Despites their low concentration, the impact of steroid estrogens such as estrone, 17β-estradiol and ethinylestradiol are often more serious than other synthetic endocrine-disrupting chemicals (EDCs) since their endocrine-disrupting potency is much higher. While their existence in waterways is of increasing concern, nanofiltration (NF) and reverse osmosis (RO) are likely to play an important role in removal of these compounds. This paper describes the mechanisms involved in the retention of estrogen estrone using NF and RO.

NF/RO membranes may adsorb trace contaminant estrone, which may result in an initially high retention. If the pore size of the membranes is larger than the estrone molecules, breakthrough can be observed when the membrane adsorptive sites are saturated. Although there is negligible effect of ionic strength on estrone adsorption by the membrane, it is strongly influenced by pH near the pKa value of estrone (10.4). While static adsorption experiments give a linear adsorption isotherm, higher estrone adsorption in the filtration process with a large pore size membrane (TFC-SR2) suggests that adsorption can also occur inside the membrane active layer.

Depending on the pore size to molecule size ratio, the transport of trace organics across the membrane active layer can be described as diffusive and/or convective. A modified diffusion model is proposed to assess the degree of diffusive to convective transport of trace contaminant estrone across the membrane.

**Keywords**

Endocrine disrupters, hormones, nanofiltration, reverse osmosis, adsorption, water and wastewater treatment.
INTRODUCTION

The effects of endocrine-disrupting chemicals (EDCs) on both humans and the environment are of increasing concern. The European Commission (1996) has defined an EDC as “an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to endocrine function”. Over the last few years, intensive attempts have been made to study a wide variety of effects that has been attributed to EDCs. A multitude of environmental effects already observed include increase vitellogenin levels, which is used as a bio-indicator of femininity in fish, in male and juvenile female fish in and immediately downstream of the sewage effluent discharge points (Jobling et al., 1998; Purdom et al., 1994; Harries et al., 1997) and declining fertility in young alligators due to endocrine modulator DDT (Piva and Martini, 1998). Most recent studies by many researchers have confirmed the impacts of EDCs on trout at the common concentration encountered in sewage effluent (Rodgers-Gray et al., 2001; and Thorpe et al., 2001).

Amongst a vast number of EDCs the impacts of steroid estrogens such as estrone, 17β-estradiol (natural hormones) and 17α-ethinylestradiol (a synthetic hormone, the main component of the contraceptive pill) are prominent as they have far higher endocrine-disrupting potency than most synthetic EDCs. Estrone and 17β-estradiol are mainly produced in the ovary and during pregnancy in the placenta. They control the development of the secondary female sex characteristics in women and together with the gestagens, control the reproductive process (Turán, 1995). Being excreted by humans, such steroid estrogens are ubiquitous in aquatic environments receiving sewage effluent. They were frequently detected in Canadian and German sewage treatment plants (STP) discharge effluent within the lower ngL⁻¹ range. Estrone concentration of up to 70 ngL⁻¹ in STP effluent was also reported (Ternes et al., 1999). The performance of conventional wastewater treatment plants with regards to removal of steroid estrogens varies greatly and, in consequence, concentrations of some steroid estrogens in secondary effluent often remain high enough to harm wildlife such as fish in particular (Johnson and Stumpf, 2001). Dose response curves are to date largely unknown and so are effects on humans.

In spite of the magnitude of this problem, research on the removal of EDCs in water and wastewater has been limited to date due to their relatively low concentration and the associated analytical difficulties. This is particularly true for steroid estrogens as only at a few ng/L, 17β-estradiol may cause distinctive effects on fish (Purdom et al., 1994). The accumulation of synthetic and natural hormones in the environment is largely unknown. Given the seriousness of possible effects (fertility, development, behaviour) the understanding of removal of such contaminants in water and wastewater is of utmost importance for water and wastewater treatment.

