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- [14] Li, Q. and M. Elimelech, *Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms*. Environmental Science & Technology, 2004. **38**(17): p. 4683-4693.
- [15] Schäfer, A.I., *Natural Organics Removal using Membranes: Principles, Performance and Cost*. 2001: CRC Press Boca Raton.
- [16] Judd, S.J. and P. Hillis, *Optimisation of combined coagulation and microfiltration for water treatment*. Water Research, 2001. **35**(12): p. 2895-2904.
- [17] Aoustin, E., A.I. Schäfer, A.G. Fane, and T.D. Waite, *Ultrafiltration of natural organic matter*. Separation and Purification Technology, 2001. **22-23**: p. 63-78.
- [18] Waite, T.D., A.I. Schäfer, A.G. Fane, and A. Heuer, *Colloidal fouling of ultrafiltration membranes: impact of aggregate structure and size*. Journal of Colloid and Interface Science, 1999. **212**(2): p. 264-274.
- [19] Lee, N., G. Amy, J.-P. Croue, and H. Buisson, *Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM)*. Water Research, 2004. **38**(20): p. 4511-4523.

Critical Risk Points of NF/RO Membrane Filtration Processes in Water Recycling Applications

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Abstract

NF/RO membrane filtration processes have been recognized as an important technology to facilitate water recycling. Those processes are well-proven technologies, which can be used to remove a wide range of contaminants including trace contaminants that are of particular concern in water recycling. However, risk implications in association with brine or concentrate and membrane cleaning wastewater disposal have to date not been adequately understood. This study examines the adsorption and release process of several endocrine-disrupting chemicals (EDCs) during NF/RO filtration processes. Results reported here indicate that the membrane can serve as a large reservoir for EDCs and their release may be possible during membrane cleaning or erratic pH variation during operation. Treatment of membrane cleaning solution should be carefully considered when EDCs are amongst the target contaminants in NF/RO membrane filtration.

Keywords: hormones, endocrine-disrupting chemicals (EDCs), release, membrane, nanofiltration, reverse osmosis, risk.

1. Introduction

Water recycling has been recognized as a key approach to alleviate water shortage, which has now become a worldwide issue. While available advanced technologies such as membrane filtration, advanced oxidation, and carbon adsorption have been instrumental in propelling water recycling forward, several obstacles associated with the occurrence of trace contaminants in treated effluents remain unresolved. Notorious amongst these trace contaminants is a group called endocrine disrupting chemicals (EDCs). There is concrete evidence that these EDCs can disrupt the endocrine system of vertebrates even at a very low concentration, resulting in numerous adverse health effects [1, 2]. A substantial amount of dedicated research work has attempted to apply advanced treatment processes to remove such EDCs in water recycling. While results are generally promising, numerous uncertainties and knowledge gaps persist [3]. Removal of many compounds is incomplete or results in other problems and risks. This is arguably because new and unconventional technologies are being applied on an emerging group of trace contaminants. Advanced oxidation processes or oxidation treatment technology in general can sometimes result in degradation byproducts, very often with unknown toxicological properties. Some byproducts may be even more potent than their parent compounds. The use of carbon adsorption technology may entail complicated treatment of spent adsorbent, while treatment and disposal of concentrate (or retentate/brine) remains a major issue for nanofiltration/reverse osmosis (NF/RO) filtration processes.

NF/RO membrane filtration is a well-proven technology to remove trace contaminants such as EDCs in water recycling [4-6] and has been applied at large scale.

Luggage Point, Water Reclamation and Management Scheme at Sydney Olympic Park, Port Kembla water recycling projects (in Australia), and the Newater project (in Singapore) are some typical examples [7]. However, risk implications in association with concentrate and spent cleaning solution disposal are to date not adequately understood. This study emphasises such critical points of risk. Focusing on the adsorption and release processes of EDCs during membrane filtration, this study highlights potential risks associated with the treatment, disposal of concentrate and membrane cleaning wastewater as well as provides orders of magnitudes of concentrations to be expected. Estimations are based on research investigations and assumptions realistic for large scale applications.

