

Removal of the Natural Hormone Estrone from Aqueous Solutions using Nanofiltration and Reverse Osmosis

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Published in Environmental Science & Technology

ABSTRACT

The ability of a variety of nanofiltration and reverse osmosis membranes to retain the natural hormone estrone are examined here as a function of solution conditions. While size exclusion dominates retention with the tighter membranes, both size exclusion and adsorptive effects appear to be instrumental in maintaining high retention on nanofiltration membranes that otherwise exhibit relatively low ion retentions. These adsorptive effects may be driven by hydrogen bonding between estrone and the membrane. Electrostatic attraction appears to aid retention with an apparent slight decrease in retention at high NaCl concentrations. Deprotonation of estrone leads to a significant decrease in retention, most likely as a result of the effect of strong electrostatic repulsive forces decreasing the proximity of the negatively charged estrone to the negatively charged membrane surface and thus lowering the potential for adsorptive retention. This deprotonation effect is absent for tight RO membranes. The results reported here indicate that while open nanofiltration membranes may be effective in retaining estrone under some conditions, the extent of retention may be very susceptible to maintenance of adsorptive capacity at the membrane surface and depend on solution chemistry.

KEYWORDS

Endocrine disrupters, nanofiltration, natural hormone estrone, reverse osmosis, water and wastewater treatment.

1 INTRODUCTION

Endocrine disrupters are compounds which interfere with the endocrine system by either mimicking hormones and triggering responses or by blocking receptors and therefore preventing hormone responses in wildlife and humans. Several thousand natural and synthetic compounds have been identified to be endocrinologically active including natural and synthetic hormones as well as certain pharmaceuticals, food additives, many synthetic chemicals and pesticides (1). The release and accumulation of such contaminants in the environment is of great concern. As early as 1973, Norpoth *et al.* (2) indicated that the use of contraceptives may cause severe long term problems due to the high persistence and biological activity of those compounds in the environment. Indeed, ample evidence now exists that estrogenic compounds and pharmaceuticals are widespread in the effluents of sewage treatment plants. Desbrow *et al.* (3) detected hormones in domestic effluent samples in concentrations up to 80 ngL⁻¹. In Las Vegas surface waters, estradiol was detected in concentrations of 2 to 3 µg/L (4). In contrast, these compounds can be active in human blood at concentrations as low as 0.5 ng/L (5), (p69). According to Desbrow *et al.* (3), natural and synthetic hormones are the major contributors to the estrogenicity of sewage effluents. While industrial chemicals are often found in higher concentrations, the potency of compounds like pesticides, nonyl-phenol or bisphenol A is up to a million times lower than that of hormones (6),(7). While hormones are excreted in urine in a conjugated and inactive form, the compounds are commonly reactivated by bacteria (8). Estrogenic activity in rivers downstream from sewage treatment plants has been shown to cause detrimental effects on wildlife (1).

A number of studies have been devoted to the examination of the environmental fate of such endocrine modulators, mostly focusing on compounds of significant concern such as estrone and 17β-estradiol (9, 10). Studies of the removal of these compounds in wastewater treatment have been limited due to their relatively low concentration and the associated difficulty in analysis. Removals of polar drug residues of between 6 and 71% by a biological filter and between 34 and 83% by activated sludge treatment have been reported with extent of removal dependent on the compound (11). Removal efficiencies of 60-70% for the hormone 17β-estradiol in conventional treatment have also been reported (12). A significant scatter in reported data should be noted which illustrates a high dependence of removal on local conditions.

Given the apparent difficulty in effectively removing endocrinologically active compounds from wastewaters by conventional means, scope exists for use of membranes in improving their removal. Near complete retention of low molecular weight organic compounds, particularly pesticides, by nanofiltration (NF) and reverse osmosis (RO) has been reported by many researchers (13-15). Both, NF and RO are pressure driven membrane processes, where an applied transmembrane pressure forces water through the 'pores' and contaminants are retained due to charge and size interactions. NF is a newer process and is defined as a process lying between porous ultrafiltration (UF) and RO. Both processes are used extensively in water and wastewater treatment, and RO is also used in desalination. NF distinguishes itself from RO in that it only retains multivalent ions, which makes it a very economic alternative where the retention of monovalent salts is not required. The main motivation to use those processes in water and wastewater treatment is the removal of trace pollutants such as endocrine modulators. The retention of such compounds is to date not well understood.

