane, and at neutral pH there are no charge effects associated with the molecule. The experiment was repeated at a lower concentration to determine whether the time required to reach saturation is dependent on feed concentration. The data points shown for the lower concentration experiment represent the middle of the 4 minute sampling period. While considering the uncertainty associated with taking samples over a 4 minute time period, there does not appear to be a significant difference in the operation time required to exceed the membrane's adsorptive capacity, even when the feed concentration is 200 times lower.

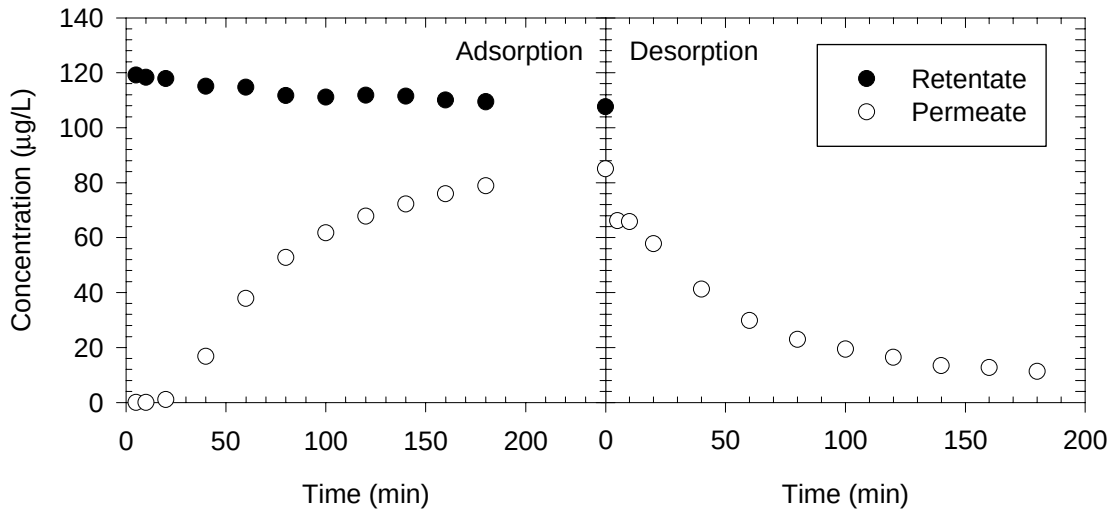


Experimental conditions: 100 µg/L E2 in 1mM phosphate buffer at pH 7, 25°C, pressure: 20 psi, cross-flow velocity: 0.4 m/s, permeate flux: 455 LMH

FIGURE 3. Rejection of E2 by Saehan UE2010 (UF) Membrane at High (Left) and Low (Right) Concentrations of E2

UF Membrane - Sterlitech GH

Because the initial UF membrane (Saehan UE2010) did not show any significant steady-state rejection, a UF membrane with small pore size, Sterlitech GH, was also tested (Figure 4). Both adsorption to, and desorption from, the membrane were monitored, following the two-phase procedure described previously. Other processes (i.e. desorption, size exclusion, etc.) may occur during the first, "adsorption", phase of each experiment, and "desorption" is not the only process occurring during the second phase of each experiment. The terms "adsorption" and "desorption" are here simply used to describe the first and second phase of each experiment, and to indicate that adsorption dominates desorption during the first phase and vice versa.



Experimental conditions: 100 µg/L E2 in 1mM phosphate buffer, pH 7, 25°C, pressure: 140 psi, cross-flow velocity: 0.4 m/s, permeate flux: 38 LMH (adsorption) and 39 LMH (desorption), $MgSO_4$ Salt Rejection: 75% at 32 LMH, 140 psi

FIGURE 4. High Early Adsorptive Capacity and Low Long-Term Rejection of E2 Shown by Sterlitech GH (UF) Membrane

At the beginning of the experiment the permeate concentration was zero, but the concentration rose slowly over the course of several hours. When the adsorption phase of the experiment was stopped at 240 minutes, steady-state conditions had not been reached; the permeate concentration was almost as high as the feed concentration, and was still climbing.

A sigmoidal curve similar to that observed here is commonly associated with breakthrough of granular activated carbon columns, and thus the two underlying phenomena could be similar. A contaminant is initially adsorbed to the front of the column (or membrane), which eventually becomes saturated. Desorption then releases contaminant further into the column, until it eventually reaches the permeate at a low initial concentration. When the entire column is saturated, the concentration exiting the column will be the same as the concentration entering the column. In this respect a

membrane can behave differently, as clearly shown in subsequent sections by the high steady-state rejection of NF membranes. While an activated carbon column achieves contaminant removal by adsorption only, size exclusion or other mechanisms can contribute to removal by membranes.

This membrane demonstrated the capacity to adsorb a large amount of E2 and had high rejection through the first hour of operation, but like the first UF membrane it had little rejection after being operated for a long time. The amount of E2 adsorbed to the membrane was large enough that a decrease in feed (retentate) concentration was easily observed over the course of the experiment. A decrease in feed concentration could also be observed during later experiments with NF membranes, although the decrease in feed concentration for these membranes was more subtle. All membranes samples were relatively small (140 cm^2 active area) compared with the total mass of E2 in the 14 L feed tank. A larger decrease in feed concentration would be expected if experiments were conducted with a greater membrane area (for example using a spiral wound module), or a smaller solution volume in the recirculating feed tank.

When the feed solution was removed and replaced with Milli-Q water, the hormone remaining adsorbed on the membrane desorbed into the permeate at a rate similar to the rate observed for adsorption. The feed solution concentration for the desorption phase of the Sterlitech GH experiment was 1.5 µg/L (not shown). Using the permeate flux and graphical integration of the desorption curve (following a procedure similar to that presented in Appendix F), the total amount desorbed can be calculated as at least 0.3 $\mu g/cm^2$ membrane area. However, the experiment was stopped before desorption was complete, and the total amount which could desorb is probably much

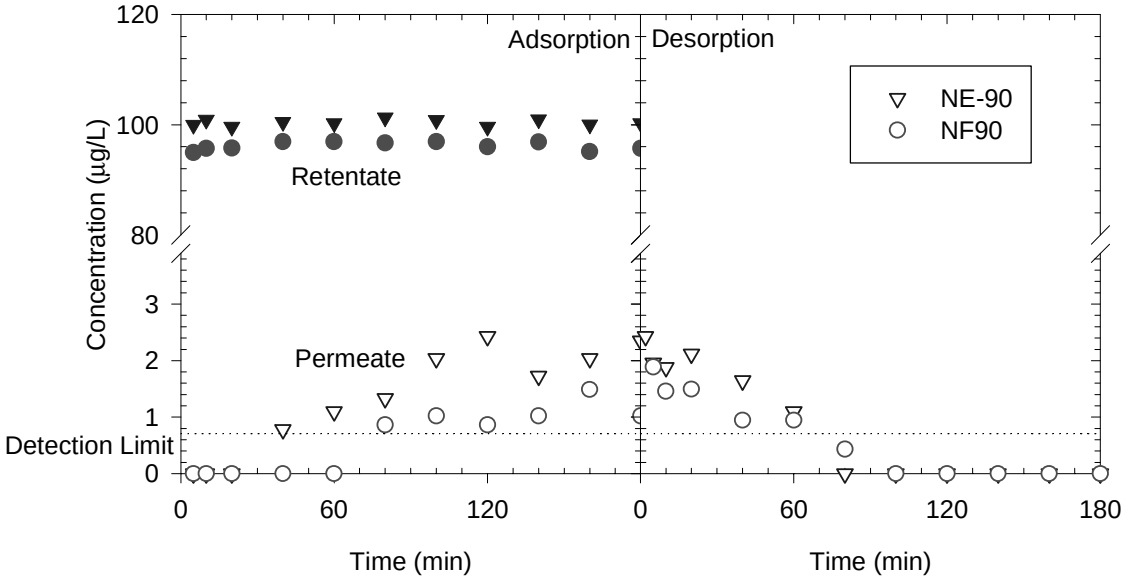
higher. Based on the observed decrease in feed concentration during the adsorption phase (following a procedure similar to that presented in Appendix D), it is estimated that a total of 1.1 $\mu g/cm^2$ membrane area of E2 was adsorbed. Solution pH was unadjusted during the second phase of all experiments (pure Milli-Q water pH approximately 5.5).

