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Nanofiltration of Hormone Mimicking Trace Organic Contaminants

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Abstract: The removal mechanisms of three hormone mimicking organic compounds by nanofiltration (NF) membranes have been examined. Two NF membranes having different pore sizes were used in laboratory-scale nanofiltration experiments with feed solutions spiked with a hormone mimicking compound—nonylphenol, tert-butylphenol, or bisphenol A. Retention of the compounds was determined at various solution chemistries, namely aqueous solution pH, ionic strength, and presence of natural organic matter. The nanofiltration behavior of the selected hormone mimicking compounds appears similar to that of natural hormones as reported in our previous work. While the solution pH can dramatically influence the retention of hormone mimicking compounds by a loose NF membrane, ionic strength does not affect the nanofiltration of such contaminants. However, in the presence of natural organic matter in the feed solution, ionic strength appears to play a significant role in solute-solute and solute-membrane interactions, resulting in increased retention due to partitioning of the hormone mimicking compounds onto organic matter at a higher ionic strength.

Keywords: Endocrine disrupting chemicals (EDCs), bisphenol A, nonylphenol, nanofiltration, trace organic contaminants

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INTRODUCTION

The presence of hormone mimicking compounds in secondary wastewater effluents and in freshwater bodies has caused great concern over their potentially adverse health impact on humans and wildlife. Most of these compounds are of significant industrial importance. Prominent amongst them are alkylphenol ethoxylates (APEs) and bisphenol A (BPA). APEs are a group of nonionic surfactants extensively used as industrial cleaning and wetting agents, emulsifiers, and domestic detergents. Despite a significant environmental concern over the use and disposal of these chemicals, the demand for APEs grows steadily with a current annual production estimated to be approximately 500,000 tons (1). Similarly, BPA is extensively employed in the production of epoxy resins and polycarbonates. The annual BPA production is reported to be in excess of 1 million tons (2).

APEs together with some BPA enter the aquatic environment primarily as components of industrial and domestic wastewater. During the biological wastewater treatment process, APEs degrade into a complex mixture of several biorefractory metabolites, mostly consisting of short chain alkylphenols such as nonylphenol and octylphenol (3). Unfortunately, these metabolites are often more persistent, toxic, and bio-accumulative than their parent compounds. Swiss researchers, who followed the transformation of APEs in 11 sewage treatment plants in Switzerland, reported that up to 40% of the initial APE load could reach the aquatic environment via secondary effluent, mostly in alkylphenol forms (3, 4). This finding is supported by numerous studies conducted in several other countries, consistently demonstrating the ubiquitous and widespread presence of hormone mimicking compounds in secondary wastewater effluents and receiving waters (5, 6). Alkylphenols and BPA are commonly detected in secondary effluent and sewage impacted water bodies throughout the world at concentrations within the lower microgram per liter (ppb) range, although concentrations up to several hundred micrograms per liter have also been reported (5, 7, 8).

Although endocrine disrupting potency and other chronic effects of alkylphenols and BPA are very well documented in the literature (1, 9, 10), there is a lack of information concerning the removal of hormone mimicking compounds prior to wastewater effluent discharge and particularly during water recycling, which has been strongly endorsed by the water industry as a sound approach to combat water shortage (11, 12). Nanofiltration may potentially be an effective technology to address the water recycling issue, particularly when trace contaminants are a concern. The effectiveness of NF membranes in removing low molecular weight organics such as pesticides has been recently demonstrated (13–16). Promising retention values of hormone mimicking compounds such as nonylphenol and BPA have also been reported in several studies (17, 18). However, the removal mechanisms and the influence of solution chemistry on the retention of hormone mimicking compounds by NF membranes remain poorly understood.

The purpose of this study is to elucidate the removal mechanisms of hormone mimicking compounds by NF membranes and to examine the influence of solution chemistry, namely pH, ionic strength, and organic matter content, on the separation process. Experiments were carried out with two NF membranes whose pore sizes have been previously characterized. Retention was related to the membrane characteristics and the compound physicochemical properties. Solution chemistry effects were investigated by considering the resulting behavior of hormone mimicking compounds and their interactions with the membrane and the natural organic matter in the feed solution during the nanofiltration process.