Adsorption of these compounds on the membrane has been found to be an important factor affecting their retention. Little is known however of the removal efficiencies of natural hormones by membranes since their concentrations may be several orders of magnitudes lower than those of other organic compounds (e.g. pesticides) that have been examined. In this paper, we report results of studies of the initial removal of the natural hormone estrone from aqueous solution by NF and RO as a function of solution conditions including estrone concentration, pH and ionic strength. Estrone has been selected for this study because of its high persistence, high potency and moderate

concentrations in wastewaters. In addition, estrone is the metabolic product of 17β-estradiol.

2 MATERIALS AND METHODS

2.1 Membranes

Eight commercially available membranes were selected from two manufacturers. Four membranes were supplied by Koch Membrane Systems (former Fluid Systems Cooperation), San Diego, CA and four by Trisep Corporation. Koch supplied the TFC-S, TFC-ULP, TFC-SR1 and TFC-SR2 membranes which are all polyamide on polysulfone support. Trisep supplied the X-20, ACM-4, TS-80 and XN-40 which are all polyamide-urea composite membranes. The X-20 and XN-40 membranes were of particular interest as they are currently used in the water reuse demonstration plant in Queensland. Membrane characteristics are summarised in Table 1.

2.2 Chemicals, Organics and Background Electrolyte

All chemicals were of analytical grade. Estrone-2, 4, 6, 7-³H(N) was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA) with a specific activity of 74 Ci mmol⁻¹ and a concentration of 1.05 mCi mL⁻¹ in ethanol solution. The solution was stored at <4 °C in the dark. Stock solutions were prepared by adding 26.06 µL estrone solution into MilliQ water for every 100 ng required.

As an example, estrone lot 80K9642 had a purity of 92% when assayed in early 2001. The purity decreases over time as it is an unstable product. It is estimated that the activity decreases approximately 5% per year (16).

Carbonate buffer was selected as a natural matrix. The background electrolyte consisted of 1 mmolL⁻¹ NaHCO₃ and 20 mmolL⁻¹ NaCl unless otherwise stated. CaCl₂ was added as required and pH was adjusted with 1 molL⁻¹ NaOH and HCl.

2.3 Equipment and Filtration Protocol

All experiments were carried out in magnetically stirred batch cells (volume of 185 mL, membrane area 21.2 · 10⁻⁴ m²) at pressures of 500 and 1000 kPa, pressurised with instrument air. All experiments were stirred at 400 rpm (measured with a Philips PR 9115/00 stroboscope). A reservoir of 1.5 L volume was connected to the stirred cell to supply extra MilliQ water if needed. Balances connected to PCs were used to measure and calculate permeate fluxes.

A new membrane was used for each experiment. Membranes were compacted for 1 hr at 10 bar followed by pure water flux determination for 30 mins at 5 bar, both using MilliQ water. Reservoir and stirred cell were then emptied. A feed solution of 185 mL in volume was placed in the stirred cell and the filtration process was conducted at 5 bar for TFC-SR1, TFC-SR2, TFC-S, TFC-ULP and XN-40 membranes until 6 permeate samples, each of a volume of 20 mL, were collected and hence a total of 120 mL of the feed solution was filtered. A pressure of 10 bar was applied for the X-20, TS-80 and ACM-4 membranes in order to achieve compatible flux values with the other membranes examined. Initial and final flux values (J_i and J_f) were recorded at the beginning and end of the filtration process respectively.

2.4 Analytical Methods

2.4.1 Scintillation Counting

A Packard Instruments Scintillation counter was used for analysis of the ³H estrone. The samples were counted for 5 mins and standards were prepared in concentrations of 0, 0.01, 0.1, 1, 10, 100, 1000 and 10 000 ngL⁻¹ estrone, prepared from the fresh compound and used throughout the entire set of samples. The detection limit of the method was 0.1-0.2 ngL⁻¹.

The scintillation liquid was composed of 0.5% 2,5 diphenyloxazole (ppo) and a 1:2 ratio of triton-x emulsifier and toluene X 100 (17). Scintillation vials of 20mL volume were used and filled with 1mL sample and 9mL scintillation liquid. Vigorous shaking was applied to dissipate the emulsion.

2.4.2 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

A Perkin Elmer Optima 3000 ICP-AES instrument was used to determine the cation content of

solutions. Samples were diluted with 5% nitric acid. All vials used were cleaned with 1 M sulfuric acid.