Membrane processes have been widely accepted of being able to comply with more stringent requirements in water and wastewater treatment. Given the potential impacts of EDCs such as estrone and 17β-estradiol, and inadequate and inconsistent performance of conventional wastewater treatment in regard to such compounds, nanofiltration (NF) and reverse osmosis (RO) are likely to play an important role in the removal of EDCs. Retention of trace organics by NF/RO membranes has been the subject of considerable research (Chian et al., 1975; Bauer et al., 1987; Duranconau et al., 1997; Berg et al., 1997; Kiso et al., 2001; Schäfer et al., 2001). Depending on their affinity to the membrane material, retention of trace organics by NF/RO membranes can be governed by a complex fashion according to the chemistry of the solute-membrane interactions. In such circumstances, molecular weight of organic solutes and salt retention of the membranes may be a poor predictor of the retention (Wiesner and Buckley, 1996; Schäfer et al., 2001).

It has been reported that NF/RO processes are capable of removing trace organics including a wide range of pesticides, synthetic organic compounds and natural hormones (Chian et al., 1975; Duranconau et al., 1997; Berg et al., 1997; Kiso et al., 2000; Kiso et al., 2001; Schäfer et al., 2001). In our previous work, removal of the trace contaminant estrone and 17β-estradiol using eight different nanofiltration and reverse osmosis membranes has been studied. It was found that some membranes could adsorb such trace organics and may subsequently give an impression of high retention (Ngheim et al., accepted). Retention behaviour of such trace organics is often explained by the solution diffusion model (Wiesner and Buckley, 1996). According to this model, solute transport across the membrane is a two step process: firstly, the solute is adsorbed or dissolved by the membrane; secondly, it migrates across the membrane by diffusion or convection. Molecular characteristics such as water solubility, hydrogen bonding, acidity and branching can affect both the adsorption and the migration processes (Reinhard et al., 1986). Jones and O'Melia (2000) developed a rate model to investigate the adsorption of macromolecules, bovine serum albumin (BSA) and human IgG, on NF/RO membranes. This model also suggests a two stage process which is diffusion of the organics to the proximity of the membranes followed by adsorption on the membrane surface. Being large macro-molecules, it is anticipated that BSA and large humic acid molecules are rejected by UF membranes mostly due to size exclusion and adsorption of such compounds can only occur on the membrane surface. On the other hand, steroid estrogens are much smaller; thus, penetration of these compounds into the pores of NF and even some RO membranes may be possible. Consequently, physico-chemical interactions between the membrane polymer and steroid estrogens are likely to play an important role in governing the adsorption process. While in the study by Jones and O'Melia adsorption of BSA was induced by hydrophobic interaction, steroid estrogens adsorption on NF/RO membranes may be mainly governed by specific interactions such as hydrogen bonding.

This paper investigates the adsorptive behavior of the natural hormone estrone on eight different NF and RO membranes in an attempt to establish a relationship between adsorption, pore size and retention of the membranes and the removal of the trace contaminant estrone. Given the seriousness of the problem and the variability of the conditions in which the membranes are used, a range of different possible interactions between the estrogens and the membrane polymer under various pH and ionic strength values of the feed solution and their effects on estrone adsorption by the membranes were examined. A modified diffusion model developed by Jones and O'Melia (2000) was adapted to depict the diffusive/convective transport of estrone across the membranes in order to gain further understanding of the estrone retention mechanisms by NF/RO membranes.

Materials and Methods

Membranes

Eight commercially available membranes were selected for this study, namely TFC-S, TFC-ULP, TFC-SR1, and TFC-SR2 supplied by Koch Membrane Systems (San Diego, USA) and X-20, ACM-4, TS-80, and XN-40 supplied by Trisper Corporation (Goleta, USA). Membrane types, materials, pure water fluxes at 5 bar and membrane resistances are summarised in Table 1. It has been shown in our previous work that all membranes are negatively charged near pH neutral (Schäfer et al., submitted).

Filtration System and Protocol

Filtration experiments were carried out in a 185 mL stainless steel stirred cell. Details of the filtration system were described elsewhere (Schäfer et al., 2001). The inner diameter was 56.6 mm resulting in a membrane surface area of 21.2 cm². An Amicon magnetic

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Stirrer was used and the stirrer speed was set at 400 rpm to minimize concentration polarisation effects. Instrument grade air was used to pressurize the stirred cell. The membranes were gently washed using MilliQ water to remove the protective coating and a new membrane was used for each experiment. Three membranes with varying retentions were selected.

