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THE ROLE OF ENDOCRINE DISRUPTERS IN WATER RECYCLING – RISK OR MANIA?

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Abstract The widespread occurrence of endocrine disrupting chemicals (EDCs), such as steroid hormones, in secondary wastewater effluents has become a major concern in the water recycling practice. This paper investigates the risk of steroid hormone breakthrough during nanofiltration membrane filtration in water recycling applications. The results indicate a dynamic equilibrium between adsorption and desorption of steroid hormone with regard to the membrane. This equilibrium can be pH dependent and there is a possibility for release of steroid hormones at high pH during membrane cleaning procedures or erratic pH variations. Increase in water recovery can severely increase the hormone breakthrough concentration. The results also indicate a possibility of accumulation of steroid hormones in the NF membrane, followed by subsequent release.

Keywords endocrine disrupting chemicals; nanofiltration; steroid hormones; water recycling

INTRODUCTION

Recycling of domestic wastewater effluent is rapidly becoming a necessity for water utilities throughout the world to augment our limited fresh water supply, which is currently under tremendous pressure to due exponential population growth (Freeman and Morin, 1995; Asano and Levine, 1996; Levine, 1999). However, concern over contaminants that may present in wastewater effluent is still a major obstacle to water recycling practice (Higgins et al., 2002). In addition to the microbiological risks, there has also been a significant focus on trace contaminants, which have endocrine disrupting properties (Higgins et al., 2002). Prominent amongst these endocrine disrupting contaminants are steroid hormones, which are excreted continuously by humans and animals. Due to incomplete removal during primary and secondary treatment processes, they are ubiquitous in secondary wastewater effluents at concentrations in the lower ng/L range (Harries et al., 1999; Ternes et al., 1999). Despite their low concentration, these contaminants are of a major health concern because of their extremely high endocrine disrupting potency (Table 1). While a direct "cause and effect" linkage between these contaminants and the recent decline in male sperm counts, and increasing incidence of testicular, prostate, and breast cancer is still debatable (Colborn et al., 1997), the environmental effects of endocrine disrupting chemicals on wildlife has been confirmed by various laboratory and field studies (Purdom et al., 1994; Rodgers-Gray et al., 2001; Ottinger et al., 2002).

Table 1: Relative endocrine disrupting potency and threshold to fish of several endocrine disrupting chemicals

EDCs	Relative Potency	Threshold (ng/L)	Reference
Estradiol	1	1	(Purdom et al., 1994)
Estrone	10^{-1}	10	(Thorpe et al., 2003)
Butyl phenol	1.6×10^{-4}	6.25×10^{3}	(Jobling and Sumpter, 1993)
Nonyl phenol	0.9×10^{-5}	1.11×10^{5}	

Nanofiltration (NF) and reverse osmosis (RO) membrane filtration processes have been widely used in water recycling due to their reliability and capacity to effectively remove a wide range of contaminants (Levine, 1999; Van der Bruggen and Vandecasteele, 2003) or where trace contaminants such as pesticides need to be removed (Ventresque and Bablon, 1997). However, the removal mechanisms of steroid hormones by NF/RO membranes are not yet fully understood. Particularly, the risk of steroid hormone breakthrough in NF/RO filtration has not been adequately examined. In our previous work, it was found that some membranes could adsorb steroid hormones to a significant extent, which may appear as high retention by loose NF membranes (Schäfer et al., 2003). This paper investigates the risk of steroid hormone estradiol and estrone accumulation on the membrane due to adsorption/partitioning and possible breakthrough of such contaminants in NF/RO membrane filtration processes.

MATERIALS & METHODS

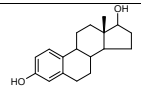
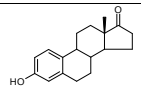
Three thin-film composite NF membranes — TFC-SR2, TFC-S and NF-270 — were selected for this study. The first two membranes were supplied by Koch Membrane Systems (San Diego, USA), while the last one was supplied by Dow Chemicals (Minneapolis, USA). TFC-SR2 is a loose NF membrane with less than 15 % sodium chloride retention while the NF-270 and TFC-S are tighter membranes with sodium chloride retention of approximately 40 % and 85 %, respectively.

A dead end stirred cell and a SEPA® crossflow cell were used in this study. The stirred cell was made of stainless steel with a volume of 185 mL. The stirred cell inner diameter was 56.6 mm, which results in a membrane area of 21.2 cm^2. An Amicon magnetic stirrer was used and the speed was set at 400 rpm to minimize concentration polarization. The cross flow filtration system includes a SEPA® cross flow cell (Osmonics), a feed pump, a recirculation pump, and a flowmeter. Crossflow velocity was set at 7.3 cm/s. The effective membrane surface area is 139 cm^2 and the channel height is 0.86 mm. Prior to each experiment, the membrane was compacted for 1 hour at 10 bar using DI water. The feed solution was then introduced and pressurized at 5 bar. Unless otherwise stated, feed solution for all experiments contained 100 ng/L of steroid hormone estradiol or estrone.