MATERIALS AND METHODS

NF Membranes

Two commercially available NF membranes, denoted NF-270 and NF-90 (FilmTec Corp., Minneapolis, MN), were used in this investigation. The membranes were received as flat sheets and were stored in deionized (DI) water (NanoPure II, Dubuque, IA) at 4°C. According to the manufacturer, both membranes are polyamide thin-film composite with a microporous polysulfone supporting layer. Some key properties of these membranes have been described elsewhere (22, 24–26).

Contact Angle Measurement

The captive bubble method was employed to measure the contact angle of the clean membranes. Measurements were performed with an NRL contact angle goniometer (Rame Hart, Mountain Lakes, NJ). Details on the measurement technique are described elsewhere (19).

Hormone Mimicking Organic Compounds

Three hormone mimicking compounds, namely nonylphenol (NP), tert-butylphenol (TBP), and bisphenol A (BPA), were selected for this investigation (Fig. 1). These compounds are amongst the most prominent emerging wastewater contaminants that have to date been identified. As seen in Fig. 1, a characteristic feature of these compounds is the presence of phenolic functional groups with a hydrophobic alkyl chain. Stock solutions (1 g/L) of all three compounds were prepared in pure methanol. The stock solutions were stored at <4°C and were used within 1 month.

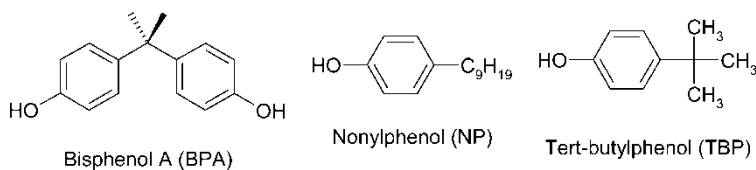


Figure 1. Molecular structure of the three hormone mimicking compounds used in this study.

NF Membrane Bench-Scale Unit

A laboratory-scale, cross-flow membrane filtration test unit was used in this study. The unit utilizes a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing pressures up to 68 bar (1000 psi) and a cross-flow of up to 4.2 L per minute. The temperature of the feed solution was controlled using a refrigerated circulator (Neslab RTE 111). A duplicate plate-and-frame membrane cell was used, each housing a membrane coupon with an identical effective surface area of 7.7 cm × 3.0 cm. The permeate flow rate was monitored by a digital flow meter connected to a PC, and the cross-flow rate was monitored by a rotameter. All test unit parts in contact with the solution are made of stainless steel or Teflon to minimize adsorption of the organic compounds.

Membrane Filtration Protocol

Prior to each experiment, the membrane was stabilized at 12 bar (176.4 psi) using deionized (DI) water for at least 16 h until the permeate flux attained a constant value. The feed reservoir temperature was kept at $20 \pm 0.1^\circ\text{C}$ throughout the experiment. After stabilizing the membrane, the feed reservoir was emptied and 4 L of DI water was introduced to the feed reservoir. The cross-flow velocity and the permeate flux were adjusted to 30.4 cm/s and 15 $\mu\text{m/s}$ (54 L/m²h or 32.4 gfd), respectively. The membrane permeability was then determined. Test compounds were spiked into the feed reservoir to make up a concentration of 500 $\mu\text{g/L}$. Unless otherwise stated, the permeate and retentate were recirculated back to the feed reservoir. Feed and permeate samples (approximately 2 mL each) were taken for analysis at specified time intervals.

Suwannee River natural organic matter (SRNOM) supplied by the International Humic Substances Society (St. Paul, MN) was used to represent natural organic matter (NOM) in some experiments. In such experiments, the NOM concentration in the feed solution was 10 mg/L. The NOM concentration was confirmed by measuring the total organic carbon (TOC) of the feed solution. SRNOM was selected because of its high concentration of dissolved

organic carbon and low concentration of inorganic salt (ash content of 7%). Contribution of this ash to the solution ionic strength is assumed to be negligible. When necessary, certified grade NaCl and NaOH or HCl (Fisher Scientific, Pittsburgh, PA) were added to the feed solution to adjust the ionic strength and pH, respectively.

Membrane calcium and sodium retentions were obtained by challenging the membranes with a single salt solution (i.e., CaCl_2 or NaCl). Calcium and sodium concentrations of the feed solution were 1 mM and 10 mM, respectively. The applied pressure was 5 bar and the experiments were conducted at pH 6.

