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FACTORS DRIVING REJECTION OF MICROPOLLUTANTS (XENOESTROGENS AND PHYTOESTROGENS) DURING REVERSE OSMOSIS/NANOFILTRATION TREATMENT

Mariusz DUDZIAK [a], Michał BODZEK [b]

[a] Dr.; Faculty of Energy and Environmental Engineering, The Silesian University of Technology,
ul. Konarskiego 18, 44 – 100 Gliwice, Poland
E-mail address: *mariusz.dudziak@polsl.pl*

[b] Prof.; Faculty of Energy and Environmental Engineering, The Silesian University of Technology,
ul. Konarskiego 18, 44 – 100 Gliwice, Poland

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Abstract

The research investigated the rejection of 12 xenoestrogens and phytoestrogens (low-molecular weight organic compounds) during reverse osmosis and nanofiltration, using membranes of a wide cut-off range and different degree of NaCl retention. The paper describes statistically the correlation between rejection and selected physico-chemical parameters characteristic of the compounds removed. The removal of micropollutants depends on the type of membrane processes and membranes. Rejection of both tight and loose nanofiltration membranes is mainly dependent on compound hydrophobicity described by logK_{ow}. This confirms the participation of adsorption in the separation mechanism. The removal of a compound by loose nanofiltration membranes is also dependent on its molecular weight and Stokes radius. Reverse osmosis produced a 75% removal of the micropollutants and retention depend on the dipole moment of the compound.

Streszczenie

Badano retencję 12 małocząsteczkowych związków organicznych z grupy ksenoestrogenów i fitoestrogenów w procesie odwróconej osmozy i nanofiltracji z użyciem membran o szerokim zakresie cut-off i różnym stopniu zatrzymania NaCl. Statystycznie opisano korelację retencji i wybranych parametrów fizyko-chemicznych charakteryzujących usuwane związki. Usunięcie mikrozanieczyszczeń zależy od rodzaju procesu membranowego oraz membrany. W przypadku zwartych jak i otwartych membran nanofiltracyjnych retencja uzależniona jest głównie od hydrofobowości związku określanej poprzez logK_{ow}. Potwierdza to udział zjawiska adsorpcji w mechanizmie separacji. W przypadku otwartych membran nanofiltracyjnych na usunięcie związku ma wpływ również jego masa molowa i promień Stokes'a. W procesie odwróconej osmozy mikrozanieczyszczenia usuwane były w ponad 75%, a retencja uzależniona była od momentu dipolowego związku.

Keywords: **Micropollutants; Reverse osmosis; Nanofiltration; Rejection mechanism.**

1. INTRODUCTION

The mechanism of compound separation during reverse osmosis (RO) and nanofiltration (NF) is based on dissolution and diffusion. However, the rejection of hydrophobic compounds is dependent on adsorption [1] and the process has a two-step separation mechanism i.e. a compound is adsorbed on the surface of a membrane in the first step and then passes through it by diffusion and/or advection. This is determined by the affinity of the compound with the polymer the membrane is made of or its ability to dissolve. Adsorption increases during membrane filtration and causes deterioration in the removal of low–molecular weight compounds [2]. In case of nanofiltration membranes, their susceptibility to adsorption is associated with the removal of NaCl, which indicates the separation properties of those membranes [3-4].

The phenomenon of adsorption is more intensive for reverse osmosis which uses more compact membranes than nanofiltration [5]. The intensity of adsorption also depends on the type of removed compound and its concentration in water [3].

Papers [5-7] revealed the effect of adverse phenomena that accompany membrane filtration on micropollutants rejection i.e. concentration polarization, membrane fouling and scaling. An increase in the concentration of a removed pollutant in the area of polarization layer causes a decrease in the retention coefficient of low-molecular weight organic compounds during reverse osmosis. It is unlike nanofiltration in which the rejection of micropollutants increases under the conditions of concentration polarization [5], which is caused by the higher porosity of nanofiltration membranes compared to the reverse osmosis ones. Membrane contamination with organic and inorganic matter i.e. fouling and scaling

Table 1.
The selected factors driving rejections of micropollutants during reverse osmosis and nanofiltration treatment

Factor	Membrane process	
	Reverse osmosis	Nanofiltration
	Change in rejection of micropollutants *R*	
Adsorption	R↓	R↓
Concentration polarisation	R↓	R↓
Fouling or/and Scaling (membrane contaminated)	R↑	R↑
Inorganic substances in treatment water (Na^+, Ca^{2+})	-	R↓
Organic substances in water (Humic acid)	R↑	R↑

Table 2.
Estrogenic compounds examined

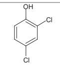
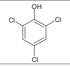
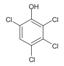
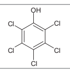
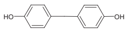
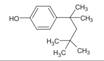
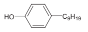
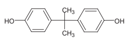
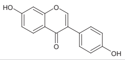
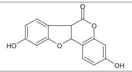
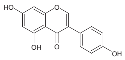
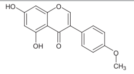
Compound	Classification	Structures	Concentration in water, µg/dm^3	Extraction method	Method detection limit, µg/dm^3(ng/dm^3)
2,4–dichlorophenol (2,4–DCP)	xenoestrogens		100	Liquid–Liquid Extraction LLE	0.3
2,4,6–trichlorophenol (2,4,6–TrCP)					
2,3,4,6–tetrachlorophenol (2,3,4,6–TeCP)					0.6
Pentachlorophenol (PCP)					1.2
Bisphenol F (BPF)			40	Stir Bar Sorptive Extraction SBSE	1
4–*tert*–octylphenol (OP)					1
4–nonylphenol (NP)					5
Bisphenol A (BPA)					1
Daidzein (Daid)	phytoestrogens		5	Solid Phase Extraction SPE	(3)
Coumestrol (Coum)					(3)
Genistein (Gen)					(6)
Biochanin A (Bio–A)					(9)