Each experiment was conducted in three steps. The membranes were compacted for 1 hour using MilliQ water at 10 bar. Pure water flux was then determined at 5 bar. In the third step, the reservoir was emptied and the cell filled with the test solution. The solution was filtered at 5 bar or 10 bar for Koch (TF-SR2 and TFC-S) and Trisep (X-20) membranes respectively, to obtain comparable flux values. Unless otherwise stated, six permeate samples of 20 mL each were collected from the filtration of a feed volume of 185 mL. Feed and concentrate samples were also collected for analysis.

**Static Adsorption Experiments**

Adsorption experiments were performed in an automatic incubator shaker (Bioline, Edwards Instrument Company, Australia). A membrane area of 21.2 cm² was gently washed using MilliQ water as for filtration experiment. Since estrone can approach the membrane from both sides, double the membrane area (42.4 cm²) was used for calculation. The support layer was neglected for adsorption as it cannot form hydrogen bonds. The membrane was then cut into small pieces and placed in a conical flask. 50 mL of test solution containing 1 mM NaHCO₃, 20 mM NaCl at pH 8.0 and the required concentration of estrone was introduced to the flask. The flask was immediately placed into the shaker and 1 mL of sample was taken for every measurement as the experiment progressed. The flask was covered with nylon film to avoid evaporation and shaken at 100 rpm to ensure a homogeneous solution. A temperature of 25 °C was maintained throughout the experiment.

**Solution Chemistry and Chemicals**

All chemicals were of analytical grade. Radiolabelled estrone-2,4,6,7-³H(N) was purchased from Sigma Aldrich (Saint Louis, Missouri, USA). The background electrolyte consisted of 1 mM NaHCO₃, and 20 mM NaCl. pH was adjusted using 1M HCl or 1M NaOH.

**Natural Hormone Characteristics and Analysis**

Estrone has a very low solubility in water (Merck, 1996) with a molecular weight of 270 g/mol. Diameter of the equivalent sphere of the molecule is estimated to be about 0.8 nm using the Stokes-Einstein equation. The acid dissociation constant, pKa, of estrone is 10.4 (Schäfer et al., submitted). Hydroxyl and carbonyl functional groups of estrone can facilitate the formation of hydrogen bonding between the molecule and the membrane surface. Theoretically, estrone can be either a proton-donor or a proton-acceptor species. Molecular structure of estrone and possible hydrogen bonding formations with the membrane functional groups are shown in Figure 1.

- Feed solution was prepared by spiking estrone into background electrolyte solution to an estrone concentration of 100 ng/L, which presents a typical concentration of natural hormones often encountered in water and wastewater treatment. Estrone was analysed using a Packard Instruments scintillation counter.
- Adsorption of estrone by the membranes was determined by mass balance calculation. The mass balance equation is defined as:

\[
C_pV_p = A\Gamma + V_f \sum C_n + C_vV_v \tag{1}
\]

where \(A\) is the membrane area (cm²); \(\Gamma\) is the amount of estrone adsorbed per surface area (ng/cm²) and \(n\) is the number of permeate samples; \(C_p\), \(C_v\), \(C_c\) and \(V_p\), \(V_f\), \(V_c\) are concentration and volume of feed, permeate and concentrate respectively.

Adsorption was also determined by cutting the membrane into small pieces at the conclusion of each experiment. The membrane was then placed into a scintillation vial to which 5 mL of acetone was added. The vial was shaken vigorously and left for 1 hour for all estrone to dissolve. 1 mL of solution was extracted into another vial for air-drying. The residue was redissolved with 1 mL of MilliQ water and analysed after adding 9 mL of scintillation liquid. Both methods produced similar results.