Analytical Methods

A Shimadzu high-performance liquid chromatography (HPLC) system was used to analyze the three hormone mimicking compounds: nonylphenol, bisphenol A, and tert-butylphenol. The system comprised an autosampler (model SIL-10ADvp), a solvent delivery system, and a UV-Vis detector (SPD-10AVvp). The solvent delivery system included two HPLC pumps, a degaser, and a gradient mixer. A reversed phase column (Discovery® C18 with pore size, length, and diameter of 5 μm , 250 mm, and 4.6 mm, respectively) supplied by Supelco was used. The UV wavelength was set at 280 nm. DI water and acetonitrile (ACN)—delivered at a constant flow rate of 1 mL/min—were used as the mobile phase for gradient elution. The gradient program of the mobile phase was adapted from a method reported by Ying and Kookana (20): 30% ACN and 70% water at 0 min, 80% ACN and 20% water from 12 to 24 min, 100% ACN at 24 min, and 30% ACN and 70% water at 30 min. Each analysis lasted 35 min, and the injection volume was 50 μL . The detection limit was approximately 20 $\mu\text{g/L}$ for these contaminants. Analysis was conducted immediately following the nanofiltration experiments.

TOC was measured with a Shimadzu TOC- V_{CSH} analyzer (Shimadzu Corporation, Kyoto, Japan). A Perkin Elmer Optima 3000 ICP-AES Instrument was used to measure calcium and sodium concentrations. Samples were diluted 1:1 with 5% analytical grade nitric acid prior to analysis.

RESULTS AND DISCUSSIONS

Membrane Characteristics

Results of contact angle measurements indicate that both membranes are relatively hydrophobic (Table 1). The NF-270 membrane has a very thin semi-aromatic piperazine-based polyamide active layer (21), which results in a relatively smooth surface (22, 23). This is possibly the reason for the

Table 1. Several characteristics of the selected NF membranes

Membrane	Permeability ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Contact angle ($^{\circ}$)	Average roughness ^a (nm)	Calcium retention ^b (%)	Sodium retention ^c (%)	Average pore radius ^d (nm)
NF-270	13.5	55.0	5.5	43	40	0.42
NF-90	6.4	42.5	69.9	95	85	0.34

^aData from reference (22) (measured on a $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ area).

^bExperimental condition: 1 mM CaCl_2 at 5 bar, pH = 6.

^cExperimental condition: 10 mM NaCl at 5 bar, pH = 6.

^dData from reference (25).

excellent performance of the membrane, specifically its high-water permeability and organic matter retention (24). On the other hand, the NF-90 membrane consists of a fully aromatic polyamide active layer. As a result of these subtle differences in the polymer composition and morphology of the active layers, the NF-90 membrane is less hydrophobic (represented by a lower contact angle) than the NF-270 membrane, as shown in Table 1.

Average pore radii and zeta potentials of both membranes have been determined in our previous studies (25, 26). Results from these studies reveal that the NF-270 is a relatively loose NF membrane while the NF-90 is a tight NF membrane. Both membranes have a slightly positive zeta potential below pH 3.5 and are negatively charged above this pH (26). While Ca^{2+} retention by the NF-90 membrane is considerably higher than that of Na^+ , the NF-270 membrane shows a similar selectivity for the divalent (Ca^{2+}) and monovalent (Na^+) ions (Table 1). In the latter case, the trend is not in accord with the size of the hydrated ions. When Donnan exclusion is the predominant mechanism for salt retention, counterions have a higher concentration in the membrane pores than in the bulk solution because of electrostatic attraction between the negatively charged membrane and the oppositely charged counterions (27). Consequently, counterions with a higher valence are less retained by the membrane despite their larger hydrated radius. This behavior is typical for a loose, negatively charged NF membrane (27, 28). In our case, it appears that the NF-270 membrane exhibits certain Donnan exclusion behavior, with electrostatic interactions playing an important role in salt retention. On the other hand, the salt retention mechanism by the NF-90 appears to be predominantly governed by steric (size) exclusion.

