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. It is a well-proven technology, 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 is be possible during membrane cleaning or erratic pH variation during operation. Treatment of membrane cleaning wastewater should be carefully considered when EDCs are amongst the target contaminants in NF/RO membrane filtration.

Keywords hormones, 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 to some extent. 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. The results are promising; however, numerous knowledge gaps persist. This is arguably because new and unconventional technologies are being applied on an emerging group of trace contaminants. Advanced oxidation or oxidation treatment technology in general can sometime result in degradation byproducts, very often with unknown toxicological properties. In the worst case, some byproducts are 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 NF/RO filtration processes.

NF/RO membrane filtration is a well-proven technology to remove trace contaminants such as EDCs in water recycling [3-5]. However, risk implications in association with concentrate and spent cleaning solution disposal have to date not been adequately understood. This study emphasises such critical points of concern. Focusing on the adsorption and release processes of EDCs during membrane filtration, this study highlights potential risks associated with the treatment and disposal of concentrate and membrane cleaning wastewater.

2. Materials & Methods

2.1. Membranes

Four thin-film composite NF membranes ― denoted as NF-270, TFC-SR2, TFC-S, and X-20 were selected for this study. 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 [6] 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.

Table 1 Characteristics of the selected membranes (data from a previous study [7]; [a] data obtained in this study)

Membrane	Average Permeability [$Lm^{-2}h^{-1}bar^{-1}$]	Contact Angle (^{o})	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; and estrone (E1), estradiol (E2), progesterone (P), and testosterone (T) presenting natural steroid hormones. These compounds are commonly found at trace levels in both surface waters receiving treated effluents and secondary wastewaters [8-13]. 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.
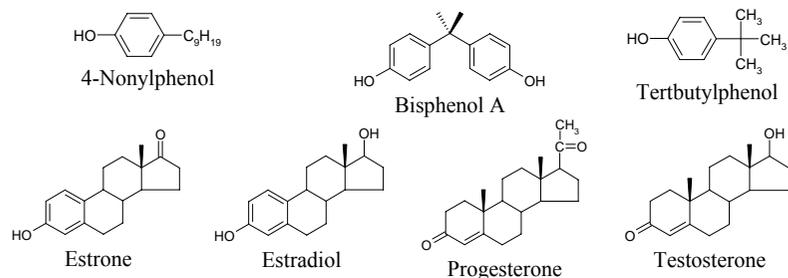
Figure 1 Molecular structure of trace organic contaminants selected in this study.

Molecular weight and several other physicochemical properties including solubility in water, pK_a, and log K_{ow} of the selected EDCs are presented in Table 2. As can be seen 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 log K_{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 (Log K_{ow} was determined using a commercial software Pallas 3.0 [14], na: data not available or not applicable)

Compound	Molecular weight (g/mol)	Solubility (mg/L)	pK_a	Log K_{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-[3]H(N) and progesterone-2-4,6,7-[3](H)(N) were purchased from Sigma Aldrich (Saint Louis, MO) and estradiol-2,4-[3](H)(N) and testosterone-2,3-[3](H)(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 [7]. 4-Nonyl phenol, 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-V detector at a wavelength of 280 nm. The mobile phase contained DI water and HPLC-grade acetonitrile. The gradient program was optimized 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 and dead end filtration stirred cells were used in this study. Both of them have been described in detail previously [7, 15]. 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. 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. Permeate samples were consequently collected in 20 mL scintillation vials.

2.4. Static adsorption experiments

For all static adsorption experiments (where static refers to adsorption without applied pressure and hence permeation), 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. Mass balance calculations

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

$$\mathrm{Re}\,c = \frac{Q_P}{Q_F} \tag{1}$$

$$\mathrm{Re}\,t = 100 \times \left(1 - \frac{C_P}{C_F}\right) \tag{2}$$

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:

$$C_P = \left(1 - \frac{\mathrm{Re}\,t}{100}\right) \times C_F \tag{3}$$

$$C_C = \frac{\left(C_F - C_P \times \mathrm{Re}\,c\right)}{\left(1 - \mathrm{Re}\,c\right)} \tag{4}$$

The concentration of EDCs in spent membrane cleaning solution can be calculated as follows:

$$C_{Spent} = \frac{\Gamma \times A}{V} \tag{5}$$

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

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 last approximately 24 hours in typical conditions. Adsorption of EDCs used in this study (per one square meter) to the NF 270 membrane is presented in Figure 2. Three hormone mimicking compounds (HMCs) adsorbed significantly more to the NF 270 membrane than the steroid hormones. This probably reflects the fact that initial HMC concentration was 6,000 times higher than that of steroid hormones. Although all EDCs in this study have quite similar log K_{ow} values, ranging from moderate to high, there is a weak correlation between the amounts 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 Kow, other physicochemical parameters of the organic solute such as dipole moment and dielectric constant may also influence adsorption [16].