This result demonstrates that adsorption and desorption must be considered as dynamic processes in the removal of hormones by membrane processes. When the concentration of hormone in the feed solution is high, adsorption will dominate, and the permeate concentration will rise until an equilibrium between adsorption and desorption is achieved. If the concentration in the feed solution decreases, desorption will dominate, until a new equilibrium is reached. Hence, under continuous operation at varying feed concentrations, one would expect to see a delay of at least several hours between changes in feed concentration and the corresponding changes in permeate concentration. In cases where desorption dominates, membrane rejection, as traditionally defined, may actually be negative. In other words, it is possible for the permeate concentration to be temporarily higher than the feed concentration.

Unless there is significant adsorption of hormones to larger particles which can be more easily removed, UF membranes with MWCO greater than 1000 kDa are unlikely to remove large quantities of hormones when operated at steady-state. Because both UF membranes tested had a low steady-state rejection of E2, the remainder of the experiments focused on nanofiltration membranes.

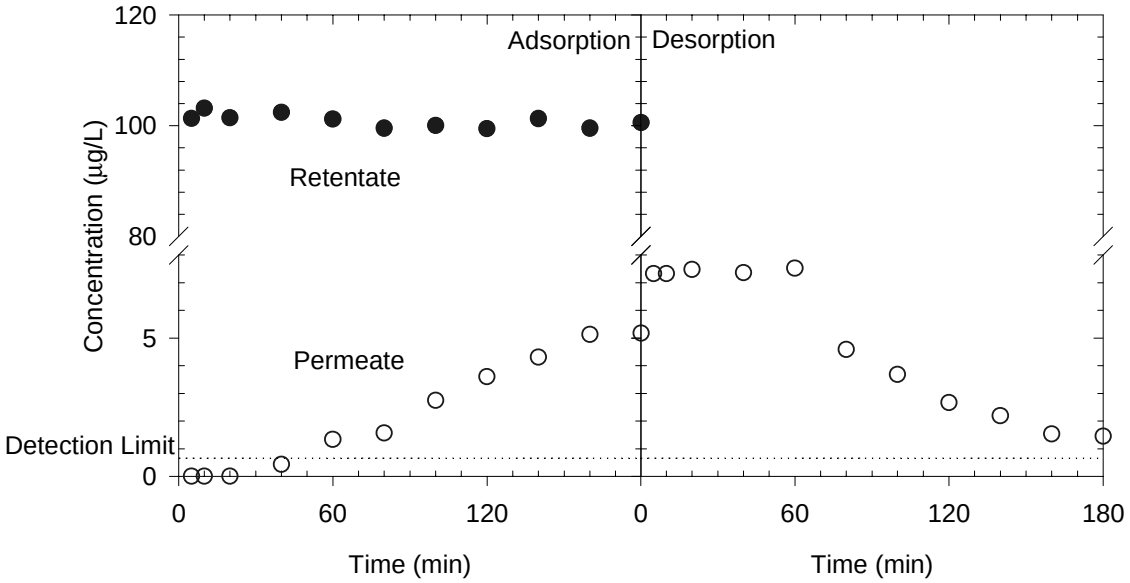
Tight NF Membranes (FilmTec NF90, Saehan NE-90, & Saehan NE-70)

Several of the nanofiltration membranes tested showed a very high rejection of E2. The FilmTec NF90 and the Saehan NE-90, both had a rejection of greater than 97% after 3 hours of operation (Figure 5). The Saehan NE-70 membrane also showed a high rejection of E2, greater than 90% after 3 hours (Figure 6). The scatter in these data is likely due to the fact that the permeate concentration was near the HPLC detection limit of 0.7 µg/L. Sample concentrations below detection limits are plotted as zero, although the true concentration is likely somewhere between zero and the detection limit. Similar adsorption and desorption phenomena were observed for these tight NF membranes as with other NF and UF membranes, however a much smaller amount was adsorbed than with the Sterlitech GH membrane. One feed sample was taken during the desorption phase of each NF experiment. Each of these samples was below the HPLC detection limit (< 0.7 µg/L).



Experimental Conditions: 100 µg/L E2 in 1mM phosphate buffer, pH 7, 25°C, pressure: 70 psi (NE-90) and 135 psi (NF90), cross-flow velocity: 0.4 m/s, permeate flux: 47 LMH (adsorption) and 54 LMH (desorption) (for NE-90), 66 LMH (adsorption) and 69 LMH (desorption) (for NF90), $MgSO_4$ Salt Rejection: 98% at 32 LMH, 70 psi (for NF90), 98% at 38 LMH, 70 psi (for NE-90)

FIGURE 5. High Rejection of E2 for Tight NF Membranes (Saehan NE-90 and FilmTec NF90) at High Feed Concentration

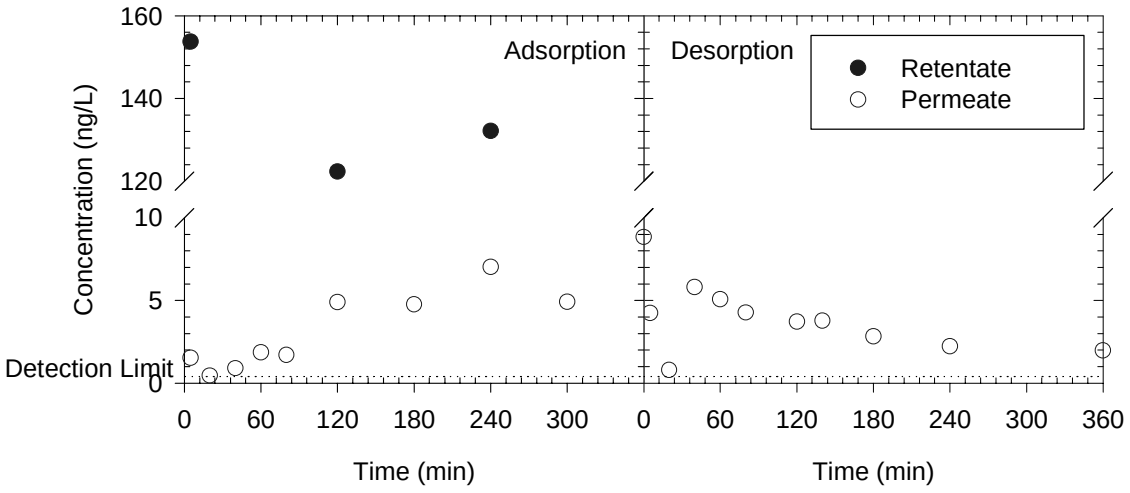


Experimental conditions: 100 µg/L E2 in 1mM phosphate buffer, pH 7, 25°C, pressure: 70 psi, cross-flow velocity: 0.4 m/s, permeate flux: 31 LMH (adsorption) and 34 LMH (desorption), MgSO4 Salt Rejection: 99.1 % at 23 LMH, 70 psi

FIGURE 6. High Rejection of E2 for Tight NF Membrane (Saehan NE-70) at High Feed Concentration