**RESULTS AND DISCUSSION**

**Breakthrough Observations**

In our previous studies, we have shown that estrone can be adsorbed by polyamide membranes, presumably due to hydrogen bonding (Schäfer et al., submitted; Nghiem et al., accepted). Adsorption and convection will dominate the transport of estrone across the membranes, if their pore sizes are larger than estrone molecule. Due to adsorption, estrone transport is retarded across the membrane layer and consequently estrone retention depends on the adsorption process until the material is saturated. To investigate this relationship between adsorption and the pore size of the membrane, filtration experiments were conducted with a series of fresh feed solutions for TFC-S and X-20 membranes. The Result of these experiments is presented in Figure 2. A breakthrough curve is apparent for the TFC-S membrane, of which the pore size is speculated to be in the same order of the estrone molecule. As the size of the molecule is reduced, the permeate concentration of TFC-S membrane becomes stable below the feed concentration, which indicates some degree of retention due to a sieving mechanism. A breakthrough curve is not observed for the X-20 membrane. For tight membranes, diffusion controls the rate of trace organic transfer across the membrane and the separation process can be achieved through sieving mechanism.

**pH and Ionic Strength Effects**

Batch filtration experiments were performed to investigate the effect of solution condition (pH and ionic strength) on the adsorption of estrone. A new membrane was used for each pH and ionic strength condition. Adsorption in nanograms (10⁻⁹ g) of estrone per membrane surface area (cm²), from a 100 ng/L solution by TFC-SR2, TFC-S and X-20 membranes as a function of pH is shown in Figure 3. Variation in pH of the solution can result in conformational changes of the estrone molecules and the membrane structure or the electrostatic interaction between estrone and the membrane surface, which will ultimately influence estrone adsorption onto the membrane. A trend of slight reduction in adsorption as pH increased at pH below the dissociation constant of estrone (pKa = 10.4) is observed. Adsorption of estrone decreases dramatically as the pH exceeds the pKa value of estrone, which suggests that site-specific adsorption plays a more important role in this case. Estrone adsorption by the X-20 membrane is considerably less than that by the TFC-S and TFC-SR2 membranes. Consequently, a sudden reduction in adsorption when pH exceeds the pKa value of estrone was not observed with this membrane. As proposed in our earlier work, when dissociated, estrone loses its proton and become a negative species; it is unable to form hydrogen bonds with the membrane functional groups, resulting in a sudden reduction in adsorption (Schäfer et al., submitted). A more gradual reduction in hydrophobic adsorption of bovine serum albumin (BSA) on regenerated cellulose
membranes when pH exceeds the isoelectric point (IEP) of BSA was observed by other researchers (Jones and O'Melia, 2000).

Figure 4 shows estrone adsorption from a 100 ngL\(^{-1}\) feed solution onto a TFC-SR2 membrane as a function of NaCl concentration at pH near neutral. The NaCl concentration may partially screen electrostatic potentials and polarity. While modification of molecular structure is important for large molecules, the effect with estrone is likely to be minimal. Similarly, the ionic strength may reduce the electrostatic interaction between the molecules and the surface functional groups of the membrane. Both phenomena can influence hydrophobic interactions between estrone molecule and the membrane surface. Although, there is some variation in adsorption as NaCl concentration varies from 0 to 100 mM, no obvious trend can be observed. This further indicates that site-specific interaction dominates the adsorption mechanism.

Retention of estrone by TFC-SR2 as a function of pH and NaCl concentration resembled the curve presented in Figure 3 & Figure 4 (data not shown). High initial estrone retention (above 90\%) at low pH and low estrone retention (about 55\%) clearly indicate that retention in this case was mainly governed by adsorption. Drop in adsorption resulted in a milder decline in retention of estrone by TFC-S membrane. Whereas, no decline in retention of estrone by the X-20 membrane was observed when estrone adsorption decreased. As the membrane pore size (based on salt retention studies) is in the order TFC-SR2-TFC-S-X-20, these results show that effect of adsorption on retention of estrone by NF/RO membranes can be pore size dependent. The data is published by Schäfer et al. (submitted).