Physicochemical Properties of Hormone Mimicking Compounds

Numerous studies have demonstrated the capacity of alkylphenols and bisphenol A to interact with hormone receptors in similar and sometimes

precisely the same mechanisms as natural hormones (10, 29, 30). Physicochemical properties of the selected hormone mimicking compounds in this study are also quite similar to those of natural hormones. They all have phenolic groups with a comparable pK_a value, in a range of 10.1–10.3. Below pH 10, these compounds are neutral in charge, and interactions between their polar centers and the membrane fixed charge groups are expected to be negligible, given their relatively low dipole moments (31) (Table 2).

The octanol–water partitioning coefficients ($\log K_{ow}$) of these compounds vary from moderately high (BPA and TBP) to very high $\log K_{ow}$ (NP), corresponding to relatively low to very low solubility in water, as can be seen in Table 2. This indicates that they readily adsorb to hydrophobic materials. However, given the presence of the proton donor and acceptor functional groups of the compounds, hydrogen bonding can also play an important role in governing the interaction between these hormone mimicking compounds and the membrane polymers (25, 32).

Nanofiltration of Hormone Mimicking Compounds

Nanofiltration of hormone mimicking compounds is quite similar to that of natural hormones as we reported before (25). The compounds investigated in this study are undissociated at the pH of the experiments (pH 6). As we delineated previously, interactions between the compound polar centers and the membrane surface are expected to be minimal. Consequently, removal is predominantly governed by steric (size) exclusion and adsorption.

Due to adsorption of the hormone mimicking compounds to the membrane polymer, their concentrations in the feed decrease and then stabilize as an equilibrium is attained (Figures 2–4). Nonylphenol (NP)

Table 2. Physicochemical parameters of the selected organic contaminants

Compound	Molecular weight (g/mol)	pK_a	Solubility in water (mg/L)	Log K_{ow}	Dipole moment (D)
Bisphenol A	228	10.1 ^a	120 ^b	3.32 ^e	1.0 ^e
Tert-butylphenol	150	10.2 ^a	700 ^c	3.31 ^e	1.0 ^e
Nonylphenol	220	10.3 ^a	5.0 ^d	5.77 ^e	1.4 ^e

^aEstimated using Pallas 3.0 software (43).

^bReference (9).

^cReference (44).

^dReference (45).

^eEstimated using Hyperchem 7.1 software (46).

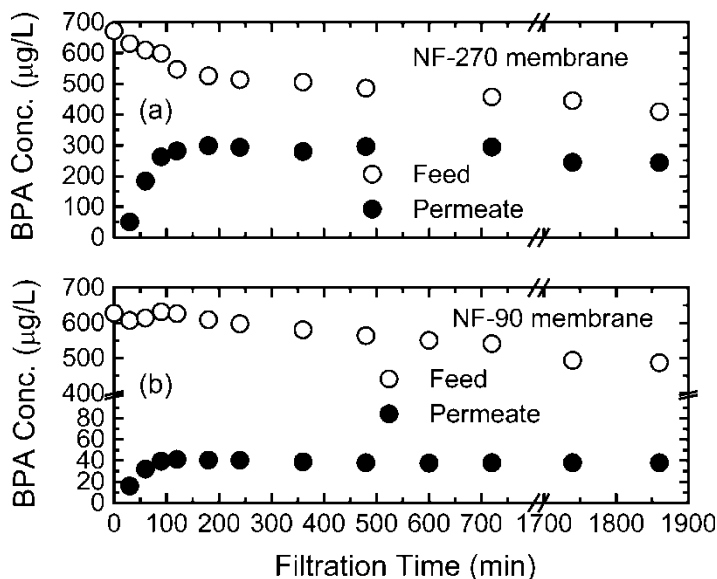


Figure 2. Permeate and feed concentrations of bisphenol A (BPA) as a function of filtration time for the (a) NF-270 and (b) NF-90 membranes. The feed solution contained approximately 500 µg/L of BPA in deionized water. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 µm/s (54 L/m² h), pH = 6, and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

adsorbed strongly to both membranes and the feed concentration was completely depleted after approximately 4 h (Fig. 4). No NP was detected in the permeate samples and therefore only feed concentrations are presented in Fig. 4. This behavior is attributed to the compounds very high log K_{ow} value (Table 1), which results in a strong hydrophobic interaction with the membrane polymer. For all compounds in this study, the partitioning process reached equilibrium in a much shorter time than that of natural hormones as we reported previously (25). It should be emphasized, however, that the initial concentrations of the hormone mimicking compounds used in these experiments (500 µg/L) were about 3 orders of magnitude higher than those with the natural hormones in our earlier work (100 ng/L) (25).

