A R C H I T E C T U R E C I V I L E N G I N E E R I N G E N V I R O N M E N T
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REMOVAL OF XENOESTROGENS FROM WATER DURING REVERSE OSMOSIS AND NANOFILTRATION – EFFECT OF SELECTED PHENOMENA ON SEPARATION OF ORGANIC MICROPOLLUTANTS

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Abstract

Reverse osmosis and nanofiltration are membrane separation processes used to remove low – molecular weight organic micropollutants from water. Investigations in this field focus on the effect of unfavourable phenomena concomitant with membrane filtration, such as adsorption, fouling and concentration polarization on membrane separation of removed organic micropollutants. This study investigated the effect of adsorption and concentration polarization on the removal of four xenoestrogenic compounds i.e. 4 – *tert* – octylphenol, 4 – nonylphenol, bisphenol A and bisphenol F. Furthermore, a reservoir of micropollutants adsorbed on the membrane surface was desorbed. Reverse osmosis yielded much better results in xenoestrogens removal compared to nanofiltration carried out for comparative reasons. However, the osmotic membrane showed high sorptive properties towards the xenoestrogens. The fundamental feature of adsorption is the formation of hydrogen bridges between membrane polymer and a compound being removed, and the process itself is reversible. The desorption of adsorbed micropollutants involved filtration of an electrolyte solution of pH > pK_a of the compound. It has been found that concentration polarization brings about a decrease in xenoestrogens retention during reverse osmosis. For nanofiltration at similar filtration conditions, retention of micropollutants increased probably due to the mixed separation mechanism in the process i.e. sieve mechanism with accompanying concentration polarization and fouling.

Streszczenie

Odwrócona osmoza i nanofiltracja to procesy separacji membranowej stosowane do usuwania małocząsteczkowych mikrozanieczyszczeń organicznych z wody. Prowadzone badania w tym zakresie związane są z określeniem wpływu zjawisk niekorzystnych towarzyszących filtracji membranowej takich jak adsorpcja, *fouling* oraz polaryzacja stężeniowa na separację membranową usuwanych związków organicznych. W pracy badano wpływ zjawiska adsorpcji i polaryzacji stężeniowej na usuwanie czterech związków z grupy ksenoestrogenów tj. 4 – *tert* – oktylofenol, 4 – nonylofenol, bisfenol A i bisfenol F. Dokonano także próby desorpcji rezerwuaru zaadsorbowanych mikrozanieczyszczeń z powierzchni membrany. Znacznie wyższe usunięcie ksenoestrogenów uzyskano, w procesie odwróconej osmozy w stosunku do badanej porównawczo nanofiltracji. Jednakże, membrana osmotyczna wykazała wysoką zdolność sorpcyjną, w stosunku do badanych ksenoestrogenów. U podstaw zjawiska adsorpcji leży tworzenie mostków wodorowych pomiędzy polimerem membrany a usuwanym związkiem, a sam proces ma charakter odwracalny. Desorpcji zaadsorbowanego ładunku mikrozanieczyszczeń organicznych dokonano filtrując roztwór elektrolitu o pH > pK_a związku. Wykazano, że zjawisko polaryzacji stężeniowej powoduje obniżenie retencji ksenoestrogenów, w procesie odwróconej osmozy. W przypadku nanofiltracji, dla zbliżonych warunków filtracji, retencja mikrozanieczyszczeń rosła prawdopodobnie z uwagi na mieszany mechanizm separacji w tym procesie tj. mechanizm sitowy przy współudziale zjawiska polaryzacji stężeniowej i *foulingu*.

Keywords: **xenoestrogens; membrane processes; water; adsorption; concentration polarization; fouling.**

1. INTRODUCTION

Xenoestrogens are man – made chemical compounds discharged into water environment which are currently the focus of attention among scientists due to their high biological activity [1]. The wide group of xenoestrogens includes alkylphenols i.e. 4 – *tert* – octylphenol, 4 – nonylphenol, bisphenol A and bisphenol F. Those micropollutants have not been monitored so far since they were not subject to legal regulations; they were not even regarded as hazardous.