### Adsorption Isotherms

Estrone adsorption as a function of feed concentration (1, 10, 100, and 1000 ngL\(^{-1}\)) on log scale for the TFC-S and TFC-SR2 membranes in stirred cell filtration experiments are presented in Figure 5. Both membranes show a linear curve with a similar partition coefficient K of 48 Lm\(^{-2}\). The adsorption isotherms of TFC-SR2 and X-20 membranes are obtained using static adsorption experiment (membrane pieces in flasks) and presented Figure 6. While the adsorption isotherms of the two membranes are also linear, which is common in very dilute system (Do, 2001), partition coefficients are significantly lower, 8.1 and 4.0 for TFC-SR2 and X-20 membranes, respectively.

During the filtration process, hydraulic resistance is overcome by convection since the pore size of TFC-S and TFC-SR2 is similar or larger than estrone molecule. Estrone can penetrate into the active membrane layer, where site-specific adsorption, presumably due to hydrogen bonding, can occur. In contrast, diffusion is the only driving force in the static adsorption process. Due to the small pore size of the active layer, hydraulic resistance reduces the penetration of estrone and adsorption occurs mainly at the surface. Consequently, a much smaller amount of estrone is adsorbed as can be observed in the static adsorption experiments. The difference in partition coefficient of TFC-SR2 (very loose NF) and X-20 (RO) membrane can be attributed to the fact that the pore size of the X-20 membrane is smaller than the estrone molecule and adsorption can only occur at the surface of the active layer. Although it is possible for the supporting layer to adsorb estrone, results reported here also indicate that the active layer indeed dominates the adsorption process as previously suggested by Chian et al., (1975) and William et al., (1999) for other membranes. The Pore size of the supporting layer is in the order of 100 nm (William et al., 1999), thus, hydraulic resistance is expected to be negligible and the partition coefficient obtained in filtration and static adsorption experiment would be similar if adsorption to the supporting layer dominates (in static experiments the contaminants can adsorb from both sides of the membrane). This is consistent with the results reported by William and co-workers (1999) who found that the majority of trichlorophenol was adsorbed by the active layer of FT30-BW membrane (polyamide on polysulphone support) and subsequent flux decline was observed as an indication of site specific adsorption. However, flux decline could not be observed in our experiments due to very low concentrations of estrone.

### Adsorption & Desorption Kinetics

The results from the study of the adsorption kinetics in static flask experiments are shown in Figure 7. After about 200 minutes the adsorption of estrone by the TFC-SR1, TFC-SR2 and X-20 has attained the plateau value, while this takes significantly longer for the TS-80, ACM-4 and X-20 membranes. Despite the fact that all membranes are made of the same similar polymer, this indicates some difference in physical characteristics of the membranes.

Unlike adsorption kinetics, desorption kinetics of all membranes follow the same pattern and reach equilibrium at 200 minutes. However, considering the adsorption isotherms of the TFC-SR2 and X-20 membranes (see Figure 6), it can be seen in Figure 8 that the desorption process is not complete. This may present an irreversibility factor at this experimental condition, as desorption is lower than what would be expected from the equilibrium established due to the concentration in the bulk after desorption.

### Diffusive versus Convective Transport

In pressure driven membrane filtration processes, the transport of uncharged microporous organic compounds, which have high affinity to the membrane material, across the membrane active layer can be convective and/or diffusive, depending on the pore size of the membrane. The transport of trace organic compounds can be convective while an ideal RO membrane is diffusive. For a real membrane convention and diffusion co-exist. To assess the degree of convective to diffusive transport of trace contaminant estrone in NF/RO membranes, a modified diffusion model developed by Jones and O'Melia (2000) can be applied using the experimental data from static adsorption kinetics experiments. A solution to the one-dimensional diffusion equation was used to describe adsorption at the thin film interface between bulk solution and the membrane surface. Fick's law yield for one-dimensional isothermal diffusion in homogeneous films of a sufficiently large area is:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_{(w)} \frac{\partial C}{\partial x} \right)
\]