Assuming purely steric solute-membrane interactions and negligible polar interference, the observed retention of inert organics with a given radius can be predicted for the NF-270 and NF-90 membranes based on the pore transport model described in our previous study (25). Figure 5 shows the observed retention of BPA and TBP taken at the end of the filtration experiments (ca. 30 h) when a partitioning equilibrium has been reached. The

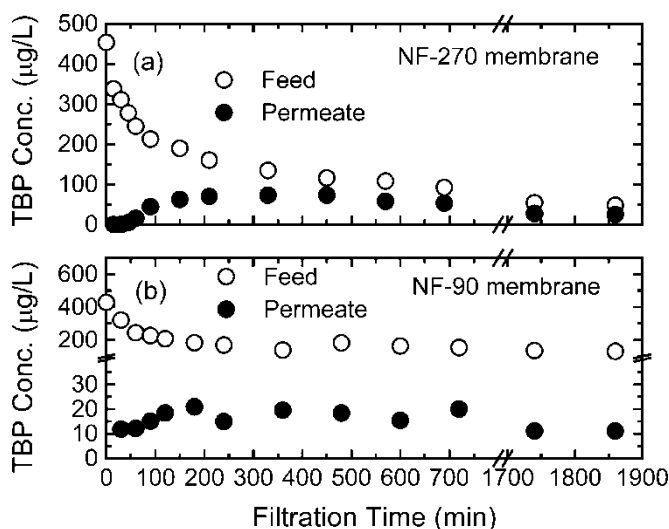


Figure 3. Permeate and feed concentrations of tert-butylphenol (TBP) for the (a) NF-270 and (b) NF-90 membranes. The feed solution contained approximately 500 µg/L of TBP in deionized water. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 µm/s (54 L/m²h), pH = 6, and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

predicted observed retention of inert organics and hormone retentions obtained from our previous study are also included in this figure (25).

Retention of hormone mimicking compounds is lower than the predicted value based purely on a steric (or size) exclusion mechanism (Fig. 5). This is

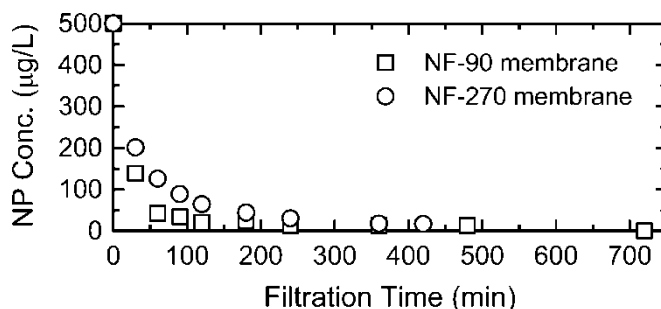


Figure 4. Feed concentrations of nonylphenol (NP) as a function of filtration time for the NF-90 and NF-270 membranes. The feed solution contained approximately 500 µg/L of NP in deionized water. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 µm/s (54 L/m²h), pH = 6, and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