CHEMICALS

All chemicals were of analytical grade. Both estradiol and estrone have low solubility in water, moderate octanol water partitioning coefficients, and pK_a values of approximately 10.4. Their molecular structure and physiochemical characteristics are summarized in Table 2. Radiolabeled estradiol-2,4-^{3}H(N) and estrone-2,4,6,7-^{3}H(N) were purchased from Sigma Aldrich (Saint Louis, USA). Estradiol and estrone were analyzed using a Packard Instruments scintillation counter. The detection limit of this technique is approximately 0.1 ng/L.

Table 2: Physical and chemical characteristics of estradiol and estrone

	Molecular Structure	MW (g/mol)	Solubility (mg/L) at 20°C [a]	Log K_{ow} [b]	pK_a [c]
Estradiol		272.4	13	4.01	10.4
Estrone		270.4	13	4.54	10.4

[a] (Lai et al., 2000); [b] calculated using HyperChem Software; [c] estimated based on molecular structure analogy (Perrin, 1980).

RESULTS & DISCUSSION

Short term adsorptive interactions between membranes and steroid hormones

In our previous study, it was reported that estrone adsorption and retention by NF membranes were strongly affected by pH (Schäfer et al., 2003). In this study, we investigated the pH dependence of estradiol adsorption and retention by the NF membrane TFC-SR2. Given a pKa of 10.4, the speciation of estradiol as a function of pH will vary following a sigmoidal curve. At pH greater than 10.4, negatively charged ionic estradiol will be the dominant species, whereas at pH less than 10.4, non-ionic estradiol will dominate. As can be seen from Figure 1A, retention decreases dramatically at pH higher than the estradiol pKa value. The pH dependence of estradiol retention is similar to that of estrone as we reported previously (Schäfer et al., 2003). This can be attributed to the similarity in their molecular structures. A mass balance was carried out to determine the amount of estradiol adsorbed onto the membranes. At high pH, due to charge repulsion between the negatively charged estradiol molecule and the negative membrane surface, one would expect adsorption to be minimum. It was found that estradiol adsorption onto the membrane also depends on pH (Figure 1B). Figure 2 shows a strong linear correlation between estradiol adsorption and retention, which indicates that retention by the loose TFC-SR2 membrane is mainly due to adsorption. While the membrane can act as an estradiol sink to a limited extent, there is a risk of steroid hormone release, as it is a common practice to raise the pH to 11 during membrane cleaning.

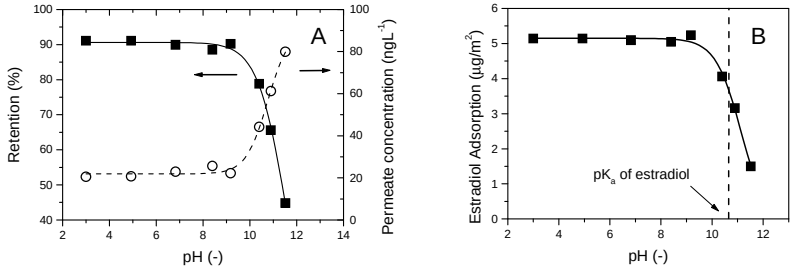


Figure 1: pH effect on permeate concentration, retention, and adsorption of estradiol by the TFC-SR2 membrane (feed solution: 100 ng/L estradiol, 1 mM $NaHCO_3$, 20 mM NaCl)

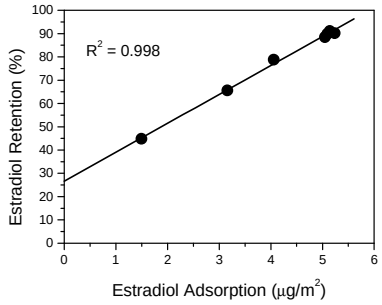


Figure 2: Correlation between retention and adsorption of estradiol by the TFC-SR2 membrane at the initial stages of filtration.

Breakthrough phenomena in nanofiltration

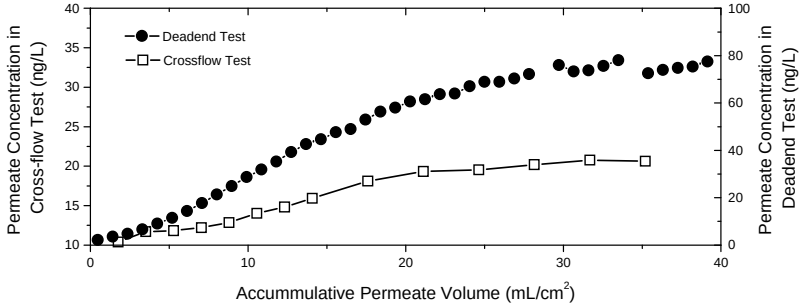


Figure 3: Permeate concentration of estrone in dead end and crossflow filtration with the TFC-S membrane as a function of permeate volume (feed solution: 100 ng/L estrone, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