Adsorption can also be influenced by several factors related to the membrane properties including the nature of the polymeric membrane material, membrane hydrophobicity (represented

by contact angles), 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 suggest that the membrane is a loose NF membrane with open pore size (see Table 2). Not surprisingly, it adsorbs estrone considerably more than the others.
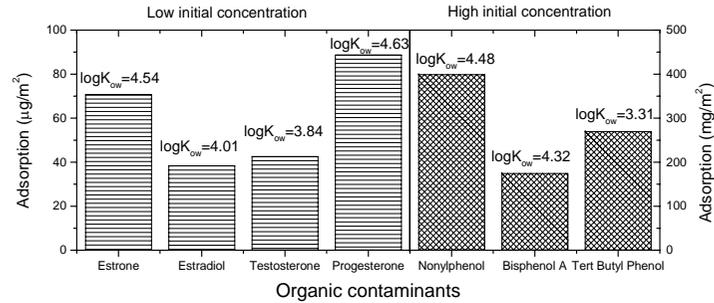
Figure 2

Estimated adsorbed amount of trace contaminants to the NF 270 membrane. Initial solution concentration for steroid hormones 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.
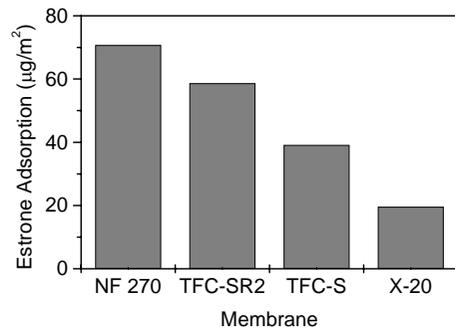

Figure 3 Adsorbed amount of estrone on four membranes in this study. Initial solution contains 100 ng/L of estrone in a background solution containing 20 mM of NaCl, and 1 mM of NaHCO₃, pH ~ 8.0.

Initial concentrations used in this study probably presents a worst case scenario and actual environmental concentration of these contaminants can be significantly lower, typically in the range of 1 ng/L or less [8-10, 17]. Results reported in Figure 2 and Figure 3 demonstrate a considerable risk of EDCs release from the membrane during cleaning or erratic operating conditions. At a concentration of only 1 ng/L, estradiol can show a distinctive endocrine disrupting effect on fish. Membrane area in a typical 8-inch module is approximately 37 m^2 [17]. If released, the amount of estradiol adsorbed to 10 membrane modules would 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. It must be emphasized that this is a new and difficult issue, which is still attracting hotly debates from the scientific world.

3.2.   *Release of EDCs during operation*

The accumulation of hormone in an NF membrane and subsequent release was simulated. Estradiol and progesterone solutions were constantly agitated in a stirred cell containing a NF-270

membrane sample without pressurization. Hormone concentration in the stirred cell at a specified interval is presented in Figure 4.
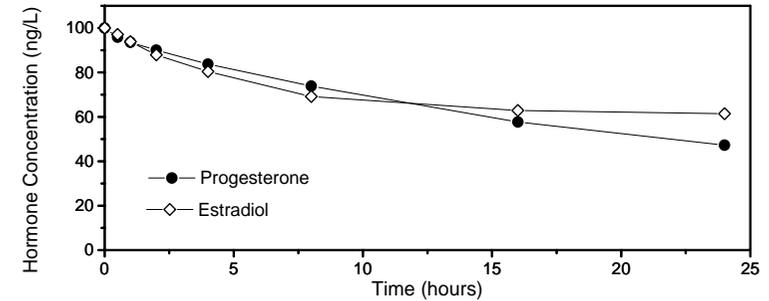

Figure 4 Static adsorption of estradiol and progesterone onto the NF-270 membrane (feed solution: 100 ng/L hormone, 1 mM NaHCO₃, 20 mM NaCl, and pH 8.0).
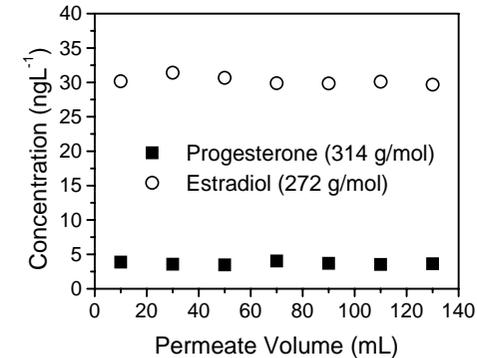

Figure 5 Permeate concentration of estradiol and progesterone as functions of permeate volume after pre-adsorption (feed solution: 1 mM NaHCO₃, 20 mM NaCl, and pH 8.0).