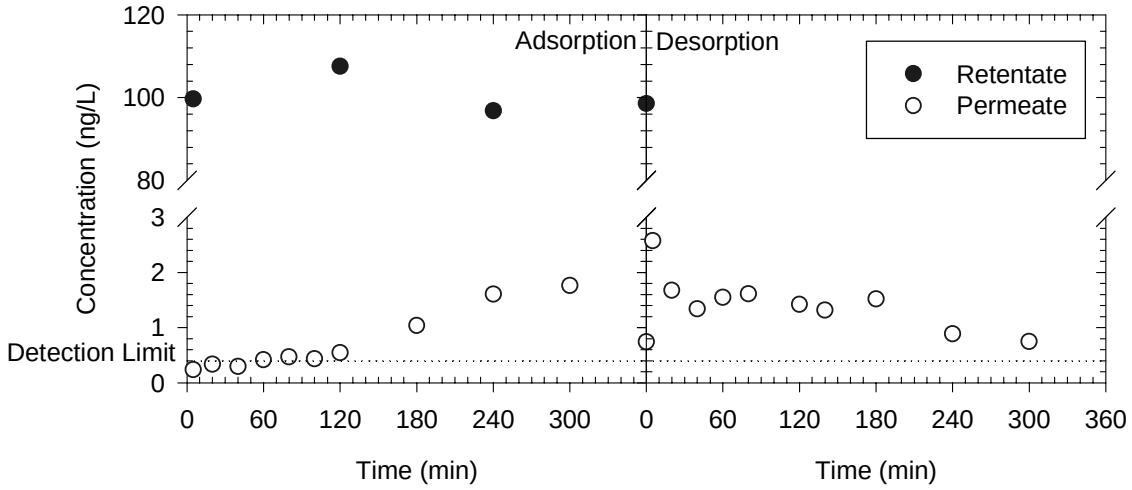
Two of these tight NF membranes, Saehan NE-90 and NE-70, were also tested at a much lower concentration of E2, in order to determine whether the results obtained under high feed concentrations are applicable to the lower concentrations typically encountered in treatment plants (Figures 7 & 8). The feed concentration in the low concentration experiments was a factor of 1000 lower than in the high concentration experiments, or 100 ng/L instead of 100 µg/L. This concentration of 100 ng/L is comparable to concentrations frequently reported for secondary wastewater effluent. Because the concentrations of these samples were far below the HPLC detection limit, SPE and ELISA were used for analysis. The percentage rejection observed after several hours of operation is similar to that observed for the high-concentration experiments. Analytical problems led to some data scatter, and the precise cause of these problems was

not determined. The scatter makes it difficult to determine whether the system has reached steady-state, but the permeate concentration clearly increases during the adsorption phase of the experiment and decreases during the desorption phase, as was observed for the high-concentration experiments. These results indicate that membrane performance at elevated feed concentrations should not be drastically different than those at much lower concentrations. For this reason, and because of the analytical difficulties associated with conducting experiments at low concentrations, most of the remaining experiments were conducted at elevated feed concentrations. Further experiments should be conducted at low feed concentrations to confirm this result and to determine whether changes in feed concentration affect the time required to reach steady-state. Experiments conducted by Ng et al. (2004) with a starting E2 concentration of 100 ng/L showed decreasing rejection even after 110 hours of operation, suggesting the possibility that adsorption kinetics at low concentrations may be very slow.



Experimental conditions: 100 ng/L E2 in 1 mM phosphate buffer, pH 7, 25°C, pressure: 70 psi, cross-flow velocity: 0.4 m/s, permeate flux: 35 LMH (adsorption) and 40 LMH (desorption), MgSO4 Salt Rejection: 98.4% at 30 LMH, 70 psi

FIGURE 7. High Rejection of E2 for Tight NF Membrane (Saehan NE-70) at Low Feed Concentration (Results Similar to High Concentration)

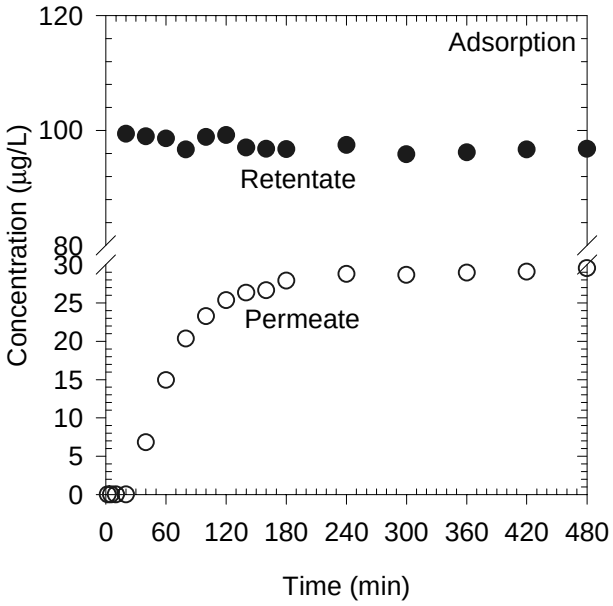


Experimental conditions: 100 ng/L E2 in 1 mM phosphate buffer, pH 7, 25°C, pressure: 70 psi, cross-flow velocity: 0.4 m/s, permeate flux: 44 LMH (adsorption) and 48 LMH (desorption), MgSO4 Salt Rejection: 99.4 % at 35 LMH, 70 psi

FIGURE 8. High Rejection of E2 for Tight NF Membrane (Saehan NE-90) at Low Feed Concentration (Results Similar to High Concentration)

Loose NF Membrane (FilmTec NF270): Initial Experiment

The FilmTec NF270 membrane was used for the remainder of the experiments because it showed a rejection of E2 that was intermediate between the tight NF membranes, which showed almost complete rejection, and the UF membranes, which showed almost no rejection. For the initial experiment, permeate and feed samples were collected over an eight-hour period (Figure 9) to determine the time required to reach the membrane's adsorptive capacity (steady state, or saturation). From this experiment, it was determined that steady state was reached after four hours of operation, and subsequent adsorption experiments were conducted over a four-hour time period.



Experimental conditions: 100 µg/L E2 in 1 mM phosphate buffer, pH 7, 25°C, pressure: 70 psi, cross-flow velocity: 0.13 m/s, permeate flux: not measured (estimate 70 LMH based on later experiments), MgSO4 Salt Rejection: 98.2% at 56 LMH, 69 psi

FIGURE 9. Moderate Rejection of E2 for Loose NF Membrane (FilmTec NF270)

The steady-state rejection of approximately 70% observed during this experiment was significantly lower than that observed for the same membrane during later experiments under similar conditions (80-85%). However, the salt rejection observed for this membrane coupon (~98.2%) was lower than that measured for later NF270 membrane coupons (generally >99%), and both the salt rejection and hormone experiment were conducted at a lower cross-flow velocity (0.13 m/s) than later experiments (0.40 m/s). A low level of hormone rejection would be expected for a membrane exhibiting a low level of salt rejection, and a low cross-flow velocity may lead to a low rejection of both salt and hormone. This is because a high cross-flow velocity may decrease the build-up of salt or hormone at the membrane surface (concentration polarization) which may in turn lead to a lower permeate concentration. The NF270

membrane had a significantly lower steady-state rejection than the other NF membranes (approximately 70-85% rejection for the NF270 as compared with >97% rejection for the NF90 and NE-90 and >90% for the NE-70). This is likely due to larger pores in the NF270 membrane, but it should also be noted that this membrane had the highest contact angle of the membranes tested, and may therefore be more hydrophobic and have a greater capacity for hydrophobic adsorption. Interestingly, this conflicts with the results of Nghiem et al. (2004b), who did not observe a difference in rejection between the NF270 and NF90 membranes.

Loose NF Membrane (FilmTec NF270): Quantification of amount adsorbed

Later experiments with NF270 membranes were replicated several times in order to quantify the amount of hormone adsorbed to, or desorbed from, membranes. The adsorptive capacity of the NF270 membrane was estimated by four methods, as described below. From each of these methods, the amount adsorbed or desorbed was estimated to be between 0.1-0.2 $\mu g/cm^2$ when operated under steady-state conditions at a feed concentration of 100 µg/L. While this amount is significant, it is considerably less than the total amount adsorbed to the Sterlitech GH membrane (>0.3 $\mu g/cm^2$) at a similar feed concentration.

The amount adsorbed to the membrane can be estimated by the decrease in feed concentration over the course of the 240-minute adsorption phase of each experiment. While the decrease in feed concentration observed for the FilmTec NF270 membrane is much smaller than that observed for the Sterlitech GH membrane, it is noticeable and consistent over several replicate experiments. Assuming that the decrease in feed

concentration is caused by adsorption to the membrane, a mass balance was performed to estimate the mass adsorbed per unit membrane area (calculations in Appendix D). The average decrease in feed concentration was approximately 1.6 µg/L. For a 14 L feed tank and 140 cm^2 active membrane area, this decrease in feed concentration corresponds to approximately 0.16 µg adsorbed per square centimeter of membrane area.

