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MEMBRANE FILTRATION IN WATER RECYCLING – REMOVAL OF NATURAL HORMONES

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1. INTRODUCTION

Recent detections of endocrine-disrupting chemicals (EDCs) in effluent are of great concern by sections of the community associated with the issue of reclaimed water recycling. In vitro and in vivo studies by many researchers have confirmed the impacts of EDCs on trout at the common concentration encountered in sewage effluent. Amongst many types of EDCs the impacts of steroid estrogens such as estrone, estradiol (natural hormones) and ethinylestradiol (a synthetic hormone) are prominent as they have far higher endocrine-disrupting potency than other synthetic EDCs (Johnson and Stumpter, 2001). Performance of conventional wastewater treatment of different plants on removal of these compounds varies greatly and, concentrations of some steroid estrogens in secondary effluent are still able enough to harm wildlife such as fish in particular (Johnson and Stumpter, 2001). In spite of the magnitude of this problem, research on the removal of EDCs in water and wastewater treatment remains to date very limited due to their relatively low concentration and the associated analytical difficulties.

Table 1: Membrane types and pure water flux

Membrane Type	Average Pure Water Flux* [$Lm^{-2}h^{-1}$]	Membrane resistance [m^{-1}]	Membrane material
TFC-S	55.0 ± 7.3	$3.3 \cdot 10^{13}$	Polyamide on
TFC-SR2	77.0 ± 25.2	$2.3 \cdot 10^{13}$	Polysulfon support

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

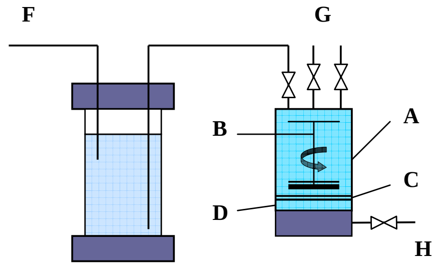
Given the continuous developments in membrane technology, tertiary treatment using membrane processes has been identified as a promising technology to provide a safeguard to water recycling practice and to protect the environment. Several researchers have shown that nanofiltration is capable of removing trace organics including natural hormones and a wide range of pesticides (Kiso et al, 2001; Schäfer et al, 2001; Kiso et al, 2000). In our previous work, removal of trace contaminant estrone using eight different nanofiltration and reverse osmosis membranes, which cover a wide pore size range, has been studied. It was found that estrone could be adsorbed to the surface by some membranes. This adsorptive phenomenon is of concern as it may result in contaminants leakage or bulk release when desorption occurs. This paper investigates retention and adsorptive behavior of natural hormones estrone and estradiol on two low pressure nanofiltration membranes TFC-SR2 and TFC-S.

2. MATERIALS AND METHODS

2.1 Membranes and filtration process

TFC-S and TFC-SR2 were selected for this study due to their excellent permeability at low pressure. They were supplied by Fluid System (San Diego, USA). Membrane types and pure water flux at 5 bar are summarised in Table 1. TFC-S is expected to have a smaller pore size as compared to TFC-SR2 due to its higher salt retention (data is not shown) and pure water flux differences.

A schematic of the filtration system is shown in Figure 1. Experiments were carried out in a 185 mL stainless steel stirred cell. The inner diameter was 56.6 mm resulting in a membrane surface area of 21.2×10^{-4} m^2. An Amicon magnetic stirrer was used and the stirrer speed was set at 400 rpm. Instrument grade air was used to pressurize the stirred cell. A new membrane was used for each experiment.



A Stirred cell
B Magnetic stirrer
C Membrane
D Stainless steel porous support
E 2 L reservoir
F Pressurised instrument air inlet
G Feed inlet, safety and release valves
H Permeate outlet

Figure 1: Membrane filtration stirred cell set-up

After compacting the membranes using MilliQ water at 10 bar for 1 hour, feed solution was filtered at 5 bar and six permeate samples of 20 mL each were collected from a feed volume of 185 mL. A retentate sample was also collected for analysis.

Parameters used to quantify the efficiency of a membrane were flux (J) and solute retention (R) where the flux is defined as $J \equiv \frac{1}{A}\frac{dV}{dt}$ and retention as $R = 100 \cdot (1 - \frac{c_P}{c_B})$.

2.2 Chemicals and analysis

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 $NaHCO_3$, and 20 mM NaCl. pH was adjusted using 1M HCl or 1M NaOH.

2.3 Natural Hormone Characteristics and Analysis

Both estrone and estradiol are hydrophobic compounds and have a very low solubility in water (Merck, 1996). The acid dissociation constant, pKa, of estrone is 10.4 (Schäfer et al, (submitted)). Estradiol has a very similar molecular structure as estrone; thus, it is expected to have the same pKa value. Hydroxyl and carbonyl functional groups of estrone and estradiol make them capable of participating in hydrogen bonding, as a proton-donor or proton-acceptor species.

Feed solution was prepared by spiking estrone or estradiol into background electrolyte solution to make up 100 ng/L of estrone or estradiol, respectively. This is a typical concentration of natural hormones often encountered in surface waters and wastewaters.

Estrone was analysed using a Packard Instruments scintillation counter.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on adsorption of estrone

As indicated previously, eight membranes were screened for estrone retention and from that result two membranes were selected for further study; the TFC-SR2 and TFC-S due to an expected difference in pore dimension based on pure water flux (see Table 1) and salt retention.