Since the adsorption (or partitioning) process was accomplished via weak form of secondary bonding, desorption and adsorption can simultaneously occur. At the completion of the static adsorption (see Figure 4), the depleted feed solution was filter through the NF-270 under a pressure of 60 psi (4.5 bar). Given that the average pore diameter of the membrane is 0.82 nm [15] and the Stokes diameter of estradiol is estimated to be 0.80 nm [18, 19], high estradiol concentration in the permeate (see Figure 5) 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 steroid hormones after being adsorbed to the membrane surface can diffuse through a very thin layer of the nanofiltration active skin [15]. Furthermore, a high concentration gradient due to the adsorption (or partitioning) of steroid hormones to the membrane can also contribute to this diffusion. This diffusion process depends on the organic 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.

3.3. Release of EDCs during cleaning

In practice, NF membranes are regularly cleaned by a cleaning solution that has pH around 11 and usually consists of caustic soda combined with surfactant such as EDTA or sodiumdodecylsulfate and enzyme cleaners. However, given the pK_a values of several EDCs as listed in Table 2, they can dissociate and become negatively charged at this pH and a significant amount of EDCs can 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. The pH of this background solution was 11. A pressure of 60 psi (4.5 bar) was then applied. Estradiol concentration in the permeate samples is presented in Figure 6. As can be seen in Figure 6, desorption of estradiol at pH 11 occurs instantaneously. Estradiol concentration in the permeate decreases as estradiol is desorbed from the membrane polymer matrix. In practice, cleaning is usually accomplished at high cross flow velocity with negligible transmembrane pressure. Although the possibility that EDCs can desorb into the permeate side of the membrane during cleaning in minimal, results reported here clearly implies that wastewater obtained from the cleaning process may contain a significant amount of EDCs, which should be taken into account for later disposal. It is further possible that permeate will contain a higher concentration of EDCs as filtration recommences.
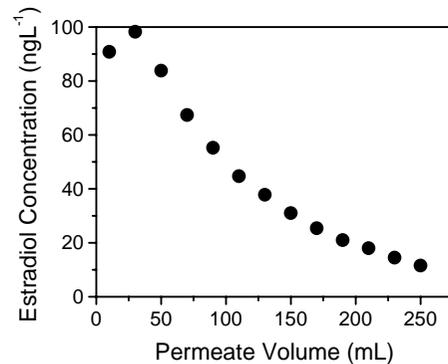

Figure 6 Permeate concentration of estradiol as a function of permeate volume after pre-adsorption (feed solution: 1 mM NaHCO₃, 20 mM NaCl, no estradiol, and pH 11.0).

3.4. Fate of EDCs in NF/RO filtration processes

Membrane filtration is purely a physical separation process, which separate contaminants from the solvent (water) and transfer them to the concentrate. Concentrate treatment and subsequent disposal have therefore become an essential issue [20], particularly when it involves high concern trace contaminants such as EDCs. 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 [21]. It is noteworthy that actual process 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 before membrane cleaning for the partitioning process to reach equilibrium. In practice, it is expected that 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.
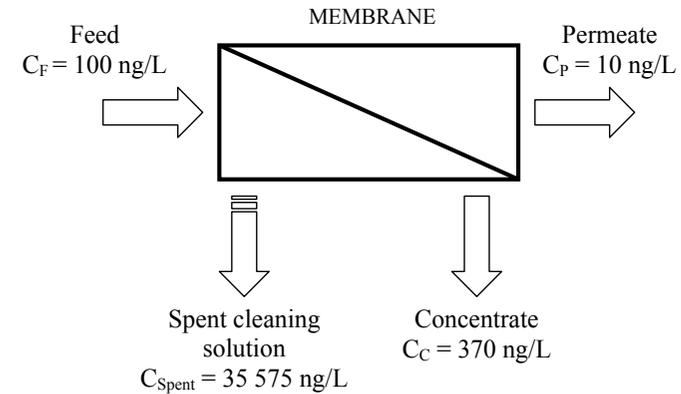

Figure 7 Estimated concentration of estradiol in different streams for assumed values of 90 % retention, recovery 0.75 and cleaning solution volume of 40 litres per one 8-inch membrane element.

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 arrangement. Typical cleaning solution volume required for one 8-inch membrane spiral wound element is approximately 40 litres [22]. 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 should 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. Results reported here indicate that the membrane can serve as a large reservoir for EDCs and their release can be possible during membrane cleaning or erratic pH variation during operation. Complete desorption of EDC to the membrane cleaning solution at high pH is assumed, which results in a very high concentration of EDCs in the spent cleaning solution. Treatment of the concentrate and the spent membrane cleaning solution should be carefully considered when EDCs are amongst the target contaminants in NF/RO membrane filtration.

5. Acknowledgements

6. Reference

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