2. Materials & Methods

2.1. Membranes

To determine the adsorption of EDCs to membrane surfaces, four thin-film composite NF membranes — denoted as NF-270, TFC-SR2, TFC-S, and X-20 were selected. The NF-270 membrane was supplied by Dow Chemicals (Minneapolis, USA). According to the manufacturer, the NF-270 is a high salt passage and high organic removal NF membrane. A recent study reported that this membrane consists of very thin active layer of polyamide of approximately 20 nm [8] on top of a porous polysulfone supporting layer. The TFC-SR2 and TFC-S membranes were supplied by Koch Membrane Systems (San Diego, CA), while the X-20 membrane was supplied by Trisep Corporation (Goleta, CA). Membrane materials and selected properties of these membranes are summarized in Table 1. Such membranes are used in large scale recycling projects.

Table 1 Characteristics of the selected membranes (data from a previous study [9]; ^a data obtained in this study)

Membrane	Average Permeability [Lm ⁻² h ⁻¹ bar ⁻¹]	Contact Angle (°)	Sodium Retention [%]	Membrane Material
X20	3.8	32.6	95.7	Polyamide-urea
TFC-S	11.0	18.7	76.5	Polyamide on polysulfone support
TFC-SR2	15.4	30.7	9.80	
NF-270	13.5 ^a	55.0 ^a	40.0 ^a	

2.2. Selected EDCs & analysis

Seven notable endocrine disrupting chemicals (EDCs) were selected for this study, namely nonylphenol (NP), tertbutylphenol (TBP), and bisphenol A (BPA) presenting hormone mimicking compounds (HMCs); and estrone (E1), estradiol (E2), progesterone (P), and testosterone (T) presenting natural steroid hormones (NSHs). These compounds are commonly found at trace levels in both surface waters receiving treated effluents and secondary wastewaters [10-15]. As can be seen in their molecular structures presented in Figure 1, these compounds possess hydroxyl or carbonyl groups and are hence capable of hydrogen bonding with a suitable substrate (in this case membranes) but also to other solids in wastewater, and hence prone to adsorption.

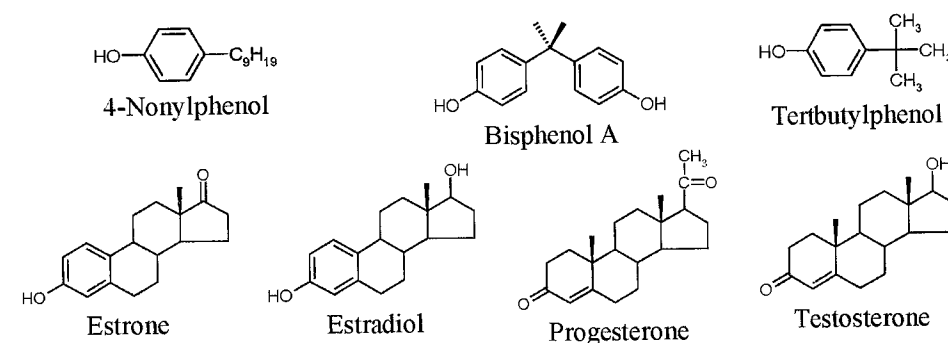


Figure 1 Molecular structure of trace organic contaminants selected in this study.

Physicochemical characteristics of EDCs strongly influence the adsorption. Molecular weight and several other physicochemical properties including solubility in water, pK_a, and logK_{ow} of the selected EDCs are presented in Table 2. These selected compounds are low molecular weight organics within the range from 150 g/mol to 315 g/mol. They have moderate to high logK_{ow} values. This indicates that they readily adsorb to hydrophobic materials such as the membrane surfaces under favourable conditions.

Table 2 Physicochemical properties of EDCs used in this study (LogK_{ow} was determined using a commercial software Pallas 3.0 [16], na: data not available or not applicable)

Compound	Molecular weight (g/mol)	Solubility (mg/L)	pK _a (-)	LogK _{ow} (-)
Tertbutylphenol	150	700	10.2	3.31
4-Nonylphenol	220	5	10.3	4.48
Bisphenol A	228	120	10.1	3.32
Estradiol	272	13	10.4	4.01
Estrone	270	13	10.4	4.54
Testosterone	288	na	na	3.84
Progesterone	315	na	na	4.63