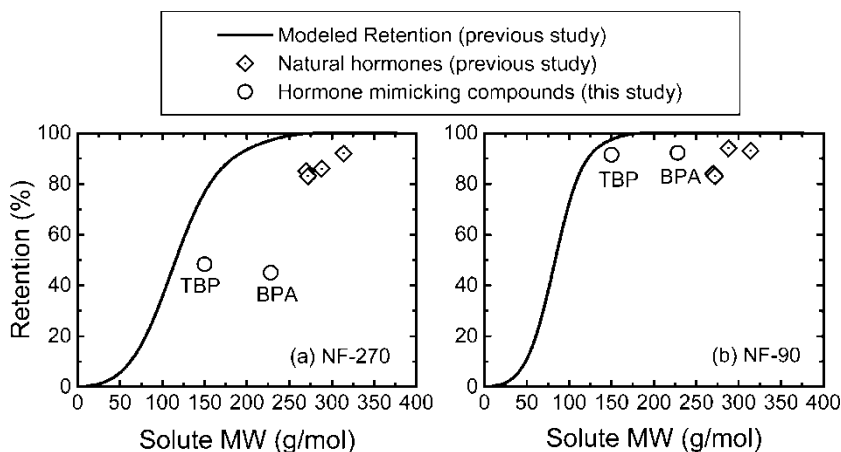


Figure 5. The measured retentions of bisphenol A (BPA) and tert-butylphenol (TBP) (open symbols) as compared to model predictions (solid line, presented in our previous publication (25)) for retention of nonadsorptive inert organics as a function of solute molecular weight by (a) the NF-270 and (b) the NF-90 membranes. Retention measurements were taken at the end of the filtration experiments (ca. 30 h) at pH 6, where these hormone mimicking compounds are neutral. Also included in the figure were measured retention of four natural hormones (solids symbols representing estradiol, estrone, testosterone, and progesterone) published previously (25). Parameters used in modeling were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 $\mu\text{m/s}$ (54 L/m²h), and temperature = 20.0°C.

attributed to the partitioning (or adsorption) and subsequent diffusion of hormone mimicking compounds in the membrane polymer phase. However, steric exclusion remains the predominant mechanism responsible for the retention of hormone mimicking compounds. Because BPA and TBP have smaller molecular weights (or molecular sizes) than the steroid hormones, their retentions by the NF-270 membrane are considerably lower (Fig. 5a). Similarly, although lower than the predicted value, BPA and TBP retentions by the tight NF-90 membrane remain quite high, indicating a central role of steric exclusion in the separation of hormone mimicking compounds (Fig. 5b).

Influence of Solution pH on Retention

Since the pK_a of BPA is 10.1, it transforms from a neutral species to a negatively charged species as pH rises to pH 11. Consequently, the retention mechanisms at pH 11 can be significantly different. As seen in Fig. 6, BPA retention by the loose NF-270 membrane at pH 11 is predominantly governed by electrostatic (charge) exclusion (33). Due to electrostatic repulsion between the negatively charged BPA and the negative membrane surface, no adsorption of BPA to the membrane is observed. Retention is almost complete and

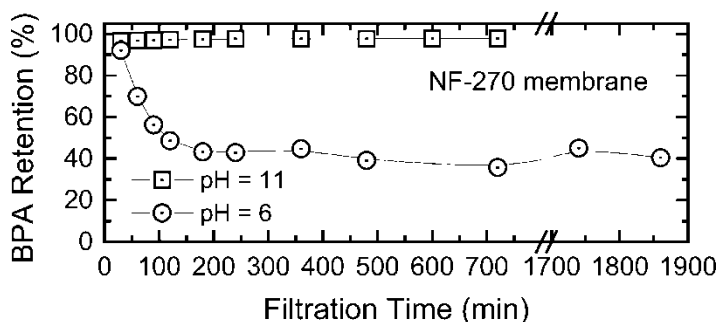


Figure 6. Retention of bisphenol A (BPA) by the NF-270 membrane at two different pH as a function of time. The feed solution contained approximately 500 $\mu\text{g/L}$ of BPA in deionized water. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 $\mu\text{m/s}$ (54 L/m²h), and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

independent of filtration time. This is consistent with our previous discussion that the loose NF-270 membrane exhibits a typical Donnan exclusion behavior and charge interaction can play an important role in the separation of negatively charged solutes. The results indicate that a significant influence of solution pH on the retention of hormone mimicking compounds is expected in the vicinity of the pK_a value due to the compound speciation.

Effect of Ionic Strength on Retention

Although ionic strength can strongly influence the electrostatic interaction between fixed charge groups of organic macromolecules and hence their conformation (34–36), its effect on the size and shape of small organic molecules such as the hormone mimicking compounds used in this study is expected to be negligible. However, because ionic strength can influence electrostatic interaction between the membrane functional groups (35), the membrane cross-linked polymer network can either expand or shrink in response to variations in solution ionic strength. Consequently, this may induce changes in the membrane pore size and thus influence retention characteristics.