An alternative method of calculating the amount adsorbed to the membrane is by a graphical integration of the adsorption curve, as shown in Figure 10 (data and calculations in Appendix E). This method should give a reasonable estimate of the amount adsorbed if it is assumed that the permeate concentration at 240 minutes is the steady-state permeate concentration, and the difference between the permeate concentration at any point in time and the steady-state permeate concentration is due to hormone adsorption on the membrane. Besides adsorption, the only other reason for the initial permeate concentration to be lower than the steady-state permeate concentration is if the time required for mixing and transport of the hormone through the system is significant. In Appendix C it was demonstrated that this amount of time was small (less than 5 minutes). The decrease in feed concentration described above was neglected for this analysis because it was less than 2%. The calculated amount adsorbed by this procedure for three data sets is 0.08, 0.11, and 0.15 ug/cm^2 (average 0.11 ug/cm^2 membrane area.)

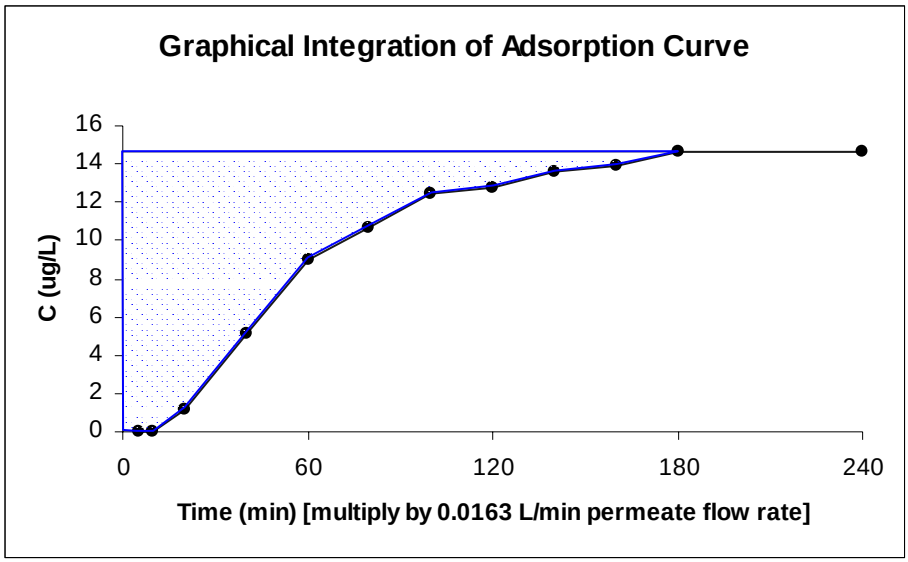


FIGURE 10. Estimation of Amount Adsorbed by Graphical Integration

The amount desorbed from the membrane can be calculated by a graphical integration method similar to the one used to calculate the amount adsorbed. It is assumed that when the feed solution is replaced with pure water, any E2 measured in the permeate is the result of desorption from the membrane. In Appendix B it is shown that the amount of E2 left in the permeate carrier and permeate tubing and the end of the adsorption phase of each experiment is insignificant compared with the total mass desorbed. The graphical integration procedure for estimating the total amount desorbed is presented in Figure 11 and Appendix F. From this procedure, conservative estimates for the amount desorbed are between 0.12, 0.14, and 0.17 ug/cm^2 (average 0.15 ug/cm^2 membrane area.)

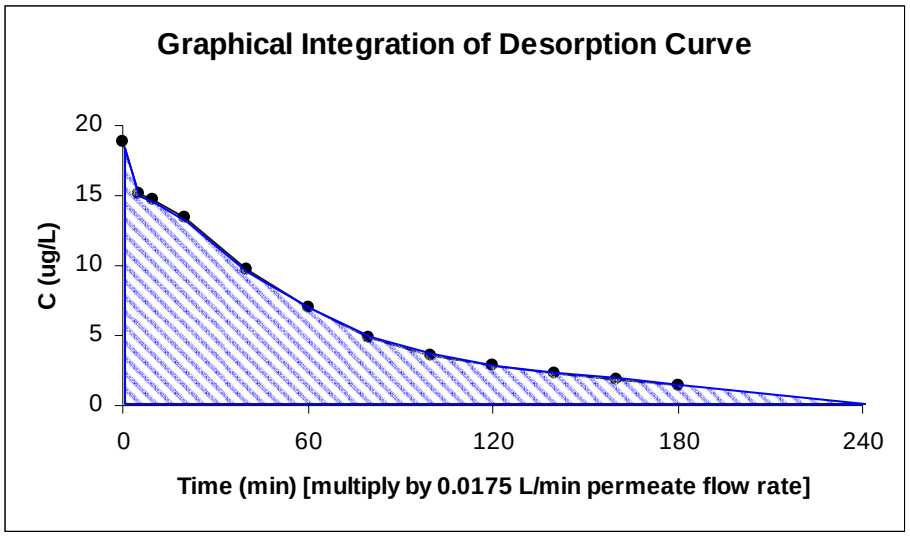


FIGURE 11. Estimation of Amount Desorbed by Graphical Integration

The amount of hormone adsorbed to the membrane during system operation was also compared to the amount desorbed from a saturated membrane in a batch experiment. For this experiment, the adsorption phase was performed on 6/3/2005 under conditions identical to the other replicate experiments. At the end of the adsorption phase the saturated membrane was removed from the cell, dipped in Milli-Q water for 1 second to rinse the hormone solution from the surface, and cut into four equal sections each with an active area of 35 cm^2. Two of these sections were stirred in methanol, one in pH 7 water, and one in pH 11 water. Each solution was 50 mL. Samples were collected at 20, 100, 450, and 2640 minutes from the start of the soaking procedure. Methanol samples were diluted with equal volume of H_2O before analysis, and measured concentrations of E2 in these samples were multiplied by 2 to determine the amount desorbed. The results of this experiment are presented in Table 3. The amount of E2 desorbed from each of the sections soaked in methanol was equivalent to 0.12 $\mu g/cm^2$ membrane area, which is in good agreement with the calculated amounts adsorbed and desorbed using the other three methods. More hormone was desorbed in the pH 11 water than the pH 7 water, but in

both cases the total amount desorbed was small. The total amount desorbed in pH 11 water may be higher than in pH 7 water because at this pH E2 is negatively charged. Charge repulsion between E2 molecules and the membrane may break some of the weak bonds holding E2 to the membrane, leading to greater desorption.

TABLE 3. Batch Desorption in pH7 water, pH 11 water, and Methanol (FilmTec NF270 Membrane, operated at 100 ug/L feed concentration)

pH 7 sample		
T(min)	C (µg/L)	(µg/cm^2)
20	1.3	0.0019
100	1.6	0.0023
450	2.3	0.0032
2640	5.0	0.0072