All chemicals used in this study were of analytical grade. Radiolabeled estrone-2,4,6,7-³H(N) and progesterone-2-4,6,7-³H(N) were purchased from Sigma Aldrich (Saint Louis, MO) and estradiol-2,4-³H(N) and testosterone-2,3-³H(N) were purchased from Perkin Elmer (Boston, MA). Steroid hormones were analysed using a Perkin-Elmer scintillation counter (Tri-Carb 2900 TR). The detection limit of this technique has previously been determined to be approximately 0.1 ng/L [9]. 4-Nonylphenol, bisphenol A, and tertbutylphenol were purchased from Sigma Aldrich (Saint Louis, MO). These hormone mimicking compounds were analysed using an HPLC system with an UV detector at a wavelength of 280 nm. The mobile phase contained DI water and HPLC-grade acetonitrile. The gradient program was optimised for each compound. The detection limit of the technique is approximately 10 µg/L.

2.3. Membrane filtration units & filtration protocol

A standard cross flow system and a dead end filtration stirred cell were used in this study. Both of them have been described in detail previously [9, 17]. In the stirred cell, a Teflon coated Amicon magnetic stirrer was used and the speed was set at 400 rpm to minimize concentration polarization. Prior to each filtration experiment, the membrane was compacted for 1 hour using DI water at 10 bar. For all experiments, estrone, estradiol, progesterone, and testosterone concentration in the initial feed solution was 100 ng/L. Likewise, bis-phenol A, 4-nonylphenol, and tertbutylphenol

concentration in the initial feed solution was 600 µg/L. All compounds were studied individually. Permeate samples were consequently collected in 20 mL scintillation vials.

2.4. Static adsorption experiments

Static adsorption refers to adsorption without applied pressure and hence permeation. This allows the examination of EDCs adsorption only to the membrane surface (active layer). Static adsorption tends to be lower than adsorption during filtration. For all static adsorption experiments estradiol and progesterone concentrations in the initial feed solution were 100 ng/L. The test solution was introduced to a stirred cell with a membrane sample in place. The solution was constantly agitated and no pressure was applied during the experiments unless otherwise stated. The samples were taken at specific time intervals for analysis.

2.5. Adsorption during filtration

When adsorption of EDCs to the membrane has reached equilibrium, concentration in the concentrate can be quantified based on a simple mass balance. The membrane recovery and retention are defined in Eq. 1 and 2, respectively.

$$\text{Rec} = 100 \times \frac{Q_P}{Q_F} [\%] \quad (1)$$

$$\text{Ret} = 100 \times \left(1 - \frac{C_P}{C_F}\right) [\%] \quad (2)$$

where Q_P , Q_F , C_P , and C_F are the feed flow rate, permeate flow rate, permeate concentration and feed concentration, respectively. From Eq. 1 and 2, the concentrations in the permeate (C_P) and concentrate (C_C) can be expressed as:

$$C_P = \left(1 - \frac{\text{Ret}}{100}\right) \times C_F [\text{g/L}] \quad (3)$$

$$C_C = \frac{(C_F - C_P \times \text{Rec}/100)}{(1 - \text{Rec}/100)} [\text{g/L}] \quad (4)$$

While permeate concentration is usually measured in recycling applications, concentrate characteristics are rarely monitored.

2.6. Spent cleaning solution concentration

Cleaning in Place Programs (CIPs) are designed to remove deposits on the membrane surface and restore water flux. Specific chemical formulae will target different foulants including microorganisms, scales, as well as gel layers or adsorbed organic compounds [18]. Of interest here is the desorption of EDCs that have previously adsorbed to the membrane, and their likely concentration in the spent cleaning solution. The concentration of EDCs in spent membrane cleaning solution can be calculated as follows:

$$C_{\text{Spent}} = \frac{\Gamma \times A}{V} [\text{g/L}] \quad (5)$$

where C_{Spent} is the EDC concentration in the spent cleaning solution, Γ is the amount adsorbed to the membrane per meter square, A is the membrane area, and V is the cleaning solution volume.