The separation techniques that are taken into consideration while discussing the removal of xenoestrogens from water include pressure driven membrane operations, such as reverse osmosis (RO) and nanofiltration (NF). Their limitations in this respect result from the differences in the efficiency of low – molecular weight organic micropollutants removal in laboratory systems and those operating on a full scale [2]. This is due to the diversity of factors affecting membrane separation and associated with physical and chemical properties of the membrane (a), micropollutants (b) and treated water (c), Table 1. Those factors also include adsorption [3-7] and fouling [8-10] which usually accompany membrane filtration.

Adsorption deals with hydrophobic compounds (i.e., *n* – octanol/water partition coefficient P_{ow} values of > 2) whose hydrophobicity expressed as logP_{ow} is an important factor that affects their removal. Normally, higher removal is observed for compounds of high logP_{ow} [7]. The presence of natural organic matter NOM in water usually increases the removal of organic matter [8-10], however, it also causes fouling. Higher retention of micropollutants may result from both fouling of pores and formation of NOM – organic compound complexes [9]. Shortage of literature information concerning the effect of concentration polarization on the elimination of hydrophobic xenoestrogens necessitates further investigations into the issue.

The paper demonstrates a comparative study on the removal of selected xenoestrogens from water by reverse osmosis and nanofiltration. The retention coefficient of xenoestrogens was investigated with respect to adsorption intensity and concentration polarization. Additionally, transport properties of two composite RO and NF membranes (Osmonics Inc. USA) with thin – layer polyamide were compared.

2. MATERIALS AND METHODS

2.1. Xenoestrogens and their monitoring

A mixture of four xenoestrogens was used in the study i.e. 4 – tert – octylphenol, 4 – nonylphenol, bisphenol A and bisphenol F (Sigma – Aldrich analytical standards). Their physicochemical properties are shown in Table 2.

Table 2.
Physicochemical properties of xenoestrogens [11]

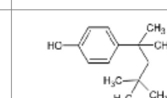
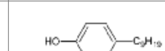
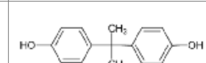
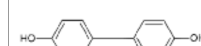
Compound	Molecular weight, (g/mol)	logP_{ow}	Molecular structures
4-*tert* -octylphenol	206.3	5.28	
4–nonylphenol	220.3	5.99	
bisphenol A	228.3	3.32	
bisphenol F	200.2	2.45	

Table 1.
Factors affecting the rejection of micropollutants during reverse osmosis and nanofiltration treatment

Membrane properties	Micropollutants properties	Physicochemical characteristics of the waters
membrne molecular weight cut–off	molecular weight (MW) and size parameter	natural organic matter (NOM)
desalting degree	geometry	inorganic matter (Na^+, K^+, Mg^{2+} and Ca^{2+})
porosity and morphology	hydrophilicity/hydrophobicity	pH value
membrane charge	molecule charge	ionic strength

The phenols were extracted from raw and filtered water samples using stir bar sorptive extractions (SBSE) and their concentrations were determined by gas chromatography. The details of the procedure are given in [12]. Concentration of individual xenoestrogens in the feed was 40 μg/dm^3.

2.2. Membranes and apparatus for membrane filtration

Commercial Osmonics Inc. (USA) RO – DS3SE and NF – DS5DL membranes were used to carry out reverse osmosis and nanofiltration respectively. Table 3 summarizes the characteristics of the two membranes. Membrane filtration was conducted in a 350 cm^3 steel membrane cell in dead – end mode with membrane surface area of 37.5 cm^2. The transmembrane pressures selected for reverse osmosis and nanofiltration were 2.0 MPa and 1.0 MPa respectively, while the temperature of the solution filtered reached 20°C.

Table 3.
Membrane properties (manufacture date)

Membrane process	Reverse osmosis RO	Nanofiltration NF
Monufacturer's symbol	DS3SE	DS5DL
Pressure, MPa	recommended: 2.7 max: 4.0	recommended: – max: 4.0
pH, –	1-11	
Temperature, °C (max)	90	
Membrane material	composite (active layer – polyamide)	
Molecular weight cut – off (MWCO), Da	–	150 – 300

Comparative filtration was carried out on deionized water that contained xenoestrogens with and without an addition of 20, 100, 500 and 1000 mg/dm^3 of powdered dextran. The nominal molecular weight of the dextran was 15 kDa (Polfa Kutno SA), and that substance was supposed to help form the polarization layer of the contaminants removed at the membrane surface.