2.4.3 Membrane Zeta Potential

The membrane zeta potential provides a measure of the electrical charge of the membrane surface and can be estimated from streaming potential measurements (18). The membrane streaming potential in background solution (10 mM NaCl, 1 mM NaHCO₃ and 0.5 mM CaCl₂) was measured using a Brookhaven Instruments Corp. BI-EKA commercial instrument. Childress and Elimelech describe the measuring cell and zeta potential calculation in detail (19). The membrane zeta potential is calculated from the streaming potential using the Helmholtz-Smoluchowski equation.

2.4.4 Contact Angle Measurements

Contact angles were determined using the conventional sessile drop technique with MilliQ water as the reference liquid. The membranes were washed with MilliQ water and then dried in an oven at 90°C for one hour. The contact angle was measured immediately after deposition of the droplet from a syringe and as a function of time.

2.5 Estrone Characteristics

The structure of estrone is shown in Figure 1A and the chemical characteristics of the molecule are summarised in Table 2. Estrone is a hydrophobic compound with a very low solubility in water. This stems partially from the fact that the pKa value of estrone is very high and the compound is uncharged in the pH range of most natural waters and wastewaters. The high octanol - water partitioning coefficient (log P) implies that estrone would readily adsorb onto particles and possibly surfaces such as membranes. Norpoth *et al.* (2) studied the solubility and stability of hormones in water and wastewater and found that the solubility in wastewater is lower than in water. While the pKa value is unavailable in the literature due to its low solubility, it can be estimated after Perrin (20) based on analogy of the structure with estriol, which has a pKa of 10.4 (21). Estrone has a double bond with an oxygen atom, which is equivalent to 2 hydroxyl groups of estriol. The pKa of estrone is thus expected to be approximately 10.4. Other chemical characteristics have been reported by Cramer *et al.* (22) and Kubli-Garifas (23). Estrone possesses a carbonyl group at C17, which is replaced by (for example) a hydroxyl group in other hormones such as estradiol. While both ends of the molecule exhibit electrostatic potential due to the hydroxyl and carbonyl groups, the carbonyl group induces a larger electrostatic potential. Estrone is a good electron acceptor and a poor electron donor (23, 24) and thus has oxidant characteristics. Estrone may also form hydrogen bonds with the membranes.

While estrone is excreted by humans in conjugated form, biological treatment processes deconjugate and reactivate the hormone to some extent. Further, estrone is a degradation product of estradiol (25) and much of the estrone found in effluents may originate from this pathway. As membrane processes are commonly used as tertiary treatment and deconjugated estrone is expected to be more difficult to retain using membranes, deconjugated estrone was selected for use in the experiments reported here. This conforms with the views of Desbrow *et al.* (3) and Johnson and Sumpter (26) who identified the group of natural and synthetic hormones as priorities.

3 RESULTS AND DISCUSSION

3.1 Membrane Characterisation

Membrane characteristics influence the performance of membranes, namely flux, retention and resistance to fouling. The selected membranes vary in pure water flux between 20 and 80 Lm⁻²h⁻¹ at 5 bar (see Table 1) with the TFC-SR2 membrane at the upper and the X-20 membrane at the lower end of this range. Pure water flux of TFC-SR2 varies significantly from one filtration experiment to another. Operating pressures of the ACM-4, X-20 and TS-80 membranes were adjusted to 10 bar to achieve a more comparable flux for all membranes.

Zeta potentials of the Koch and Trisep membranes are shown in Figure 2A and B, respectively. All eight membranes have a low positive charge at pH values below about 4 and a higher negative

charge at pH values above their point of zero charge. The structure of a basic polyamide is shown in Figure 1B, however, proprietary chemical modifications of the membrane surface may result in the presence of carboxylic functional groups.

The hydrophilicity of the membranes also varies greatly (see Figure 3). The TFC-SR1 and TFC-SR2 membranes are the most hydrophilic with contact angles between 10 and 20°. The other membranes exhibit contact angles between 30 and 45° and hence are also reasonably hydrophilic. While increased hydrophilicity would be expected to show higher flux if other membrane characteristics were identical, the eight membranes also exhibit different effective pore sizes and active layer thicknesses.

Salt retention is a further characteristic that is often used by nanofiltration and reverse osmosis membrane manufacturers to describe membrane performance. Calcium and sodium retentions for the membranes are summarised in Table 3. Flux under the experimental conditions is also a function of salt retention, as the retained ions accumulate in the boundary layer of the membrane where this concentration polarisation effect imposes an osmotic pressure, which reduces the effective driving force across the membrane.