3. Results & Discussion

3.1. Adsorption of EDCs and possible desorption

Lab-scale cross flow filtration experiments were carried out with small membrane samples to determine the adsorbed amount of EDCs to the membranes. Adsorbed amount was calculated using mass balance when membrane saturation has been achieved, which is after approximately 24 hours in typical experiments. Adsorption of EDCs used in this study (per one square meter) to the NF 270 membrane is presented in Figure 2. Results are expressed in µg or ng per m² of membrane. The HMCs adsorbed significantly more to the NF 270 membrane than the NSHs due to the fact that the initial HMC concentration was 6,000 times higher than that of steroid hormones (which corresponds to the levels found in wastewaters). Although all EDCs in this study have quite similar $\log K_{ow}$ value, ranging from moderate to high, there is a weak correlation between the amount of EDCs adsorbed to the NF-270 membrane and their $\log K_{ow}$ values. This indicates that adsorption is driven by hydrophobic interactions to a certain extent. Apart from $\log K_{ow}$, other physicochemical parameters of the organic solute such as dipole moment and dielectric constant may also influence adsorption [19], but are difficult to obtain for such compounds.

Adsorption can also depend on several factors related to the membrane properties including the nature of the polymeric membrane material, membrane hydrophobicity (represented by contact angle), and membrane surface roughness that ultimately determines the available adsorption surface. As can be seen in Figure 3, adsorption of estrone to the four membranes used in this study varies considerably. While the NF 270 membrane has the highest contact angle (most hydrophobic), it also has a relatively high permeability, which to some extent suggests that the membrane is a loose NF membrane with a more open pore size (see Table 2). Those characteristics no doubt contribute to the increased adsorption of estrone.

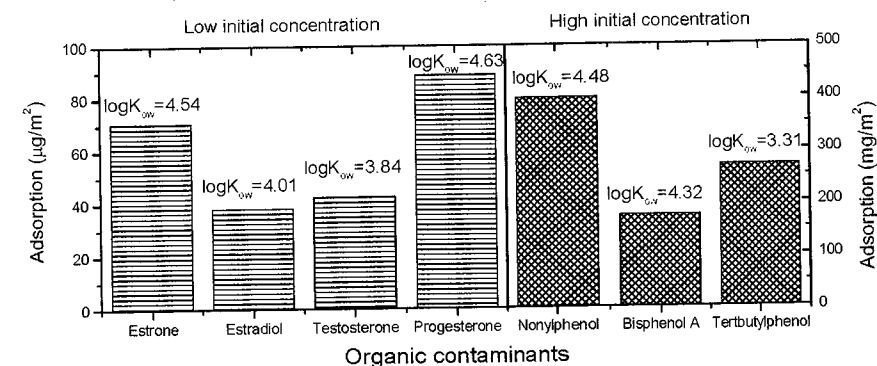


Figure 2 Estimated adsorbed amount of trace contaminants to the NF 270 membrane. Initial solution concentration for NSHs 100 ng/L or hormone mimicking compounds 600 µg/L in a background solution containing 20 mM of NaCl and 1 mM of NaHCO₃, pH ~ 8.0.

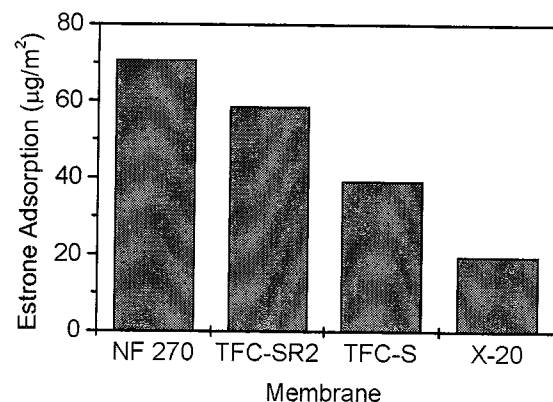


Figure 3 Adsorbed amount of NSH estrone on four membranes used in this study. Initial solution contains 100 ng/L of estrone in a background solution containing 20 mM of NaCl and 1 mM of NaHCO₃, pH ~ 8.0.