The effectiveness of filtration was assessed by measuring volumetric permeate flux (J_w – for deionized water and J_v – for model water), relative permeate flux (α) and selectivity (R) (equations 1-3, Table 4). Equations 4 and 5 were used to calculate the amount of adsorbed xenoestrogens on and in the structure of the membrane, which was examined during the filtration of deionized water with an addition of the xenoestrogens (A).

The desorption of adsorbed xenoestrogens on and in the structure of the membrane was induced by filtering an electrolyte solution (1 mM $NaHCO_3$ and 20 mM NaCl) whose pH was higher than the dissociation constant of removed compounds (pH > pK_a = 11).

Table 4.
Equations used to evaluate membrane properties and removal efficiencies

Parameter	Unit	Equations	Number
Volumetric permeate flux J_v (J_w)	m^3/m^2·s	$J_v(J_w)=\dfrac{V}{F\cdot t}$	1
Relative permeability of the membrane, α	–	$\alpha=\dfrac{J_v}{J_w}$	2
Rejection coefficient, R	%	$R=\left(1-\dfrac{C_p}{C_f}\right)\cdot 100\%$	3
Adsorption, A	%	$recovery=\left(\dfrac{C_r\cdot V_r+C_p\cdot V_p}{C_f\cdot V_f}\right)\cdot 100$ $A=100\%-recovery$	4,5
V – volume (dm^3), F – membrane area (m^2), t – filtration time (s), C – concentrations (μg/dm^3), r – retentate, p – permeate, f – feed			

Table 5.
Retention coefficients of NaCl and $MgSO_4$

Membrane	Deionized water flux $J_v \cdot 10^6$, $m^3/m^2 \cdot s$			Retention coefficient (R), %	
	Deionized water	Deionized water + NaCl	Deionized water + $MgSO_4$	NaCl	$MgSO_4$
RO–DS3SE[1]	3.94	3.03	3.35	95.1	98.2
NF–DS5DL[2]	17.6	15.8	5.54	38.2	65.3
[1] determined at 2 MPa, [2] determined at 1 MPa					

3. RESULTS AND DISCUSSION

3.1. Retention coefficient of NaCl and $MgSO_3$

Retention coefficients of NaCl and $MgSO_4$ were calculated for both membranes i.e. salts representing monovalent and divalent ions, Table 5. Membrane filtration was carried out for 1 g/dm^3 solution of a given salt at pressures amounted to 2.0 for RO and 1.0 MPa for NF. The RO – DS3SE membrane removed 95% of monovalent and divalent ions, which proves its osmotic nature. The nanofiltration NF – DS5DL membrane removed 38% of monovalent and 65% of divalent ions.

3.2. Removal of xenoestrogens

Table 6 shows retention coefficients for all the xenoestrogens investigated during nanofiltration and reverse osmosis. The osmotic RO – DS3SE membrane removed the xenoestrogens at a high level of 85-97%. Lower percentages of 54-84% were found for nanofiltration. Thus, the retention coefficients of xenoestrogens are largely dependent upon the type of membrane process. Almost complete removal of low – molecular weight organic micropollutants can be achieved solely through reverse osmosis that uses compact non – porous membranes. The authors of papers [12, 13] found that NaCl retention is the indicator of the separation properties of nanofiltration membranes to remove low – molecular weight xenoestrogens. Higher percentages of xenoestrogens removal were observed for NF membranes typical of high or medium NaCl retention, however, they simultaneously exhibited high sorptive properties towards removed micropollutants.

Table 6.
Retention coefficients (%) of the compounds tested by RO– DS3SE and NF– DS5DL

Compound	RO – DS3SE	NF – DS5DL
4 – nonylphenol	96.8	74.2
4 – *tert* – octylphenol	94.0	83.9
bisphenol A	85.3	65.7
bisphenol F	91.2	54.4

3.3. Adsorption and desorption of xenoestrogens

Papers [14-15] revealed that the adsorption of hydrophobic xenoestrogens on and in the structure of the membrane always accompanies NF separation. The mechanism of membrane separation has two stages i.e. first a compound is adsorbed on the membrane surface and then passes through it during diffusion and/or convection determined by its affinity for the polymer the membrane is made of. The data given in Fig. 1 confirm a similar mechanism for reverse osmosis. Much higher adsorption of xenoestrogens obtained for RO – DS3SE (Fig. 1) was probably caused by the fact that the second stage of separation was hindered for compact osmotic mem-