3.2 Reproducibility of Results

Two of the experiments were repeated three times with fresh membrane samples, on different days and in different analytical batches. The results are shown in Figure 4 and demonstrate only small differences in estrone retention between runs with the maximum error in the order of ± 3 %.

The decrease in retention that is observed on continued filtration is typical of many results obtained here and may reflect a retention that is dominated more by adsorptive effects than size exclusion with the adsorptive capacity decreasing (possibly due to site saturation) on continued filtration. Effects such as hydrogen bonding may account for the adsorptive retention of estrone at the membrane surface. An in depth analysis and model of the adsorptive interactions were published by Nghiem and Schäfer (27).

3.3 Comparative Retention by Membrane Type

As implied above, retention of organics can be attributed to a number of mechanisms the most common of which are size exclusion, charge repulsion and adsorption on the membrane surface. Here the retention at the initial stages of filtration is studied. Estrone at pH 6 is undissociated and only polar moieties contribute to its charge distribution within the molecule. The molecular weight of estrone is 270.4 gmol⁻¹ which translates to an approximate size of 0.4 nm (radius of equivalent sphere) using the equation of Worch (28) and the Stokes Einstein equation (not considering structural effects of the molecule) as described by Schäfer (29). Under these conditions both estrone and the membranes have a minimal charge and hydrophobic effects would be expected to dominate any interaction between them. Figure 5 shows the concentration of estrone in the permeates following filtration by the eight different membranes in MilliQ water as well as retentions calculated from permeate and feed concentrations. The retention for all membranes is high (95 to 99%) except for the XN40, which has a retention as low as 80%. Permeate concentrations are accordingly low and typically less than 5 ngL⁻¹, except for XN40 for which the permeate concentration is as high as 50 ngL⁻¹.

That the XN40 membrane exhibits significantly poorer rejection of estrone than the other membranes examined is not particularly surprising given that this membrane also exhibits the lowest sodium rejection. An observation that is perhaps more surprising is the high rejection achieved by all other membranes, even for membranes such as TFC-SR1 and TFC-SR2 for which ion rejection is not particularly high. As mentioned earlier, the consistently high rejection may well be associated with adsorption of the estrone to the membrane, even though TFC-SR1 and TFC-SR2 are two of the least hydrophobic. Again, as introduced briefly above, the mechanism driving adsorptive retention of estrone at the membrane surface is unclear but may reflect hydrophobic partitioning to the organic membrane surface or may be related to more specific interactions such as

hydrogen bonding. The fact that decreasing retention on continued filtration is observed in many instances supports the hypothesis of a more site specific interaction such as hydrogen bonding. Water flux through a dense membrane depends on the waters ability to form hydrogen bonding with the hydrophilic groups of the membrane polymer (30). Specific adsorption can result in water flux decline if organics have higher proton donor capacity than water; thus, can displace water from the hydrophilic sites of the membrane (25). Flux decline was not observed in this case. However, this is due to low concentration of estrone or more likely estrone acts as a proton acceptor and does not compete with water for interaction sites. More detailed studies of the adsorption of such compounds on NF and RO membranes was published elsewhere (27).

3.4 Effect of Estrone Concentration

The concentrations of estrone found in sewage are in the order of ng/L. Such concentrations are difficult to maintain in experiments due to analytical difficulties. However, the use of higher concentrations may not necessarily reflect the behaviour of estrone and for this reason a set of experiments was carried out to investigate concentration effects. Results are shown in Figure 6A and Figure 6B for TFC-SR2 and TFC-S membranes, respectively. These membranes were selected as representatives of low and high ion retention characteristics. The effect of concentration in the range between 1 and 1000 ng⁻¹ is minimal when retention values are compared. This result is suggestive of a constant partition coefficient for estrone between membrane and bulk solution. The maintenance of a constant partition coefficient even at the highest concentrations of estrone used indicates that saturation of the membrane surface sites is not being approached. A similar result was obtained by van den Bruggen *et al.* (15) who found that retention of several pesticides by NF was independent of the feed concentration. Considerable scatter in retention is observed at an estrone feed concentration of 1 ngL⁻¹ but high experimental errors are to be expected in this case as the permeate concentrations are close to the detection limit of the analytical method (0.1-0.2 ng/L). In light of these constraints, experimentation with a concentration of 100 ngL⁻¹ thus appears to be justified, and permeate concentrations are assumed to be proportional to the feed concentrations. Higher concentrations may be problematic due to the low solubility of estrone and the possible increase in concentration in the boundary layer.