Initial concentrations used in this study probably presents a worst case scenario while treated effluents and environmental concentrations of these contaminants can be significantly lower, typically in the range of 1 ng/L or less [10-12, 20]. However, considering the amounts adsorbed reported in Figure 2 and Figure 3, there is potentially a considerable risk of EDCs release from the membrane during cleaning or erratic operating conditions. This is particularly so when considering that a concentration of only 1 ng/L of estradiol can show a distinctive endocrine disrupting effect on fish. Other toxicological effects are largely unknown and may increase with the presence of a synergetic mixture of compounds [21]. The membrane area in a typical 8-inch module used in large scale applications is approximately 37 m² [20]. If released, the amount of estradiol adsorbed to 10 membrane modules would hence be sufficient to contaminate a water volume of 140,000 ML at 1 ng/L concentration, equivalent to the entire daily output of the Mery Sur Oise treatment plant – the world largest nanofiltration plant for drinking water production, although small quantities of highly contaminated water may also be of concern. It must be emphasised that this is a relatively new and difficult issue, which is much debated in the field at the present.

3.2. Release of EDCs during operation

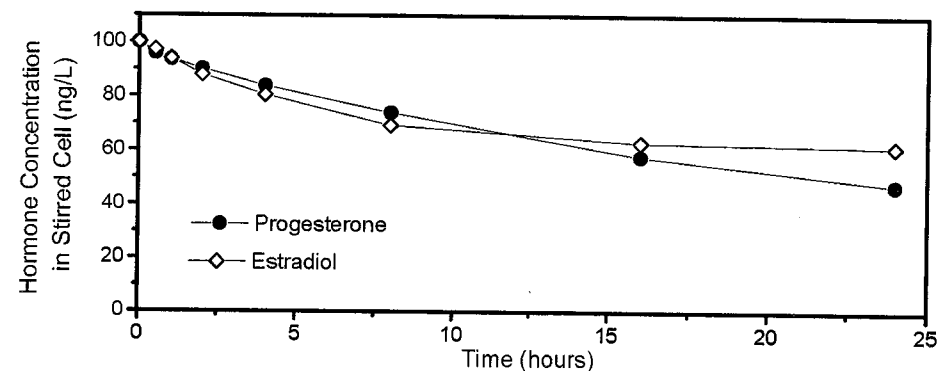


Figure 4 Static adsorption of 2 NSHs onto the NF-270 membrane (feed solution: 100 ng/L hormone, 1 mM NaHCO₃, 20 mM NaCl, and pH ~ 8.0).

Further to the above adsorption studies, the accumulation of two NSHs in an NF membrane and subsequent release was tested experimentally. Estradiol and progesterone solutions were constantly agitated in a stirred cell containing a NF-270 membrane sample without pressurization. NSH concentration in the stirred cell at a specified interval is presented in Figure 4. The decrease in concentration can be attributed to adsorption.

Since the adsorption (or partitioning) process was accomplished via weak form of secondary bonding, desorption and adsorption can simultaneously occur. Following the adsorptive saturation of the membrane, when the static adsorption has reached equilibrium, filtration is started at 60 psi (4.5 bar). The feed concentration of then approximately 60 ng/L results in relatively high permeate concentration (see Figure 5).

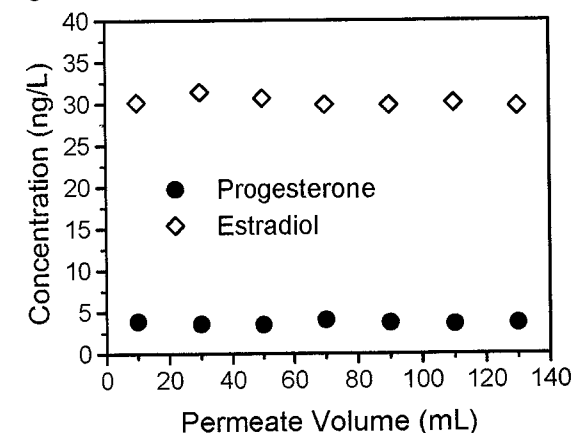


Figure 5 Permeate concentration of 2 NSHs as a function of permeate volume after pre-adsorption (see Figure 4) (feed solution: 1 mM NaHCO₃, 20 mM NaCl, and pH ~ 8.0).