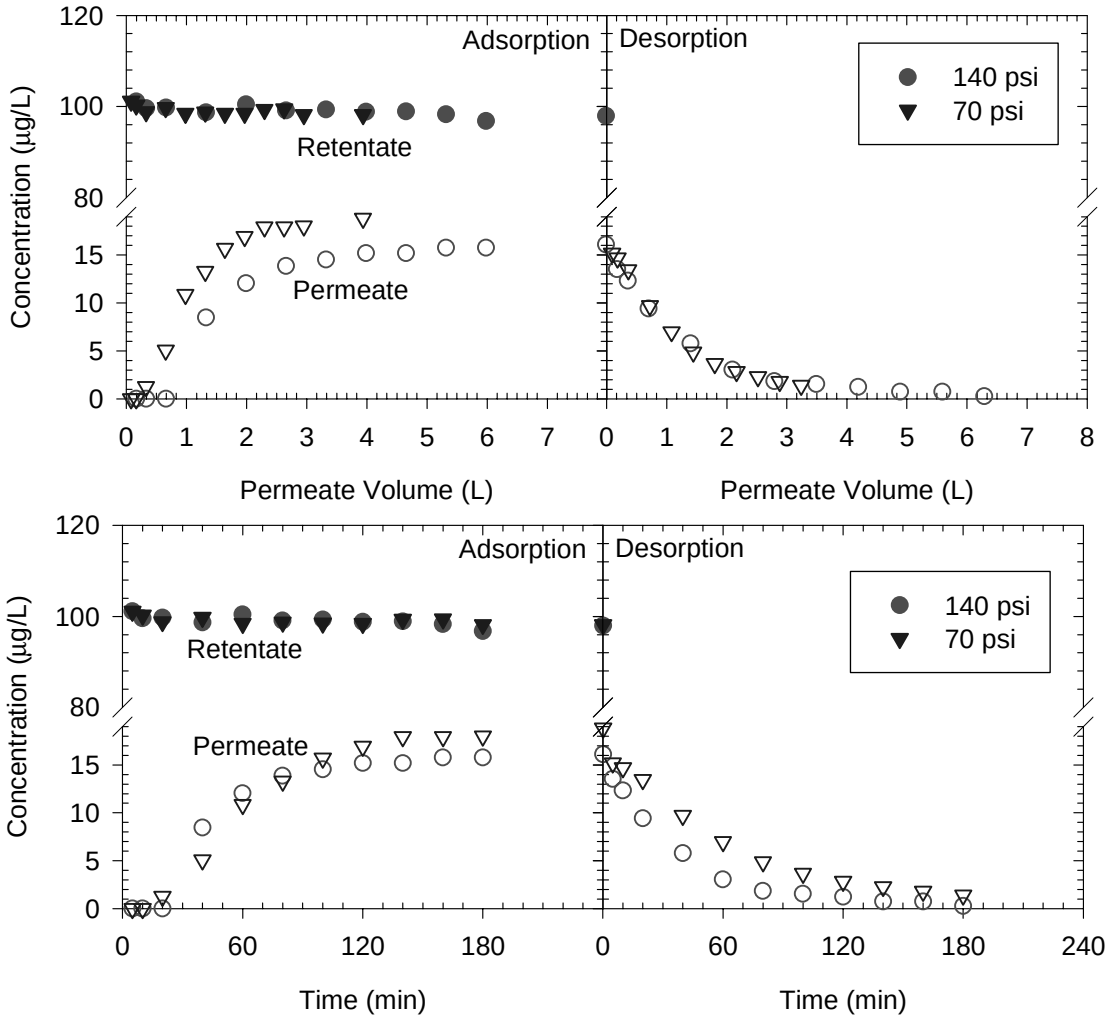
pH 11 sample		
T(min)	C (µg/L)	(µg/cm^2)
20	4.8	0.0068
100	11.6	0.0166
450	8.7	0.0125
2640	5.5	0.0078

Methanol sample #1		
T(min)	C (µg/L)	(µg/cm^2)
20	39.7	0.11
100	41.9	0.12
450	39.4	0.11
2640	41.5	0.12

Methanol sample #2		
T(min)	C (µg/L)	(µg/cm^2)
20	40.0	0.11
100	40.6	0.12
450	41.7	0.12
2640	44.0	0.13

Loose NF Membrane (FilmTec NF270): Variations in operating pressure

Experiments were conducted on the FilmTec NF270 membrane to determine the effect of changes in operating pressure on hormone rejection (Figure 12). Both graphs show the same data; the abscissa of the top graph is cumulative permeate volume rather than time to aid comparison. The data shown for 70 psi were obtained from the same membrane coupon as the data for 140 psi. The membrane was cleaned between experiments by operating the system with Milli-Q water for several hours.



Concentration as a function of: cumulative permeate volume (top) and time (bottom) Experimental conditions: 100 µg/L E2 in 1mM phosphate buffer, pH 7, 25°C, pressure: 140 psi and 70 psi, cross-flow velocity: 0.4 m/s, permeate flux: 133 LMH (adsorption) and 141 LMH (desorption) (at 140 psi), 70 LMH (adsorption) and 77 LMH (desorption) (at 70 psi), $MgSO_4$ Salt Rejection: 99% at 49 LMH, 70 psi

FIGURE 12. Effects of Variation in Operating Pressure for FilmTec NF270 Membrane

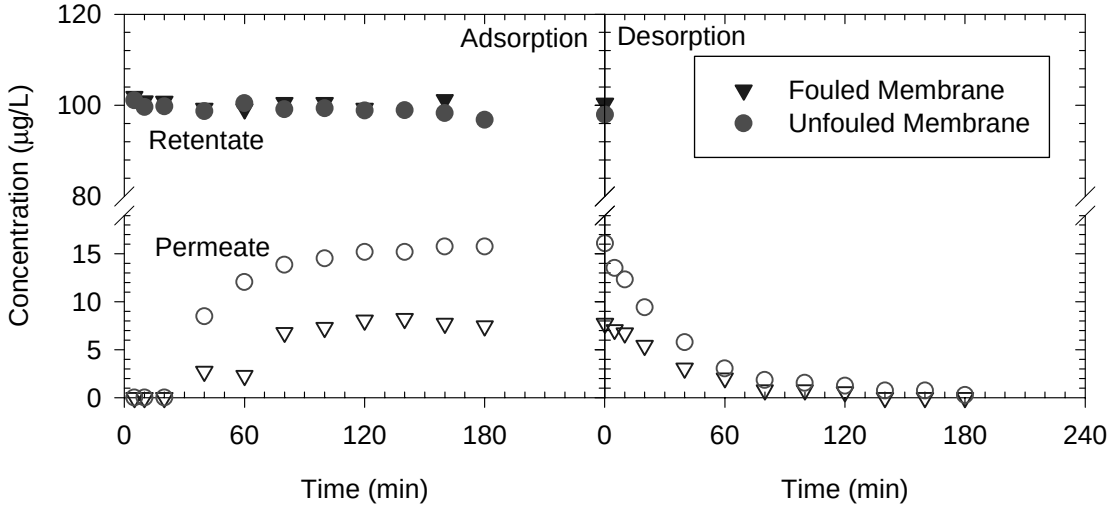
Steady-state rejection increased slightly with increased flux, which is consistent with a model presented by Nghiem et al. (2004a) for the removal of organic solutes by nanofiltration membranes. At higher flux, the membrane is saturated in less time, but saturation requires a greater volume. Diffusion of hormone from the interior of the membrane pore to the pore wall and the kinetics of hormone adsorption on the wall may

both limit the rate of adsorption. These processes may be somewhat affected by flux, but the relationship is not likely to be straightforward. Both of these limitations could explain why membrane saturation requires a greater permeate volume at higher flux. In the second phase of these experiments, hormone desorption from the membrane seemed to require the same volume of permeate regardless of flux. The fact that desorption would happen faster when the flux is higher seems intuitive, however, at this point it is unclear why the amount desorbed appears to be a simple function of permeate volume and the amount adsorbed is not. Further research is needed to confirm and better explain these results.

Loose NF Membrane (FilmTec NF270): NOM fouling of membrane

Another set of experiments was performed with the NF270 membrane to determine the effect of NOM fouling on hormone rejection (Figure 13). Both experiments shown were performed on the same membrane coupon on different days. An initial fouling solution of 10 mg/L Suwannee River Natural Organic Matter (SRNOM) in buffer solution only did not result in a noticeable decline in permeate flux (data not shown). This may be because the negatively-charged functional groups of the NOM do not easily adsorb to the negatively-charged membrane surface. Because the NOM alone did not result in noticeable flux decline, a 1 mM $CaCl_2$ solution was added to aid in bridging between the NOM and membrane surface and to enhance membrane fouling. The fouling procedure resulted in a 25% decline in permeate flux. However, it should be noted that much of this decline in flux can be attributed to the increased osmotic pressure caused by the $CaCl_2$ solution. After fouling, the steady-state hormone rejection increased,

presumably because of a decrease in the effective pore size of the membrane. Adsorption of E2 to the membrane also decreased, which may indicate that the fouled membrane has a decreased capacity for adsorption.