3.5 Ionic Strength Effects on Retention

While estrone is uncharged over most of the pH range of interest (pKa ≈ 10.4), the molecule is relatively polar as a result of the distribution of charge associated with the functional groups present (23). The presence of counter-ions in solution may partially screen the charge associated with these functional groups and thus reduce the apparent 'size' of the molecules. Similarly, solution phase counter-ions may shield the electrostatic potential generated by membrane surface functional groups and thus reduce electrostatic repulsive effects. Both effects would be expected to influence solute rejection in similar ways and cannot be easily separated.

The effect of increasing NaCl concentration is shown in Figure 7. Reasonably similar retentions are observed for NaCl concentrations from 5 to 100 mM with an apparent slight decrease at the uppermost NaCl concentration used (100 mM). As discussed above, this decrease in rejection may be indicative of some (small) impact of electrostatic effects between estrone and the membrane. That electrostatic influences on transport of estrone through the membrane are relatively minor is confirmed by the similarly minor impact of varying the concentration of calcium in solution (see Figure 8). In this case, a slight increase in rejection at the higher calcium concentrations could be surmised (possibly as a result of the ability of Ca²⁺ ions to increase retention through facilitation of bridging between estrone and the membrane) but again the effect is too minor to draw definitive conclusions (other than that size and possibly to some extent adsorption effects dominate retention). From those results it appears that concentration polarisation effects caused by salt retention of the membranes will not affect estrone retention.

3.6 Effect of pH on estrone rejection

Increase in solution pH above 3 leads to an increasingly negatively charged membrane with the

charge plateauing above pH of approximately 6. Given a pKa of approximately 10.4, the speciation of estrone will vary as shown in Figure 9A. The pH dependence of estrone speciation is mirrored almost exactly in the pH dependence of estrone retention with retention decreasing dramatically at high pH for the TFC-SR2 membrane (Figure 9B). This decrease is not due to changes in membrane characteristics due to the high pH as the flux is stable over the complete pH range examined. The result supports the earlier contention that adsorptive effects (possibly mediated by hydrogen bonding between the hydroxyl and/or carbonyl groups of estrone and the membrane) are a major contributor to retention of estrone on these membranes. One would expect adsorption to be highest under conditions where charge repulsion is lowest. At high pH adsorption would decrease and depending on the pore size, retention may drop as charge repulsion increases. This was confirmed for two further membranes, the X-20 (Figure 9C) and the TFC-S (Figure 9D). These results show clearly the decrease in pH effect as the pore size becomes smaller. The X-20 membrane retains the estrone effectively over the entire pH range showing that RO is a reliable barrier.

The above conclusion is of concern as it does suggest that the degree of estrone retention on NF membranes will be dependent upon the availability of surface sites and solution chemistry. It will be particularly interesting to examine the effects of natural and effluent organic matter on the extent of estrone retention. NOM would be expected to compete for membrane surface sites and may thus lower retention of the trace contaminant. Alternatively, given the highly hydrophobic nature of estrone, the presence of other organic compounds at the membrane surface may encourage hydrophobic partitioning into this phase with subsequent maintenance of high retention. Those parameters will be subject of further studies.

In summary, it appears that both size exclusion and adsorptive effects are instrumental in maintaining high retention of estrone on a variety of NF and RO membranes over a range of solution conditions. Adsorptive effects appear to be particularly important for retention by NF membranes exhibiting relatively low ion retentions. These adsorptive effects may be driven by hydrogen bonding between estrone and the membranes. Electrostatic repulsion appears to reduce both adsorption and retention of estrone by the membranes. Deprotonation of estrone leads to a significant decrease in retention, possibly as a result of a critical role of the estrone hydroxyl group proton in hydrogen bonding or, more likely, as a result of the effect of strong electrostatic repulsive forces decreasing the proximity of estrone to the membrane surface and thus lowering the potential for adsorptive retention if pores are large enough to allow the passage of the molecules.

ACKNOWLEDGEMENTS

The Queensland Government (DNR, EPA, Brisbane, QLD) and the Australian Research Council are thanked for project funding as is the CRC for Water Quality and Treatment who provided a summerscholarship for Long Nghiem.

We acknowledge Koch Membrane Systems (former Fluid Systems Cooperation), San Diego, CA and Trisep Corporation for providing membrane samples, the UNESCO Centre for Membrane Science & Technology, UNSW for support with streaming potential measurements and the School of Chemistry, UNSW for assistance with contact angle measurements.