To examine this effect, retention experiments were conducted in DI water and in 50 mM (or 2922 mg/L NaCl) ionic strength solution. Applied pressure was adjusted to achieve the same water flux and the solution pH was kept constant at pH 6. As seen in Fig. 7, no apparent influence of ionic strength on the partitioning of BPA and TBP to the NF-270 membrane was observed. The retention behaviors of BPA and TBP in DI water and in a high ionic strength solution with the NF-270 membrane were almost

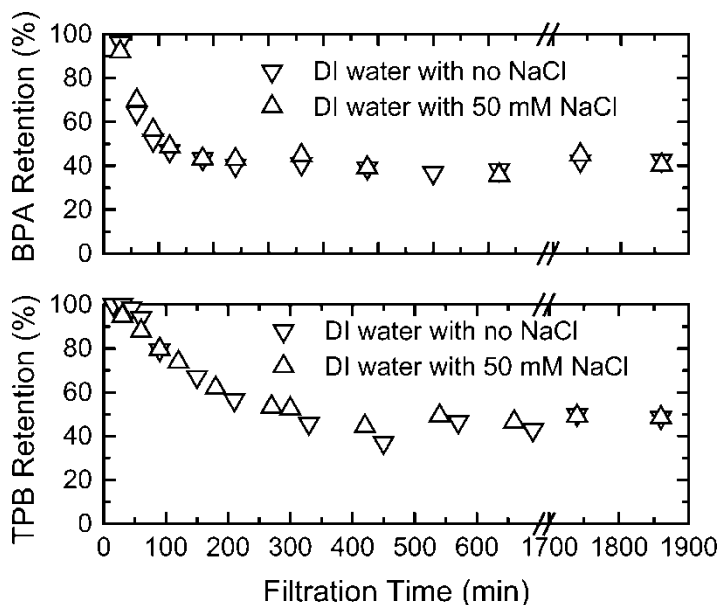


Figure 7. Effects of ionic strength on the retention of (a) bisphenol A (BPA) and (b) tert-butylphenol (TBP) by the NF-270 membrane. The feed solution contained approximately 500 $\mu\text{g/L}$ of the corresponding hormone mimicking compound in DI water or 50 mM NaCl solution. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 $\mu\text{m/s}$ (54 L/m²h), pH = 6, and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

identical. Results reported here suggest that, at the conditions examined, ionic strength has a negligible effect on nanofiltration of hormone mimicking trace organic contaminants. However, it is important to note that ionic strength can still influence the charge screening of membrane functional groups and, hence, the retention of charged organic solutes (35).

Retention in Presence of Background Natural Organic Matter

The influence of organic matter on retention of trace organics by NF membranes is complex and involves intricate combinations of solute–membrane and solute–solute interactions. This is reflected by the relatively large number of studies dealing with this subject (13, 37–40), although the results are varied and remain largely inconclusive. Several researchers revealed a small but nevertheless apparent retention enhancement of trace organics in the presence of organic matter (37–39). In contrast, Berg et al. (13) reported no increase of pesticide retention by several NF membranes

with increasing organic matter concentration. Similarly, Zhang et al. (40) showed negligible difference between simazine retention in tap water (no organic matter was detected) and in river water (COD of 56.2 mg/L). Such inconsistency in the literature underscores the need for a fundamental understanding of the interactions among trace organics, bulk organics, and the membrane surface. In this study, we attempt to delineate the effect of organic matter on hormone mimicking compound retention by also taking into consideration the effect of ionic strength.

BPA and TBP retentions by the NF-270 membrane in DI water, a solution containing 10 mg/L of NOM without any added ionic strength, and a solution containing 10 mg/L of NOM with an ionic strength (NaCl) of 10 mM are presented in Fig. 8. While the presence of 10 mg/L NOM in DI water