(2)

where C is the bulk concentration of the solute, \(t\) represents the time and \(D_{(w)}\) is the diffusion coefficient of the solute in water, \(x\) is the distance from the membrane surface. In order to solve Eq. (2) it can be assumed that the diffusion coefficient of the solute in water is constant and that the concentration of estrone at the solid/liquid boundary remains zero during the diffusion process (Jones and O'Melia, 2000). Eq. (2) then becomes:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_{(w)} \frac{\partial C}{\partial x} \right)
\]

(3)

The following initial and boundary conditions apply:

- Initial condition: \(C(x,0) = C_0\) (x=0)
- Boundary conditions: \(C(0,t) = 0\) and \(C(x=\infty,t) = C_0\)

where \(C_0\) is the initial bulk concentration of the solute. With the above conditions Eq. (3) can be solved to yield:
transport of water, estrone retention by the X-20 is high as can be confirmed by our experiment results presented earlier (Nghiem et al., accepted). In contrast, the TFC-SR2, XN-40 and TFC-SR1 membranes have high value of θ (7.7, 6.8 and 6.3 respectively). This suggests that estrone would readily penetrate into the pores of those membranes and transport of estrone across the membrane will largely depend on convection. These results are confirmed by retention results obtained in cross-flow filtration (Nghiem et al., in preparation), where those membranes showed a very low retention of estrone.

CONCLUSIONS

This study investigates the adsorptive behaviour of trace contaminant estrone by eight different NF/RO membranes using a variety of experimental designs. The membranes can adsorb trace contaminant estrone, which may result in an initially high retention, and for the loose membranes (such as TFC-S) breakthrough curves were observed when the membrane adsorptive sites are saturated. Tight membranes (RO) such as X-20 show a high potential in the removal of trace contaminant estrone, since estrone cannot penetrate into the membrane pores and adsorption can only occur at the membrane surface.

Although the effect of ionic strength on estrone adsorption by the membrane is negligible, it can be strongly influenced by pH near the pKa value of estrone (10.4). While static adsorption experiments give a linear adsorption isotherm, higher estrone adsorption during the filtration process with a large pore size membrane (TFC-SR2) suggests that adsorption can also occur inside the membrane. At this stage it is not possible to clearly differentiate between adsorption in the active layer and the support. In the experiments performed in this study, the support layer cannot engage in hydrogen bonding with the molecules and hence adsorption would be expected to be lower.

Depending on the membrane pore size, the transport of trace organics across the membrane layer can be diffusive and/or convective in nature. A modified diffusion model (Jones and O'Melia, 2000) has been adapted to quantify θ, the ratio of diffusive to convective transport of estrone across the membrane. This model may be used as an indication of trace organics retention in NF/RO membranes and to gain further understanding of their retention mechanisms.

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The Queensland Government and the Australian Research Council are thanked for project funding under the SPIRT scheme. We acknowledge Koch Membrane Systems (San Diego, USA) and Trisep Corporation (Goleta, USA) for providing membrane samples. Thomas Melin and Thomas Wintgens from RWTH Aachen, Germany are thanked for stimulating discussions.

SYMBOLS

\[ C = C_{d} \frac{x}{(4D_{(w)}t)^{1/2}} \]  
\[ J = D \frac{dC}{dt} \bigg|_{t=0} = C_{0} \frac{D_{(w)}}{\pi} \]  
\[ J = \left[ 1 - \frac{\Gamma_{0}}{\Gamma_{\theta}} \right] C \frac{D_{(w)}}{\pi} \frac{1}{\sqrt{t}} \]  
\[ J = \frac{d\Gamma}{dt} \]  
\[ \ln \left[ 1 - \frac{\Gamma_{0}}{\Gamma_{\theta}} \right] = \frac{2C_{0} \theta}{\pi} \frac{D_{(w)}}{\pi} \frac{1}{\sqrt{t}} \]