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TABLES

Table 1 Membrane characteristics (pure water flux, permeability, membrane resistance) of the membranes used.

Membrane	Average Pure Water Flux at 5 bar [Lm ⁻² h ⁻¹]	Average Permeability [Lm ⁻² h ⁻¹ bar ⁻¹]	R _M [m ⁻¹]
TFC-ULP	33.4 ± 6.7	6.7	5.4 · 10 ¹³
TFC-S	55.0 ± 7.3	11.0	3.3 · 10 ¹³
TFC-SR1	52.6 ± 9.4	10.5	3.4 · 10 ¹³
TFC-SR2	77.0 ± 25.2	15.4	2.3 · 10 ¹³
X-20	19.2 ± 2.4	3.8	9.4 · 10 ¹³
ACM-4	25.8 ± 8.0	5.2	7.0 · 10 ¹³
XN-40	42.5 ± 0.8	8.5	4.2 · 10 ¹³
TS-80	26.0 ± 12.5	5.2	6.9 · 10 ¹³

Table 2 Characteristics of estrone

Characteristic	Value	Reference
Chemical Name	3-hydroxyestra-1,3,5(10)-trien-17-one	(31)
Abbreviation	E1	
Formula	C ₁₈ H ₂₂ O ₂	
Molecular Weight	270.36	
Diameter	0.8 nm	(28), (29)
pKa	10.4	(20), (21)
Log P	1.88	(22)
Solubility in H ₂ O	30 mgL ⁻¹	(31)
Other	Metabolite of 17β estradiol UVmax 283-285nm	(31)

Table 3 Salt rejection of the membranes used (background solution pH 7.8 and 20 mM NaCl, 1 mM NaHCO₃, 0.5 mM CaCl₂). Pure water flux measured at 5 bar. Please note that pure water fluxes for different membrane samples may vary significantly.

Membrane	Calcium Rejection [%]	Sodium Rejection [%]	Pure Water Flux J _{w0} [Lm ⁻² h ⁻¹]	Final Flux J _F [Lm ⁻² h ⁻¹]	Flux Ratio J _F /J _I [-]
TFC-ULP	72.5 – 82.3	68 – 79.2	28.74	18.98	0.84
TFC-S	73.8 – 82.2	71.4 – 81.6	49.58	24.34	0.60
TFC-SR1	17.4 – 22.8	24.4 – 32.4	62.18	62.91	1.00
TFC-SR2	16.5 – 25.8	2.3 – 17.3	29.51	35.85	1.01
X-20	92.0 – 98.0	94.2 – 97.2	18.65	5.54	0.42
ACM-4	31.7 – 46.9	52.8 – 54.1	22.35	15.64	0.78
XN-40	45.2 – 55.4	21.4 – 34.5	20.3	20.46	0.99
TS-80	24.0 – 68.3	47.6 – 58.5	11.58	10.73	1.03

FIGURES

- Figure 1** Structure of estrone and membrane surface (polyamide).
- Figure 2** Membrane zeta potential measured in background solution (10 mM NaCl, 0.5 mM CaCl₂, and 1 mM NaHCO₃).
- Figure 3** Membrane contact angles.
- Figure 4** Reproducibility of results as retention and permeate concentration (TFC-S: pH 8, 100 ngL⁻¹ estrone, 10 mM NaCl, 1 mM NaHCO₃, 0.5 mM CaCl₂; TFC-SR2: pH 10, 100 ngL⁻¹ estrone, 10 mM NaCl, 1 mM NaHCO₃, no CaCl₂).
- Figure 5** Permeate concentration and retention of estrone in MilliQ water for various membranes
- Figure 6** Effect of concentration on permeate concentration and retention (A) TFC-SR2 and (B) TFC-S (pH 8, 100 ngL⁻¹ estrone, 10 mM NaCl, 1 mM NaHCO₃, 0.5 mM CaCl₂ for both membranes).
- Figure 7** Effect of NaCl concentration on estrone retention NaCl (TFC-SR2, pH 8, 1 mM NaHCO₃, and NaCl varies from 0 mM to 100 mM)
- Figure 8** Effect of CaCl₂ concentration on estrone retention (TFC-SR2, pH 8, 1 mM NaHCO₃, 20 mM NaCl, and CaCl₂ varies from 0 mM to 5 mM)
- Figure 9** Speciation of estrone (A) and effect of pH on permeate concentration and retention for membranes TFC-SR2 (B), X-20 (C) and TFC-S (D) (1 mM NaHCO₃, 20 mM NaCl, pH varies from 3 to 12)