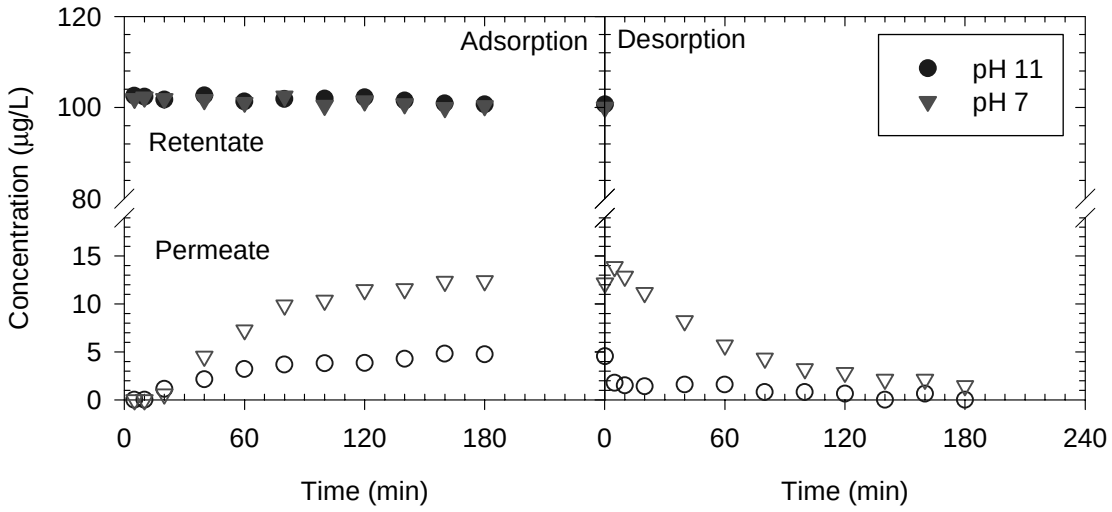
Experimental conditions: 100 µg/L E2 in 1 mM phosphate buffer, pH 7, 25°C, fouling solution also contained: 1 mM CaCl2, 10 mg/L SRNOM, pressure: 140 psi, cross-flow velocity: 0.4 m/s, permeate flux: 106 LMH (adsorption) and 142 LMH (desorption) (fouled membrane), 142 LMH (adsorption) and 150 LMH (desorption) (unfouled membrane), $MgSO_4$ Salt Rejection: 99% at 49 LMH, 70 psi

FIGURE 13. Increased E2 Rejection for NOM-Fouled NF270 Membrane

Loose NF Membrane (FilmTec NF270): pH Effect

Experiments were performed to determine the effect of increased pH on membrane performance. The pK_a of E2 is 10.4. At pH below this value, the neutral form of the molecule will predominate, while at pH above this value, the negatively-charged form will predominate. The negatively-charged molecule will likely behave differently than the neutral form, and for this reason, an elevated pH experiment was conducted at pH 11 (Figure 14). At elevated pH, the membrane showed a higher steady-state rejection of E2 and decreased adsorption, as compared with results at pH 7. This may be due to charge repulsion between the negatively-charged membrane surface and the negatively-

charged hormone molecules. The data shown for the pH 11 adsorption and desorption phases are from experiments performed on the same membrane coupon. The data shown for the pH 7 desorption are from experiments performed under the same conditions on a different membrane coupon. Solution pH was unadjusted during the desorption phase of all experiments (pure Milli-Q water pH approximately 5.5).



Experimental conditions: 100 µg/L E2 in 1 mM phosphate buffer, pH 7 or 11, 25°C, pressure: 70 psi, cross-flow velocity: 0.4 m/s, permeate flux: 78 LMH (adsorption) and 80 LMH (desorption) (pH 11), 71 LMH (adsorption), and 77 LMH (estimated) (desorption) (pH 7), $MgSO_4$ Salt Rejection: 99.5% at 55 LMH, 70 psi

FIGURE 14. Increased E2 Rejection for FilmTec NF270 Membrane at Elevated pH

Significance of Results

While the experimental conditions considered in this research are not identical to those in treatment plants, these results will help guide future research and provide a basis from which to estimate how some factors (i.e. concentration, flux, NOM, pH etc.) affect removal. Conducting experiments under conditions identical to those of treatment plants remains difficult for a number of reasons. Among these are analytical difficulties (time, cost, reliability, and accuracy of measurements in the low ng/L range), experimental

difficulties (large scale, long term), and the simple fact that surface water, STW effluent, and treatment conditions are all highly variable.

Although it has been well established that some compounds readily adsorb to membrane surfaces, the time-dependency of rejection is still frequently overlooked in studies considering contaminant removal by membranes. This can lead to a large overestimation of membrane performance, for example if only one initial sample was used to assess a UF membrane with low steady-state rejection and a high capacity for initial adsorption. It is understandable that experiments will be simplified to some extent when assessing a wide range of membranes and/or experimental conditions. Nonetheless, the results presented here reemphasize the fact that a consideration of adsorption and desorption is necessary in order to realistically assess performance.

In full-scale membrane treatment, concentrate disposal issues must be considered in addition to rejection. Membrane concentrates high in estrogenic substances may need to be subjected to additional treatment (for example ozonation) before disposal. A better understanding of sorption, biodegradation and the ultimate fate of these compounds will also help to guide decisions regarding concentrate disposal.

Although more research is needed to understand environmental and potential human health implications of EDCs, treatment alternatives (such as membranes) must be assessed simultaneously. Better information on both the effects of EDCs and methods of treatment will help to prioritize resources in the future and provide peace of mind to water consumers.

CHAPTER 5: CONCLUSION

NF and UF membranes were tested for removal of the natural hormone 17β-Estradiol under a range of conditions. Significant adsorption of hormones to the membrane was observed under all conditions, resulting in a high level of rejection during the initial phase of filtration. UF membranes tested showed little to no steady-state rejection, while the NF membranes generally showed high rejection (70% to >97%) at steady state. Permeate hormone concentrations increased with continued operation until an equilibrium between adsorption and desorption was achieved, resulting in a breakthrough curve similar to that observed with granular activated carbon columns. When saturated membranes were operated with a feed solution of pure Milli-Q water the adsorbed hormone was gradually released into the permeate stream, resulting in a temporary negative rejection. Rates of adsorption were similar to those observed for desorption, and good agreement was obtained for estimating the total amount adsorbed and desorbed by four methods. Experiments conducted at low (100 ng/L) concentrations indicated performance similar to that observed at high (100 µg/L) concentrations, though further work is needed to verify this result. Operation at increased pressure and permeate flux resulted in increased rejection, although this result should also be verified. NOM fouling of the membrane and operation at elevated pH resulted in increased rejection and decreased adsorption. Development of a dynamic model which includes adsorption and desorption to the membrane would help to better understand removal and predict membrane performance. Additional experiments should be conducted in more realistic water matrices at low concentrations of hormone. Several researchers have reported

incomplete rejection of hormones by RO membranes (Ng et al., 2004; Kimura et al., 2004), so RO membranes should also be considered in future research.

APPENDIX A: MEMBRANE CHARACTERISTICS

All data from tests performed by Saehan Industries, Inc.