Given that the average pore diameter of the membrane is 0.82 nm [17] and the Stokes diameter of estradiol is estimated to be 0.80 nm [22, 23], the high estradiol concentration in the permeate clearly indicates that estradiol which is previously partitioned to the membrane desorbs to the permeate. A much lower permeate concentration of progesterone is observed since it has a larger MW, corresponding to a larger Stokes diameter of 0.86 nm. This result is consistent with our previous findings that NSHs after being adsorbed to the membrane surface can diffuse through a very thin active layer of the nanofiltration membrane [17]. A high concentration gradient due to the adsorption (or partitioning) of NSHs to the membrane can further increase the extent of this diffusion. The diffusion process depends on the EDC diffusivity within the polymer matrix and also on the polymer density and skin layer thickness of the membranes; therefore, it may be lessened for dense RO membranes that usually have a much thicker active skin layer. However, it is possible that the membranes can act as a reservoir for EDCs and release compounds back into the concentrate stream, resulting in erratic concentration of EDCs in the concentrate, which is often observed in large scale application monitoring.

3.3. Release of EDCs during cleaning

In practice, NF membranes are regularly cleaned by a cleaning solution that has a pH around 11 and usually consists of caustic soda combined with surfactant such as EDTA or sodiumdodecylsulfate and enzyme cleaners, although sometimes an acidic cleaning step may also be included. Seeing the pK_a values of several EDCs as listed in

Table 2, those compounds can dissociate and become negatively charged at this pH and a significant amount of EDCs will hence desorb into the cleaning solution. To test this hypothesis, at the completion of the static adsorption of estradiol to the NF 270 membrane (at pH 8), the depleted feed solution was replaced by a background solution containing no estradiol, at pH 11. A pressure of 60 psi (4.5 bar) was then applied. The estradiol concentration in the permeate samples is presented in Figure 6. As can be seen, desorption of estradiol at pH 11 occurs instantaneously. Estradiol concentration in the permeate decreases as estradiol is desorbed (and hence depleted) from the membrane polymer matrix. In practice, cleaning is usually accomplished at high cross flow velocity with negligible transmembrane pressure. In which case, the estradiol would desorb into the cleaning solution but some may still leak into the permeate stream. Results reported here clearly imply that wastewater obtained from the cleaning process may contain a significant amount of EDCs, which should be taken into account for later treatment and disposal. It is further possible that permeate will contain a higher concentration of EDCs as filtration recommences after cleaning.

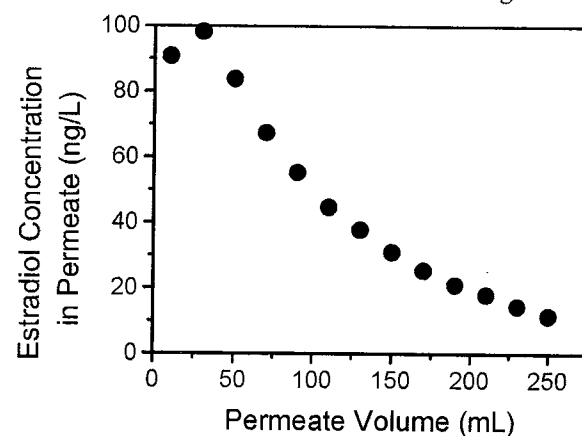


Figure 6 Permeate concentration of estradiol during cleaning as a function of permeate volume after pre-adsorption (feed solution: 1 mM NaHCO₃ and 20 mM NaCl, no estradiol, and pH 11.0).

3.4. Fate of EDCs in NF/RO filtration processes

Membrane filtration is a physical separation process, which separates contaminants from the solvent (water) and transfers them to the concentrate. Concentrate treatment and subsequent disposal have therefore become an essential issue [24], particularly when EDCs are of concern. A schematic diagram showing estimated estrone concentrations in the feed, permeate, concentrate, and spent membrane cleaning solution is shown in

Figure 7. These concentrations are in good agreement with pilot scale experimental results reported previously [25]. It is noteworthy that the actual estimation may be complicated by adsorption (and desorption) of EDCs to (and from) the membrane. In this case, it is assumed that there is sufficient filtration time at stable conditions before membrane cleaning for the partitioning process to reach equilibrium. In practice, it is expected that the concentrate concentration would increase gradually as the membrane adsorptive capacity is reducing. Concentrate concentration reaches a value as estimated in

Figure 7, when the membrane adsorptive capacity has been exhausted. As discussed in section 3.3, complete desorption may occur during membrane cleaning

with high pH solution. EDC concentration in the concentrate (and to a limited extent in the permeate) may exhibit a cyclic pattern in accordance to the cleaning regime.