Figure 2 shows that adsorption of estrone by both membranes drops drastically with the dissociation of estrone at pH 10.5. It is not surprising that adsorption capacity of the two membranes is almost identical as they are both of polyamide on polysulfon support. The experiments do not allow to distinguish between adsorption on the active layer and the support material.

Hydrogen bonding was suggested as the mechanism of adsorption of estrone by the membrane (Schäfer *et al.*, (submitted)). Hydroxyl groups are the most likely interaction sites due to the resonance structures of the aromatic groups. When dissociated, estrone loses its proton and becomes unable to participate in hydrogen bonding with membrane functional groups, resulting in a reduction in adsorption and lower retention.

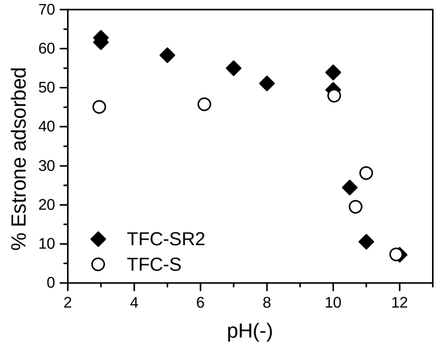


Figure 2: Estrone adsorption as a function of pH on TFC-SR2 and TFC-S membranes (100 ng/L estrone; 1 mM $NaHCO_3$; 20 mM NaCl).

3.2 Adsorption effect on estrone and estradiol retention

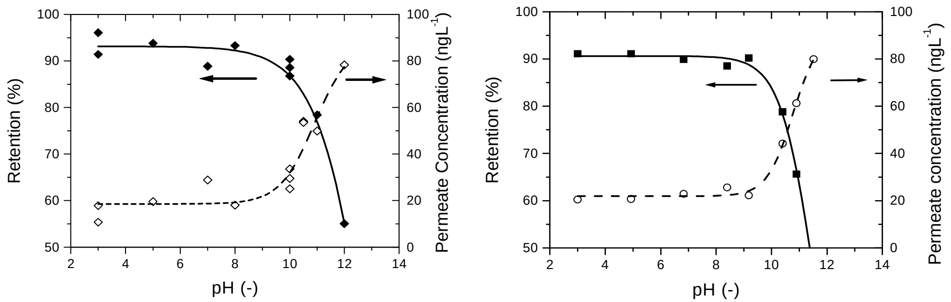


Figure 3: Permeate concentration and retention of estrone (right) and estradiol (left) by TFC-SR2 membrane as function of pH (100 ng/L estrone or estradiol; 1 mM $NaHCO_3$ and 20 mM NaCl).

Figure 3 compares retention of estrone and estradiol by TFC-SR2 at different pH. Retention of both compounds decreases drastically as pH exceeds their pKa value (10.5) in parallel with the decreased adsorption (see Figure 2 for estrone). Given the similarity between estrone, estradiol and other estrogenic compounds, this result indicates that similar adsorption phenomena by the membranes can be expected for other estrogenic compounds such as estriol or ethinylestradiol.

3.3 Time Dependence of Adsorption

It appears that adsorption of trace contaminants on membranes is a temporary effect in initial stages of filtration. While this adsorption should not be relied upon for the removal of trace contaminants, adsorption is likely to continue until the material is saturated and lead to the accumulation of large amounts of contaminants.

To investigate the limits of this adsorption and subsequent retention of saturated membranes, experiments were conducted with a series of fresh feed solutions for one membrane. Results from those experiments are presented in

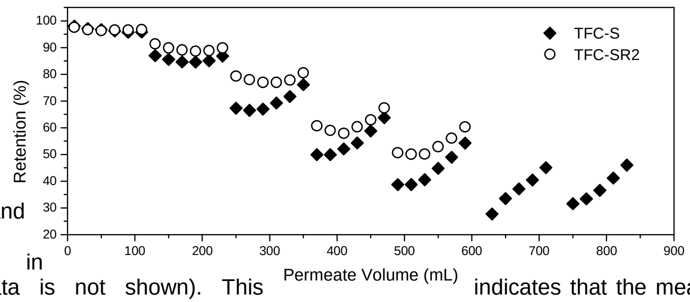


Figure 4. After 7 feed volumes of both retention and adsorption reach equilibrium and as expected retention decreases with a reduction in adsorption (adsorption data is not shown). This indicates that the measured retention is dominated by adsorption phenomena for both membranes and that retention of such polar compounds is difficult with those membranes.

Figure 4: Retention as a function of filtration volume (100 ng/L estrone; 1 mM $NaHCO_3$, 20 mM NaCl and pH 7.8).

4. CONCLUSIONS

Both estrone and estradiol could be significantly adsorbed by the membranes. pH can significantly influence the adsorption process, presumably due to hydrogen bonding. Consequently, this leads to an accumulation of trace contaminants in the membrane and possible bulk release of those contaminants when desorption is favour.

Further studies are planned to investigate the adsorption phenomena of all eight membranes to eliminate a membrane where retention is not determined by adsorption to achieve a stable retention performance, ideally in conjunction with a very low adsorption capacity to reduce the risk of a bulk release of trace contaminants.

5. ACKNOWLEDGEMENTS

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6. SYMBOLS

A:	Membrane Surface [m^2]	J:	Flux [$Lm^{-2}h^{-1}$]	V:	Permeate Volume [L]
c_B:	Bulk Concentration [mgL^{-1}]	R:	Retention [%]		
c_P:	Permeate Conc. [mgL^{-1}]	t:	Time [h]		

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