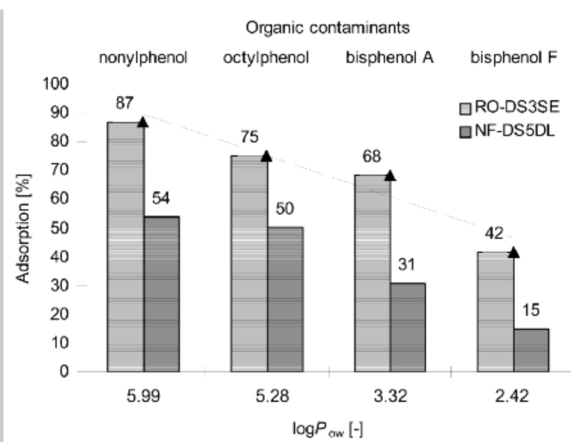


Figure 1.
Correlation of adsorption with logP_{ow} of xenoestrogens for used membranes

branes. Similarly, other authors [16] noticed the influence of hydrophobicity of a compound expressed as logP_{ow} on the degree of its adsorption. Compounds of higher hydrophobicity display higher adsorption on the membrane surface.

The NF – DS5DL membrane, initially loaded with xenoestrogens by passing a 40 μg/dm^3 solution of deionized water, has been selected to investigate the desorption of adsorbed micropollutants on and in the structure of the membrane. The process continued until 50% of the feed volume passed through the membrane. Subsequently, an electrolyte solution (pH 11) was placed in the chamber and filtration started (working pressure of 1.0 MPa). The solution initiated the release of adsorbed micropollutants from the membrane surface. The results for 4 – tert – octylphenol are depicted graphically in Fig. 2.

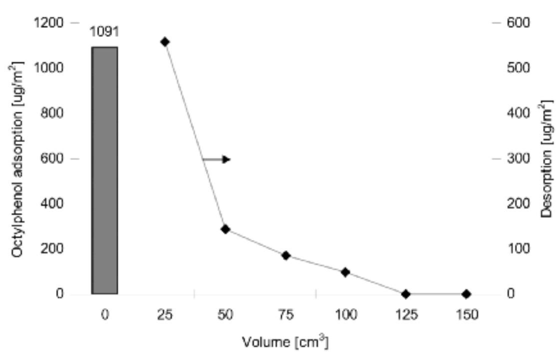


Figure 2.
Adsorption and desorption of 4 – *tert* – octylphenol (μg/m^2) as a function of permeate volume

It has been found that after 50% of the electrolyte volume passed through the membrane, 77% of the adsorbed 4 – *tert* – octylphenol (1091 μg/m^2) was released from the membrane surface. Thus, adsorption is based on the formation of hydrogen bridges between the micropollutant being removed and membrane polymer; the process is reversible. During the operation of the membrane system, the disturbances in water pH may result in adsorption and desorption taking place at the same time. The solution produced by membrane washing may contain a considerable amount of removed compounds, and this fact must be taken into account while managing it afterwards.

3.4. Impact of concentration polarisation on xenoestrogens separation

The last stage of the study focused on the filtration of deionized water containing xenoestrogenic standards with an addition of dextran to determine the impact of concentration polarization on the effectiveness of the process.

For the osmotic RO – DS3SE membrane, an increase in the dextran concentration in water brought about a decrease in the retention of the xenoestrogens, Fig. 3. The relative permeability of the membranes (α) was much lower than 1 (Table 7), which proves the formation of polarization layer of removed pollutants at the membrane surface. The decrease in membrane efficiency was also observed for the NF – DS5DL membrane (Table 7). Nevertheless, unlike the osmotic membrane, the nanofiltration one showed an increase in low – molecular weight xenoestrogens retention with increasing dextran concentration in the water, Fig. 4.