Zeta Potential: Calculated by Streaming Potential Measurements

NE-90

Electrolyte: 0.3mM NaCl	
pH	Zeta Pot. (mV)
4.75	-3.5
4.77	-3.9
3.96	-2.6
3.98	-2.6
5.96	-5.5
5.96	-5.0
7.97	-5.9
7.97	-5.3
9.15	-8.3
9.16	-7.2

Electrolyte: 1.5mM NaCl	
pH	Zeta Pot. (mV)
5.01	-12.7
5.02	-11.2
4.02	-8.0
4.04	-6.5
5.69	-15.4
5.69	-12.3
7.49	-16.0
7.47	-13.5
9.41	-14.8
9.41	-13.4

Electrolyte: 3.0mM NaCl	
pH	Zeta Pot. (mV)
5.14	-17.1
5.13	-15.4
4.16	-10.7
4.16	-10.3
5.76	-20.9
5.77	-16.7
7.23	-20.3
7.20	-17.6
9.54	-19.1
9.53	-17.0

NE-70

Electrolyte: 0.3mM NaCl	
pH	Zeta Pot. (mV)
5.15	-9.2
5.08	-10.1
4.07	-9.3
4.09	-9.4
6.17	-13.8
6.17	-14.1
8.02	-14.9
8.02	-15.2
9.25	-17.9
9.27	-17.9

Electrolyte: 1.5mM NaCl	
pH	Zeta Pot. (mV)
5.23	-24
5.24	-23.9
4.14	-18.4
4.16	-19.6
5.88	-24.6
5.88	-25.1
7.6	-24.8
7.56	-25
9.46	-23.9
9.47	-25.5

Electrolyte: 3.0mM NaCl	
pH	Zeta Pot. (mV)
5.18	-26.8
5.18	-28.2
4.24	-20.7
4.24	-22.6
5.77	-25.9
5.77	-28.3
6.82	-26.1
6.8	-28.2
9.5	-23
9.5	-26.8

NF-90

Electrolyte: 0.3mM NaCl	
pH	Zeta Pot. (mV)
5.31	-3.8
5.34	-4.7
4.37	-2.7
4.4	-3.6
6.43	-6.1
6.43	-7.4
8.06	-7.7
8.07	-9.3
9.28	-10.8
9.29	-13

Electrolyte: 1.5mM NaCl	
pH	Zeta Pot. (mV)
5.22	-10.8
5.22	-12.4
4.15	-2.8
4.16	-4.8
5.95	-12.9
5.96	-14.3
7.81	-16.4
7.79	-18.2
9.43	-17.5
9.44	-20.2

Electrolyte: 3.0mM NaCl	
pH	Zeta Pot. (mV)
5.24	-10.9
5.25	-12.6
4.22	-2.7
4.23	-4.7
5.98	-13.6
5.98	-15.1
7.68	-17.6
7.65	-18.9
9.53	-18.6
9.54	-21.4

NF-270

Electrolyte: 0.3mM NaCl	
pH	Zeta Pot. (mV)
5.13	-8.7
5.15	-10.6
4.27	-6.4
4.29	-8.5
6.16	-11.8
6.17	-13.5
8.1	-14.8
8.11	-16.6
9.48	-19.9
9.51	-21.9

Electrolyte: 1.5mM NaCl	
pH	Zeta Pot. (mV)
5.33	-21
5.34	-24.2
4.27	-12.6
4.28	-15.8
6.14	-22.2
6.14	-26.8
8.19	-26.4
8.17	-30.2
9.62	-28.5
9.62	-33.2

Electrolyte: 3.0mM NaCl	
pH	Zeta Pot. (mV)
5.43	-22.7
5.44	-26.3
4.36	-13.8
4.37	-17.4
6.13	-23.6
6.14	-27.5
7.91	-27.3
7.9	-30.9
9.63	-28.6
9.63	-34

Contact Angle, Sessile Drop Method:

	NE-90	NE-70	NF90	NF270
1	59.7	33.2	93.7	33.5
2	59.4	41.2	80.8	25.7
3	62	47.5	69.6	30.5
4	58	45.4	74.1	37.5
5	54.2	56.2	80	30.2
6	66.5	41	70.8	28.8
7	62.2	51.7	76.9	34.1
8	61	45.2	73	32.1
9	66	43.1	77.8	27.2
10	54.7	37.8	75.6	35.2
average	60.4	44.2	77.2	31.5

APPENDIX B: HORMONE REMAINING IN PERMEATE

The total mass desorbed from each membrane can be estimated by graphical integration. This mass can then be compared to the mass remaining in the permeate carrier and tubing following the adsorption phase:

For a typical FilmTec NF270 membrane at 140 psi and 100 µg/L feed concentration, the permeate flow rate is 0.55 mL/s, and the steady-state permeate concentration of E2 is 10µg/L. By graphical integration of the desorption curve, the total desorbed mass is approximately 20 µg.

The volume of water between the membrane and the end of the permeate tubing can be estimated as follows:

Permeate tubing: 50 inches × 1/8 inch O.D. × 0.028 inch wall thickness.

V in tubing = length$(1/4)(\pi)(r^2)$= $50 \times 0.25 \times \pi \times (1/8 - 2 \times 0.028)^2 = 0.187$ $in^3 = 3$ mL

V in permeate carrier = thickness × area = 0.03 cm × 287 cm^2 = 8.6 mL (this should be an over-estimate because the permeate carrier itself takes up some space)

V in permeate collection channel = 5 mL (estimated by filling with water and draining)

Total volume = 3 + 9 + 5 mL = 17 mL

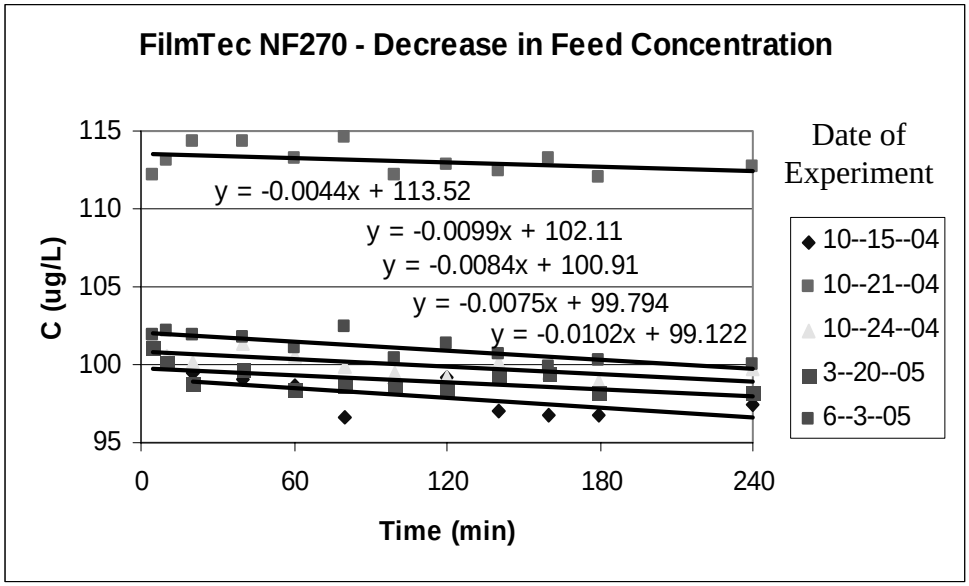
For a typical steady-state E2 permeate concentration of 10 µg/L, the mass remaining in this space at the end of the adsorption phase is 0.017 L × 10 µg/L = 0.17 µg. This is less than 1% of the total mass desorbed and was assumed to be insignificant.

APPENDIX C: NACl TRACER TEST

Experiment was conducted to determine the amount of time required for a non-adsorbing tracer to reach the permeate sampling point after spiking the feed tank. Results indicate that the tracer reached the permeate sampling point in less than 5 minutes. Therefore, the amount of time required for mixing/passage of solution through tubing is small and can be neglected.

14 L feed tank was spiked to 1 mM NaCl concentration. Conductivity was measured to estimate NaCl concentration. Because conductivity measurements require a relatively large sample volume, each sample was taken over a 4 minute time interval (2 minutes before and 2 minutes after the nominal sample time).
Feed solution before spiking NaCl: < 1 µS/cm
Permeate solution before spiking NaCl: < 1 µS/cm
Feed solution after spiking NaCl: 111 µS/cm
Permeate solution at 5 min: 19.0 µS/cm
10 min: 19.4 µS/cm
15 min: 19.3 µS/cm
20 min: 19.8 µS/cm
The same procedure typically used for hormone desorption was used and the system was restarted. Permeate samples were collected as described above.
Permeate solution at 5 min: 1.59 µS/cm
10 min: 1.05 µS/cm
15 min: < 1 µS/cm
20 min: < 1 µS/cm
The experiment was performed under the following conditions:
FilmTec NF270 membrane, unadjusted pH (~5.5), temperature 25.5°C, 70 psi
Permeate flux: 78 LMH (before addition of NaCl)

APPENDIX D: ESTIMATION OF AMOUNT ADSORBED BY DECREASE IN FEED CONCENTRATION



Shown above is a plot of the decrease in feed concentration for five replicate experiments, with a linear trend line through each data set. The small amount of scatter observed for these data points is rather large when compared with the total decrease in feed concentration. The trend lines are shown only to indicate that the decrease in feed concentration is reasonably consistent over replicate experiments, and are not intended to represent the actual data, which is unlikely to be a linear function. The actual decrease in feed concentration may be estimated by subtracting the last data point from the first data point for each data set. Because of the scatter in data, a conservative, but possibly more accurate, estimate could be obtained by subtracting the average of the last two data points from the average of the first two data points. Similarly, the average of the last three data points could be subtracted from the average of the first three data points, and so on. A decrease of 1.5-1.7 µg/L was obtained for averages of four or less data points across the five data sets.