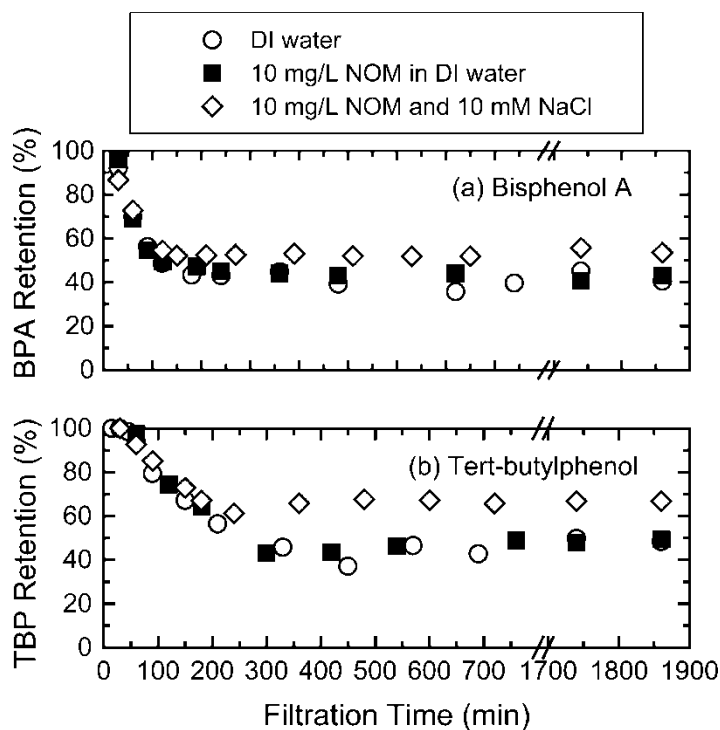


Figure 8. Effects of natural organic matter (NOM) and ionic strength on the retention of (a) bisphenol A (BPA) and (b) tert-butylphenol (TBP) by the NF-270 membrane. The feed solution contained approximately 500 $\mu\text{g/L}$ of the corresponding hormone mimicking compound in deionized water, deionized water plus 10 mg/L NOM, or 10 mM NaCl plus 10 mg/L NOM. Other experimental conditions were as follows: cross-flow velocity = 30.4 cm/s, permeate flux = 15 $\mu\text{m/s}$ (54 $\text{L/m}^2\text{h}$), pH = 6, and temperature = 20.0°C. The permeate and retentate were recirculated back to the feed reservoir during the nanofiltration run.

resulted in no increase in BPA and TBP retentions, there is a small but clear retention enhancement in the presence of organic matter at a higher ionic strength. As discussed in the previous section, ionic strength does not influence the membrane pore size and the partitioning process between trace organics and the membrane polymer. However, ionic strength is known to affect the electrostatic interactions between functional groups of both NOM and the membrane polymer (35), which can possibly influence the NOM–membrane and NOM–trace organic interactions.

Charge shielding and double-layer compression neutralize repulsive interactions among the NOM functional groups and also with the membrane negative surface. Therefore, at a sufficiently high ionic strength, NOM macromolecules are not only rigid, compact, and spherocolloidal but can also adsorb more effectively to the membrane surface (34, 35, 41). Because NOM retention by the NF-270 membrane (measured as TOC) was approximately 90% at both low and high ionic strength solutions, a layer of NOM is expected to form on the membrane surface. This layer can become denser at higher ionic strengths due to the reduction of charge repulsion among the macromolecule functional groups. Consequently, physicochemical interactions between NOM and trace organics can be enhanced. An ionic strength increase may also lead to a “salting out” effect (42), which can increase the apparent adsorption capacity of NOM for hydrophobic trace organics such as BPA and TPB to some extent, although the ionic strength used here is rather small for a significant salting out effect. Results reported here suggest the significance of solution ionic strength in influencing NOM–trace organic interactions, which is probably the cause for the ambiguity of literature data regarding the role of background organic matter in trace organic rejection.

CONCLUSION

Nanofiltration of hormone mimicking compounds such as alkylphenols and bisphenol A appears similar to that of natural hormones. Adsorption of hormone mimicking compounds to the membrane was the dominant removal mechanism at the initial stage of filtration. At later stages, adsorption and subsequent diffusion of hormone mimicking compounds in the membrane polymer resulted in lower retention than what was expected based on a steric (or size) exclusion mechanism alone. Nevertheless, it has been verified that steric exclusion is a central separation mechanism of hormone mimicking compounds using NF membranes.

Results further show that solution pH could significantly influence hormone mimicking compound retention by the loose NF-270 membrane, as charge exclusion became the dominating retention mechanism at pH higher than the pK_a value of the compound. Within the range used in this study, ionic strength did not affect the nanofiltration of hormone mimicking

compounds in the absence of organic matter. However, ionic strength appeared to play a significant role in influencing NOM–trace organic and NOM–membrane interactions. Consequently, the presence of organic matter in the feed solution in conjunction with an adequate ionic strength could discernibly enhance the retention of hormone mimicking compounds by loose NF membranes.

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