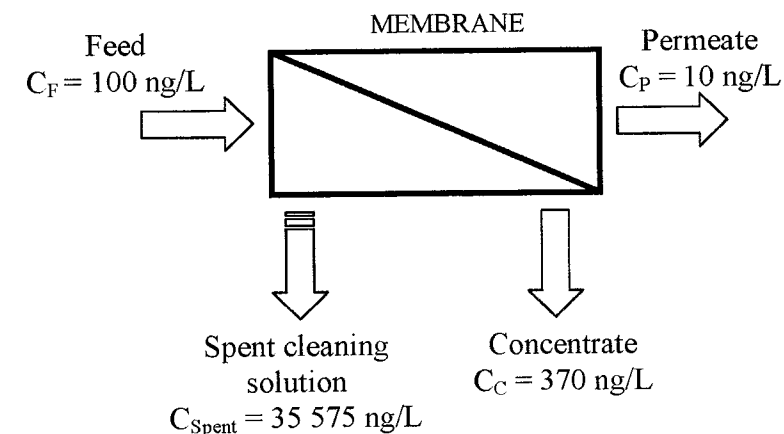


Figure 7 Estimated concentration of estradiol in different streams for assumed values of 90 % retention, recovery 75 % and cleaning solution volume of 40 litres per one 8-inch membrane element with a membrane area of approximately 37 m². Adsorbed amount of estradiol to the membrane at saturation is taken from Figure 2 (for the NF 270 membrane). Estradiol concentration in the spent solution was calculated using Eq. 5.

EDC concentration in the spent cleaning solution depends largely on the amount of EDC adsorbed to the membrane prior to cleaning and also on the volume of the cleaning solution. The cleaning solution volume for a spiral wound element should be at least adequate to fill in the volume of the membrane vessels, filters, and piping, which again depends on system design. The typical cleaning solution volume required for one 8-inch membrane spiral wound element is approximately 40 litres [26]. This value is used in this study to estimate the concentration of EDCs in spent membrane cleaning solution. As demonstrated in

Figure 7, EDC concentration in the spent cleaning solution can be extremely high. Furthermore, it is common practice to circulate the cleaning solution over a number of membrane vessels. Hence, EDC concentration in the spent cleaning solution may be even higher than estimated here. Although as mentioned earlier this probably presents a worst case scenario, due care need to be dedicated to the treatment and disposal of spent cleaning solution.

4. Conclusions

NF/RO membrane filtration processes are widely used in water recycling applications, particularly to remove trace organics such as endocrine disruptors. However, to date, risk implications in association with concentrate and membrane cleaning solution disposal have not been adequately addressed. This study focused on such critical points of concern in an attempt to quantify the scale of problems. Results reported here indicate that the membrane can serve as a large reservoir for EDCs and their release is likely during membrane cleaning or erratic pH variation during operation. Complete desorption of EDC to the membrane cleaning solution at high pH results in a high concentration of EDCs in the spent cleaning solution. Treatment of the concentrate and the spent cleaning solution need to be considered when EDCs are amongst the target contaminants in NF/RO applications.