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### TABLES

#### Table 1: Membrane Types and Pure Water Fluxes at 5 bar

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Average Pure Water Flux* [Lm⁻²h⁻¹]</th>
<th>Membrane Resistance [m⁻¹]</th>
<th>Membrane Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFC-ULP</td>
<td>33.4 ± 6.7</td>
<td>5.4·10¹³</td>
<td>Polyamide on Polysulphone support</td>
</tr>
<tr>
<td>TFC-S</td>
<td>55.0 ± 7.3</td>
<td>3.3·10¹³</td>
<td></td>
</tr>
<tr>
<td>TFC-SR1</td>
<td>52.6 ± 9.4</td>
<td>3.4·10¹³</td>
<td></td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>77.0 ± 25.2</td>
<td>2.3·10¹³</td>
<td></td>
</tr>
<tr>
<td>X-20</td>
<td>19.2 ± 2.4</td>
<td>9.4·10¹³</td>
<td>Polyamide-urea Composite</td>
</tr>
<tr>
<td>ACM-4</td>
<td>25.8 ± 8.0</td>
<td>7.0·10¹³</td>
<td></td>
</tr>
<tr>
<td>XN-40</td>
<td>42.5 ± 0.8</td>
<td>4.2·10¹³</td>
<td></td>
</tr>
<tr>
<td>TS-80</td>
<td>26.0 ± 12.5</td>
<td>6.9·10¹³</td>
<td></td>
</tr>
</tbody>
</table>

* Average values are derived from all experiments and variations are averaged.

#### Table 2: Diffusive to convective ratio (θ) and equilibrium concentration for different membranes using the modified diffusion model.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Γₑ (ngcm⁻²)</th>
<th>θ</th>
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</thead>
<tbody>
<tr>
<td>XN-40</td>
<td>0.0897</td>
<td>6.8</td>
</tr>
<tr>
<td>TS-80</td>
<td>0.0738</td>
<td>2.4</td>
</tr>
<tr>
<td>ACM-4</td>
<td>0.0702</td>
<td>2.0</td>
</tr>
<tr>
<td>X-20</td>
<td>0.0519</td>
<td>1.2</td>
</tr>
<tr>
<td>TFC-SR1</td>
<td>0.0910</td>
<td>6.3</td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>0.0962</td>
<td>7.7</td>
</tr>
<tr>
<td>TFC-S</td>
<td>0.0765</td>
<td>3.3</td>
</tr>
<tr>
<td>TFC-ULP</td>
<td>0.0853</td>
<td>4.2</td>
</tr>
</tbody>
</table>

**FIGURES**

- **Figure 1:** Schematic of possible hydrogen bonding between the estrone molecule and the membrane functional groups.
- **Figure 2:** Permeate concentration of estrone as a function of permeate volume (1 mM NaHCO₃, 20 mM NaCl, and pH 8.0).
- **Figure 3:** Adsorption of estrone as a function of pH in TFC-SR2 membrane after filtration of 120 mL (1 mM NaHCO₃, 20 mM NaCl).
- **Figure 4:** Adsorption of estrone as a function of NaCl after filtration of 120 mL (TFC-SR2 membrane, 1 mM NaHCO₃ and pH 8.0).
- **Figure 5:** Adsorption as a function of feed concentration in filtration experiment after filtration of 120 mL (1 mM NaHCO₃, 20 mM NaCl, and pH 8.0).
- **Figure 6:** Adsorption isotherm of TFC-SR2 and X-20 (static adsorption experiment, 1 mM NaHCO₃, 20 mM NaCl, and pH 8.0).
- **Figure 7:** Adsorption kinetics in static experiments (1 mM NaHCO₃, 20 mM NaCl, 100 ng/L estrone and pH 8.0).
- **Figure 8:** Desorption kinetics in static experiments (1 mM NaHCO₃, 20 mM NaCl, 100 ng/L estrone and pH 8.0).
- **Figure 9:** Transport of trace organics across "ideal" NF (convective) and RO (diffusive) membranes.
- **Figure 10:** Relationships between the logarithm ln[1-Γ(t)/Γₑ] and the square root of time, \( t^{1/2} \) (1 mM NaHCO₃, 20 mM NaCl, 100 ng/L estrone and pH 8.0).

Figure 9

Figure 10