FIG 1

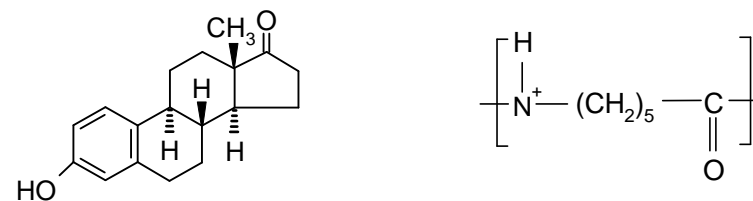


FIG 2

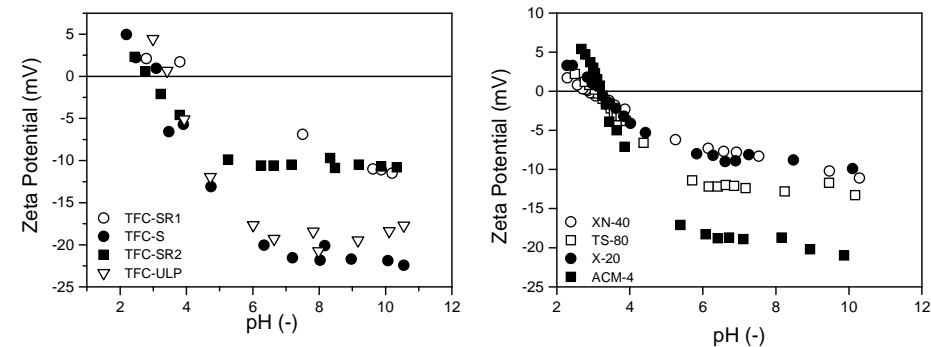


FIG 3

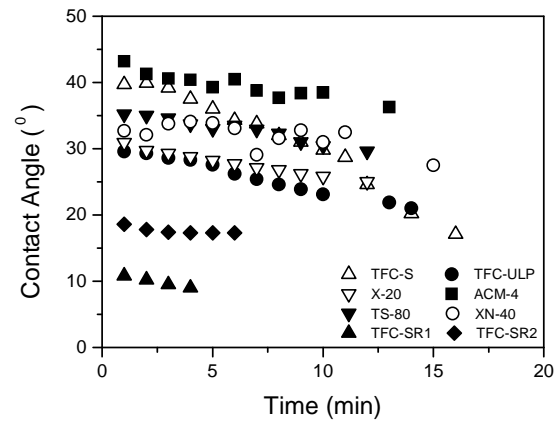


FIG 4

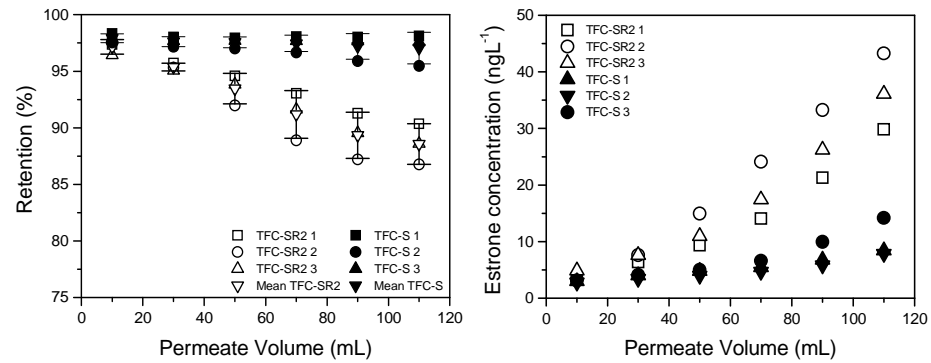


FIG 5

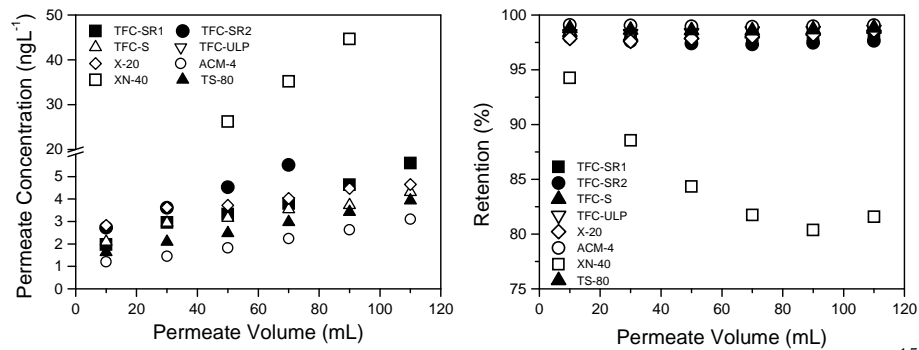