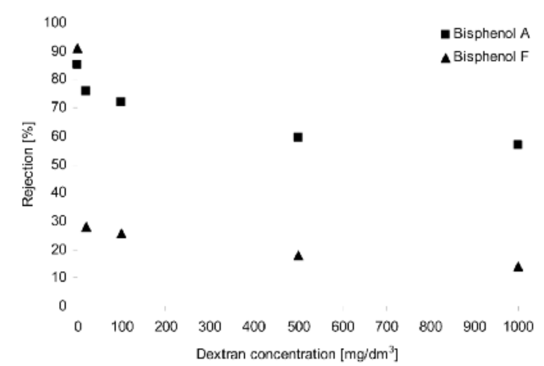


Figure 3.
Rejection of bisphenol A and bisphenol F as a function of dextran concentration (membrane RO – DS3SE)

Such various correlations under similar filtration conditions prove the different nature of the separation mechanism in those processes and the effect of adverse phenomena that accompany membrane filtration on organic micropollutants separation. For the compact and non – porous osmotic RO – DS3SE membrane, the concentration of removed pollutants in the polarization layer region was increasing, which resulted in a decrease in the retention coefficient. Filtration of the polydispersive dextran through the porous nanofiltration membrane was accompanied by concentration polarization and probably fouling of

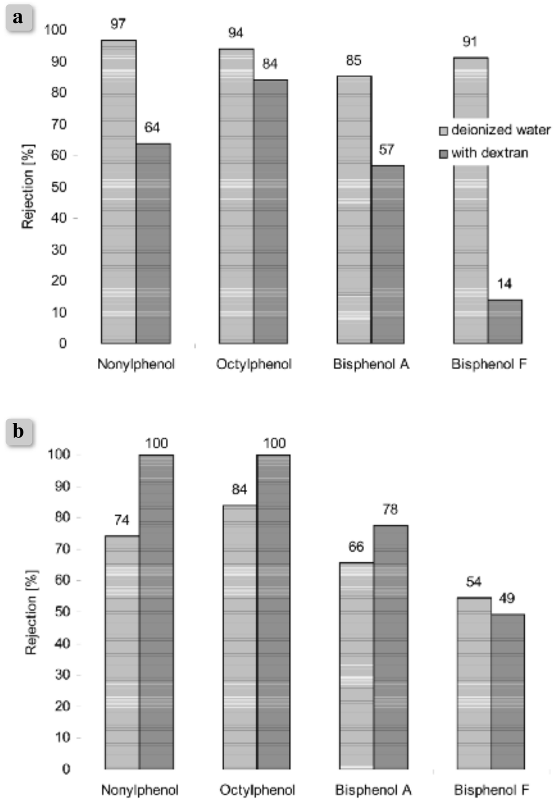


Figure 4.
Influence of dextran (1000 mg/dm³) on xenoestrogens rejection by reverese osmosis (A) and nanofiltration membrane (B)

membrane pores by dextran molecules whose size was similar or smaller than the pores. This is confirmed by the very low relative permeability of the membranes α, Table 7.

Table 7.
Relative permeability of the membrane α during dextran with xenoestrogens solutions filtration

Membrane	Dextran concentrations, mg/dm³	Relative permeability of the membrane, α
RO – DS3SE	20	0.86
	100	0.87
	500	0.78
	1000	0.60
NF – DS5DK	1000	0.16

4. CONCLUSIONS

The study compared reverse osmosis and nanofiltration which can be used to remove low – molecular weight xenoestrogens from waters. It has been found out that:

- reverse osmosis (RO – DS3SE membrane) produced higher removal of xenoestrogens of around 85-97%, however, the membrane displayed high sorptive properties towards the micropollutants,
- both osmotic and nanofiltration separation is accompanied by the adsorption of hydrophobic xenoestrogens on the membrane surface, and a reservoir of adsorbed compounds poses a real hazard during the operation of the membrane system,
- the adsorption of pollutants on the membrane surface is reversible, and desorption can occur both during the chemical washing of the membranes and change in the pH of filtered water.

The unfavourable, in terms of efficiency, concentration polarization and fouling that accompany membrane filtration cause:

- a decrease in retention coefficient for reverse osmosis filtration as a result of the increase in the concentration of the pollutant being removed in the region of polarization layer,
- an increase in xenoestrogens removal during nanofiltration due to the miscellaneous separation mechanism i.e. sieve mechanism accompanied by concentration polarization and fouling.

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