APPENDIX D: ESTIMATION OF AMOUNT ADSORBED BY DECREASE IN FEED CONCENTRATION (CONTINUED)

Raw Data:

Date	10/15/2004	10/21/2004	10/24/2004	3/20/2005	6/3/2005
Time (min)	Feed (µg/L)	Feed (µg/L)	Feed (µg/L)	Feed (µg/L)	Feed (µg/L)
5	NA	112.1	101.8	101.1	101.9
10	NA	113.1	100.6	100.2	102.2
20	99.4	114.3	100.2	98.8	101.9
40	99	114.3	101.4	99.7	101.7
60	98.6	113.2	100.5	98.4	101.1
80	96.6	114.6	99.8	98.7	102.4
100	98.8	112.2	99.5	98.5	100.4
120	99.2	112.8	99.2	98.4	101.4
140	97.0	112.5	100.1	99.3	100.7
160	96.8	113.3	99.5	99.4	99.9
180	96.7	112	98.9	98.2	100.3
240	97.5	112.7	99.7	98.2	100.0

Calculation of decrease in feed concentration:

	10/15/2004*	10/21/2004	10/24/2004	3/20/2005	6/3/2005	Decrease (ug/L)
1st minus last	1.90	-0.60	2.10	2.90	1.90	1.64
1st 2 - last 2	2.65	-0.10	1.50	2.45	2.05	1.71
1st 3 - last 3	2.40	0.50	1.50	1.43	1.93	1.55
1st 4 - last 4	2.30	0.83	1.45	1.18	1.70	1.49
1st 5 - last 5	1.72	0.74	1.42	0.94	1.30	1.22
1st 6 - last 6	1.07	1.02	1.23	0.82	1.42	1.11

*assume 5&10 minute samples = 20 minute sample

APPENDIX E: ESTIMATION OF AMOUNT ADSORBED BY INTEGRATION OF ADSORPTION CURVE

Raw Data:

Date	10/15/2004	10/21/2004	10/24/2004	3/20/2005	6/3/2005
Time (min)	Perm (µg/L)	Perm (µg/L)	Perm (µg/L)	Perm (µg/L)	Perm (µg/L)
0	< DL	< DL	< DL	< DL	< DL
5	< DL	< DL	< DL	< DL	< DL
10	< DL	< DL	< DL	< DL	< DL
20	< DL	1.3	1.2	1.2	< DL
40	6.8	5.4	5.1	5.1	4.5
60	14.9	10.4	9.0	10.9	7.3
80	20.3	13.8	10.7	13.3	9.8
100	23.2	16.1	12.4	15.7	10.4
120	25.3	17.3	12.8	16.9	11.5
140	26.3	19.0	13.6	17.9	11.6
160	26.6	19.0	13.9	17.9	12.3
180	27.9	19.2	14.6	18.0	12.4
240	28.8	20.2	14.6	18.8	12.2

*< DL = below detection limit

Use a permeate flux of 70 LMH (typical) to calculate the amount adsorbed. This corresponds to a permeate flow rate of 0.0163 L/min. “Permeate volume” is the incremental time (5, 10, 20 or 60 minutes) multiplied by the permeate flow rate. “E2 adsorbed” is the “permeate volume” multiplied by the difference between the 240 minute permeate concentration and the average of the two permeate concentrations corresponding to each “permeate volume”.

The adsorbed amount calculated for the experiment conducted on 10/15/2004 is much higher than the others, possibly because this experiment was conducted at a lower cross-flow velocity and the membrane showed a lower salt rejection, as described previously. The amount calculated for the experiment conducted on 10/21/05 may also be an overestimation, because the concentration of E2 in the feed solution was 113 µg/L rather than 100 µg/L. Averaging the amount calculated from the remaining three experiments gives approximately 0.11 µg adsorbed per square centimeter of membrane area.

APPENDIX E: ESTIMATION OF AMOUNT ADSORBED BY INTEGRATION OF ADSORPTION CURVE (CONTINUED)

Results:

Perm.	10/15/2004	10/21/2004	10/24/2004	3/20/2005	6/3/2005
V (L)	E2 ads (µg)	E2 ads (µg)	E2 ads (µg)	E2 ads (µg)	E2 ads (µg)
0.082	2.35	1.65	1.19	1.54	1.00
0.082	2.35	1.65	1.19	1.54	1.00
0.163	4.70	3.19	2.29	2.97	1.94
0.327	8.30	5.50	3.74	5.11	3.15
0.327	5.86	4.02	2.47	3.53	2.06
0.327	3.66	2.65	1.55	2.19	1.19
0.327	2.30	1.71	1.00	1.40	0.69
0.327	1.49	1.14	0.65	0.82	0.41
0.327	0.98	0.67	0.46	0.46	0.21
0.327	0.77	0.39	0.28	0.29	0.08
0.327	0.51	0.36	0.11	0.28	-0.05
0.980	0.44	0.49	0.00	0.39	-0.10
	Total (µg)	Total (µg)	Total (µg)	Total (µg)	Total (µg)
	33.71	23.43	14.93	20.51	11.58
	(µg/cm^2)	(µg/cm^2)	(µg/cm^2)	(µg/cm^2)	(µg/cm^2)
	0.24	0.17	0.11	0.15	0.08

APPENDIX F: ESTIMATION OF AMOUNT DESORBED BY INTEGRATION OF DESORPTION CURVE

Raw Data:

Date	10/22/2004	10/26/2005	3/20/2005
Time (min)	Perm (µg/L)	Perm (µg/L)	Perm (µg/L)
0*	20.2	14.6	18.8
5	16.7	13.9	15.2
10	17.1	12.9	14.7
20	14.6	11.1	13.4
40	10.4	8.2	9.7
60	8.2	5.7	7
80	5.9	4.3	4.8
100	4.9	3.2	3.6
120	3.8	2.8	2.8
140	2.7	2.1	2.3
160	2.5	2.1	1.8
180	2	1.5	1.4
240**	0	0	0

*Time = 0 minutes is the last sample from the adsorption phase

**Concentration of 0 µg/L at Time = 240 minutes is a conservative estimate. The actual concentration will typically be higher, but is frequently below the HPLC detection limit.

Use a permeate flux of 75 LMH (typical) to calculate the amount desorbed. This corresponds to a permeate flow rate of 0.0175 L/min. “Permeate volume” is the incremental time (5, 10, 20 or 60 minutes) multiplied by the permeate flow rate. “E2 desorbed” is the “permeate volume” multiplied by the average of the two permeate concentrations corresponding to each “permeate volume”.

APPENDIX F: ESTIMATION OF AMOUNT DESORBED BY INTEGRATION OF DESORPTION CURVE (CONTINUED)

Results:

Perm.	10/22/2004	10/26/2005	3/20/2005
V (L)	E2 des (µg)	E2 des (µg)	E2 des (µg)
0.088	1.61	1.25	1.49
0.088	1.48	1.17	1.31
0.175	2.77	2.10	2.46
0.350	4.38	3.38	4.04
0.350	3.26	2.43	2.92
0.350	2.47	1.75	2.07
0.350	1.89	1.31	1.47
0.350	1.52	1.05	1.12
0.350	1.14	0.86	0.89
0.350	0.91	0.74	0.72
0.350	0.79	0.63	0.56
1.050	1.05	0.79	0.74
	Total (µg)	Total (µg)	Total (µg)
	23.26	17.45	19.78
	(µg/cm^2)	(µg/cm^2)	(µg/cm^2)
	0.17	0.12	0.14

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