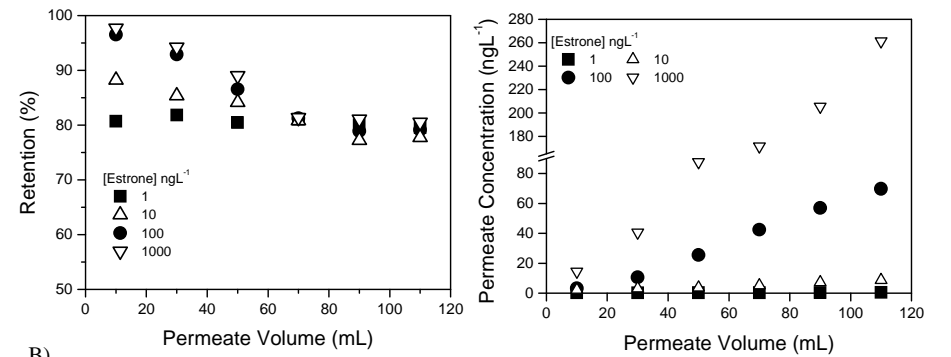


FIG 6

A)



B)

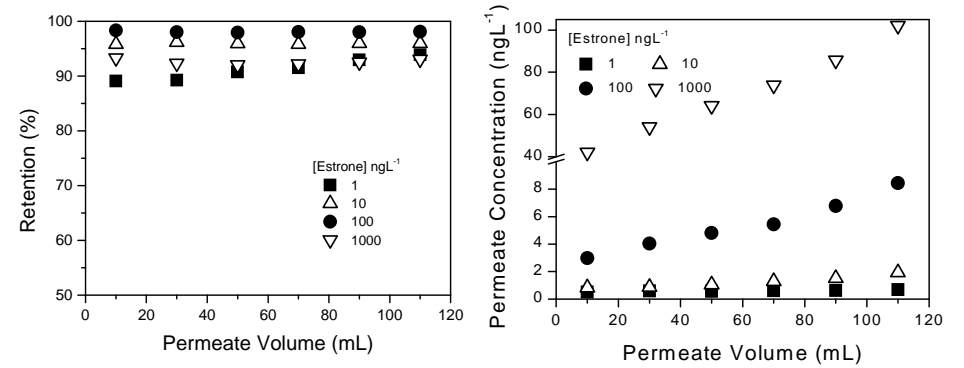


FIG 7

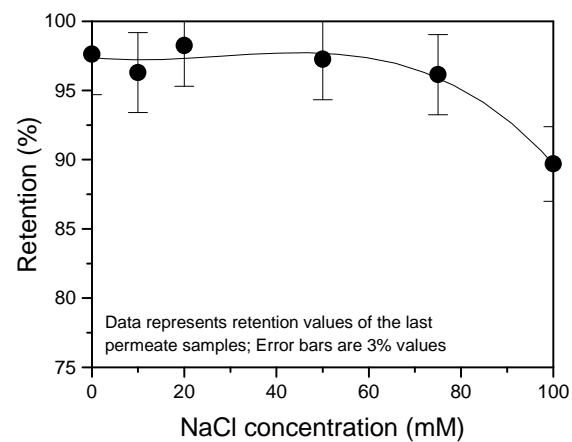


FIG 8

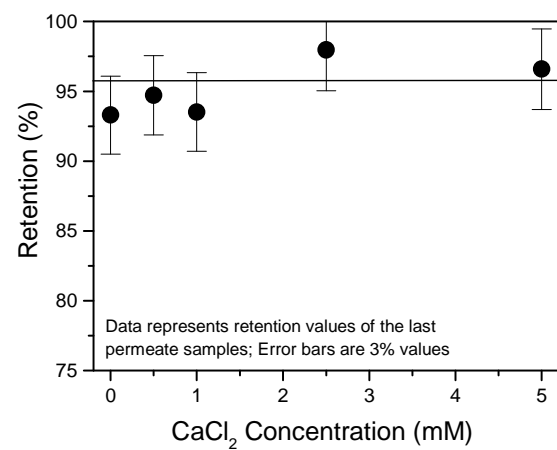


FIG 9