Acknowledgements

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Reference

- Purdom, C.E., P.A. Hardiman, V.J. Bye, N.C. Eno, C.R. Tyler, and J.P. Sumpter, *Estrogenic effects of effluents from sewage treatment works*. *Journal of Chemistry and Ecology*, 1994. **8**: p. 275-285.
- Routledge, E.J., J. Parker, J. Odum, J. Ashby, and J.P. Sumpter, *Some alkyl hydroxy benzoate preservatives (parabens) are estrogenic*. *Toxicology and Applied Pharmacology*, 1998. **153**: p. 12-18.
- Daughton, C.G. and T.A. Ternes, *Pharmaceuticals and personal care products in the environment: Agents of subtle change?* *Environmental Health Perspectives*, 1999. **107 Supplement 6**: p. 907-938.
- Kimura, K., G. Amy, J.E. Drewes, T. Heberer, T.-U. Kim, and Y. Watanabe, *Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes*. *Journal of Membrane Science*, 2003. **227(1-2)**: p. 113-121.
- Nghiem, L.D., A. Manis, K. Soldenhoff, and A.I. Schäfer, *Estrogenic hormone removal from wastewater using NF/RO membranes*. *Journal of Membrane Science*, 2004. **242(1-2)**: p. 37-45.
- Wintgens, T., M. Gallenkemper, and T. Melin, *Endocrine disrupter removal from wastewater using membrane bioreactor and nanofiltration technology*. *Desalination*, 2002. **146(1-3)**: p. 387-391.
- Radcliffe, J.C., *Water recycling in Australia*. 2004: Australian Academy of Technological Science and Engineering.
- Freger, V., *Nanoscale heterogeneity of polyamide membranes formed by interfacial polymerization*. *Langmuir*, 2003. **19**: p. 4791-4797.
- Schäfer, A.I., D.L. Nghiem, and T.D. Waite, *Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis*. *Environmental Science & Technology*, 2003. **37(1)**: p. 182-188.
- Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, and H.T. Buxton, *Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance*. *Environmental Science & Technology*, 2002. **36(6)**: p. 1202-1221.
- Ternes, T.A., P. Kreckel, and J. Mueller, *Behaviour and occurrence of estrogens in municipal sewage treatment plants - II. Aerobic batch experiments with activated sludge*. *The Science of the Total Environment*, 1999. **225**: p. 91-99.
- Ternes, T.A., M. Stumpf, J. Mueller, K. Haberer, R.-D. Wilken, and M. Servos, *Behavior and occurrence of estrogens in municipal sewage treatment plants - I. Investigations in Germany, Canada and Brazil*. *The Science of the Total Environment*, 1999. **225**: p. 81-90.
- Ternes, T.A., *Occurrence of drugs in German sewage treatment plants and rivers*. *Water Research*, 1998. **32(11)**: p. 3245-3260.
- Ying, G.-G., B. Williams, and R. Kookana, *Environmental fate of alkylphenols and alkylphenol ethoxylates - A review*. *Environment International*, 2002. **28(3)**: p. 215-226.
- Ying, G.-G., R.S. Kookana, and Y.-J. Ru, *Occurrence and fate of hormone steroids in the environment*. *Environment International*, 2002. **28(6)**: p. 545-551.
- Pallas, *PrologP*, CompuDrug Chemistry Ltd: Sedona, AZ.
- Nghiem, D.L., A.I. Schäfer, and M. Elimelech, *Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms*. *Environmental Science & Technology*, 2004. **38**: p. 1888-1896.
- Schäfer, A., N. Andritsos, A.J. Karabelas, E.M.V. Hoek, R. Scheider, and M. Nystrom, *Fouling in nanofiltration*, in *Nanofiltration - Principles and applications*, A. Schäfer, D. Waite, and A. Fane, Editors. 2004, Elsevier. p. 169-239.
- Van der Bruggen, B., L. Braeken, and C. Vandecasteele, *Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds*. *Desalination*, 2002. **147(1-3)**: p. 281-288.
- Nghiem, D.L. and A.I. Schäfer, *Trace contaminant removal with nanofiltration*, in *Nanofiltration - Principles and Applications*, A.I. Schäfer, A. Fane, and D. Waite, Editors. 2004, Elsevier Science.
- Arnold, S.F., D.M. Klotz, B.M. Collins, P.M. Vonier, L.J. Guillet Jr., and J.A. McLachlan, *Synergistic activation of estrogen receptor with combinations of environmental chemicals*. *Science*, 1996. **272(5267)**: p. 1489-1492.
- Schäfer, A.I., *Natural Organic Matter Removal using Membranes: Principles, Performance and Cost*. 2001: CRC Press.
- Worch, E., *Eine neue Gleichung zur Berechnung von Diffusionskoeffizienten gelöster Stoffe*. *Vom Wasser*, 1993. **81(289-297)**.
- Van der Bruggen, B., L. Lejon, and C. Vandecasteele, *Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes*. *Environmental Science & Technology*, 2003. **37(17)**: p. 3733-3738.
- Khan, S.J., T. Wintgens, P. Sherman, J. Zaricky, and A.I. Schäfer, *Removal of hormones and pharmaceuticals in the advanced water recycling demonstration plant in Queensland, Australia*. *Water Science and Technology*, 2004. **50(5)**: p. 15-22.
- Lavasol Membrane Cleaning Procedure* (<http://www.pwtinc.com/lavasol.htm>). Accessed on 15th Dec. 2004.