Variation in water recovery and subsequent concentration factor can also induce the release of steroid hormones. To study this possibility, estrone retention by dead end filtration was compared to that by crossflow filtration using the TFC-S membrane. Dead end filtration experiments were conducted with a series of fresh feed solutions using the same membrane sample. A crossflow filtration experiment was conducted using a SEPA® cell (Osmonics, USA). Hormone adsorption took place until adsorption/desorption within the membrane has been equilibrated. Consequently, distinct breakthrough curves (see Figure 3), as often seen in activated carbon adsorption or ion exchange of other contaminants were observed in both dead end and cross flow filtration experiments. In both cases, the permeate concentration of the TFC-S membrane became stable below the feed concentration, which indicates some degree of retention due to steric interaction mechanism. However, due to a concentration buildup at the membrane surface and ineffective back diffusion during dead end filtration, the permeate concentration by this configuration was much higher than that of cross flow filtration. Results reported here indicate that increasing recovery (which reflects a move from cross flow to more dead end type filtration) may cause a substantial increase in permeate concentration of steroid hormones. This is important for risk management where retention of micro-pollutants such as hormones is essential.

Possible release of accumulated hormones

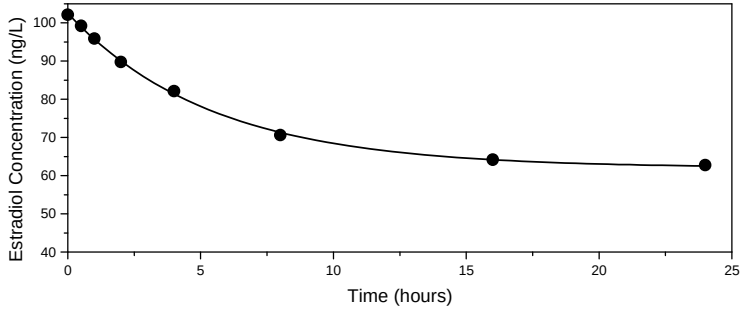


Figure 4: Static adsorption of estradiol onto the NF-270 membrane (feed solution: 100 ng/L estradiol, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

The accumulation of estradiol in an NF membrane and subsequent release was simulated. Estradiol solution of 300 mL was constantly agitated in a stirred cell containing a NF-270 membrane sample

without pressurization. Estradiol concentration in the stirred cell at a specified interval is presented in Figure 4. As there is no applied pressure and the solution does not have contact with the membrane supporting layer, the result indicates that the membrane active layer can accumulate a significant amount of estradiol.

At the end of the static adsorption experiment, estradiol concentration in the cell was 62 ng/L. A pressure of 5 bar (in dead end mode) was then applied to this solution to investigate possible desorption following accumulation. Adsorption of estradiol onto the membrane may be attributed to weak hydrogen bonding or hydrophobic interactions, which results in a dynamic and unstable equilibrium between adsorption and desorption. During membrane filtration, estradiol which has previously adsorbed onto the membrane active layer desorbs and contributes to a high permeate concentration as can be seen in Figure 5. A constant permeate concentration is also consistent with the fact that estradiol is desorbed from the membrane. The transport mechanism of estradiol through the membrane in this case is thought to be diffusion rather than convection; however, the role of water in facilitating this transport remains unclear.

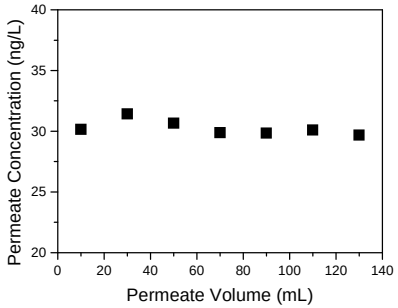


Figure 5: Permeate concentration of estradiol as a function of permeate volume after pre-adsorption (feed solution: 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

CONCLUSIONS

The risk of releasing the steroid hormones estradiol and estrone following adsorption in membrane filtration was investigated using three commercially available NF membranes. It appears that adsorption of estradiol onto the membrane strongly depends on solution pH. The low adsorption (and retention) at high pH due to charge repulsion between the negatively charged estradiol and the membrane surface raises the concern of estradiol release during membrane cleaning, where alkaline solutions at pH 11 are commonly applied. When the membrane adsorptive capacity has been exhausted, a breakthrough curve of steroid hormone was observed. Moving from crossflow to dead end filtration configuration can severely increase the breakthrough concentration. There is also a possibility of accumulation of steroid hormones in the membrane, followed by subsequent release.

The results indicate that nanofiltration may not be a complete barrier to many micro-pollutants such as hormones. This results not only in a reduced retention ability of some membranes (mechanisms are currently investigated) but also means that a release of the accumulated compounds can result in very high temporary permeate concentrations. The risks of such high concentrations require further investigation.

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