Table 3.
The selected factors driving rejections of micropollutants during reverse osmosis and nanofiltration treatment

Compound	Molecular weight, g/mol	Water solubility[a], mg/dm^3	LogK_{ow}[b]	Stokes radius[c], nm	Dipole moment[d], D	Molecular width[e], nm	Molecular length[e], nm	Molecular height[e], nm
2,4–DCP	163	4500	2.80	0.280	1.30	0	0.549	0.629
2,4,6–TrCP	197	800	3.45	0.307	1.71	0	0.529	0.629
2,3,4,6–TeCP	232	23	4.09	0.332	1.88	0	0.611	0.629
PCP	266	14	4.74	0.355	1.66	0	0.611	0.629
BPF	200	545	3.06	0.309	2.63	0.182	0.963	1.016
OP	206	5	5.28	0.314	1.84	0.413	0.760	0.729
NP	220	5000	5.92	0.324	1.40	0.395	1.558	1.599
BPA	228	120	3.64	0.329	1.00	0.792	1.035	0.668
Daid	254	11.8	2.55	0.347	3.18	0.487	1.276	0.487
Coum	268	26.2	1.57*	0.356	2.64	0	1.188	0.862
Gen	270	9.18	2.84	0.357	3.47	0.487	1.276	0.568
Bio-A	284	58.3	3.41	0.366	1.45	0.487	1.406	0.568

[a] Obtained from the Syraceuse Research Corporation (SRC) PhysProp detabase [b] logK_{ow} values as calculated from "SRC K_{ow} WIN"
[c] Calculated by the Stokes-Einstein equations [d] Estimated using the chemical modelling software, HyperChem
[e] Calculated using ChemOffice *moderately hydrophobic

result in both a decrease in membrane efficiency and increase in micropollutants rejection [6-7]. The organic and/or inorganic matter modifies the surface charge of the membrane and reduces the inside diameter of the pores by the filter cake or scale formed. This decreases the diffusion of the compound being removed [7]. The conditions of scaling also reduce the adsorption of micropollutants on the membrane surface while fouling intensifies the process which markedly affects the rejection of micropollutants [7-8].

The rejection of micropollutants during membrane processes is significantly affected by the physico-chemical composition of treated water. The removal of micropollutants from water in the presence of humic acids causes an increase in compounds retention resulting from the formation of NOM-organic compounds complexes [6-9]. On the other hand, the presence of salts containing monovalent and divalent cations in water causes a decrease in micropollutants rejection as a result of the decrease in the surface charge of the membrane [10]. The changes in micropollutants rejection during reverse osmosis and nanofiltration brought about by the factors mentioned above are shown in Table 1.

The paper is aimed at considering the effect of selected physico-chemical parameters of micropollutants on their rejection during reverse osmosis and nanofiltration. The membranes chosen for the research had a wide cut-off range and different degree of NaCl retention.

2. METHODS

2.1. Compound selection and characterization

12 low-molecular weight organic xenoestrogens and phytoestrogens have been selected for the research. The micropollutants were assayed, using extraction techniques to separate them from water, and gas chromatography-mass spectrometry (GC-MS Saturn 2100 T, Varian) to determine their concentrations. The concentrations of the micropollutants in water and methods of their separation including their detection limits are given in Table 2. The standards of the xenoestrogens and phytoestrogens tested were produced by Sigma-Aldrich (Poland). The details of the analytical methods are demonstrated in papers [7, 11-12]. Table 3 contains selected physico-chemical parameters of the micropollutants.

2.2. Membranes

Two types of flat Osmonics membrarnes i.e. a tight reverse osmosis DS-3-SE, nanofiltration DS-5-DK and a loose nanofiltration GE membrane were used in the investigations. The GE membrane had a cut–off of 1000 Da i.e. a range somewhere between nanofiltration and ultrafiltration. Their characteristics are given in Table 4. The membranes were placed in a steel membrane cell (capacity of 350 cm^3, active membrane area of 38.5 cm^2) which enabled the process to be carried out in the dead–end mode. Membrane filtration was conducted on deionized water that contained standards of the compounds of interest (the concentrations are given in Table 2) under a transmembrane pressure of 2.0 MPa. The temperature of the solution filtered was 20°C. The process was carried out until 50% of the feed was recovered and repeated four times to determine the average retention including the standard deviation of the determination. The effectiveness of the filtration was assessed by measuring the volumetric permeate flux (J_w – for deionized water and J_v – for the water with micropollutants standards added):

$$J_w(J_v) = \frac{V}{F \cdot t} \tag{1}$$

where: V – volume (dm^3), F–membrane area (m^2), t – filtration time (s)

The concentration of the micropollutants was assayed in the water being treated (feed) and purified (permeate) by membrane techniques, and the results enabled calculation of their rejection coefficients (R, %):

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \tag{2}$$

where: C – concentration (μg/dm^3), p – permeate, f – feed.

2.3. Statistical analysis

Statistical analysis was performed with the use of Statistica version 8.0. Regression analysis with one independent variable enabled us to determine the correlation between rejection and selected physico–chemical parameters that characterized the micropollutants removed (Table 3). The correlation coefficient (r) was the measure of the correlation between the variables, and the assessment was made at a significance level p of 0.05.

3. RESULTS AND DISCUSSION

3.1. Removal of micropollutants

The removal of micropollutants is dependent on both membrane processes and membrane types. The rejection of removed compounds for the membranes of interest is given in Table 5. The highest removal of micropollutants was found for reverse osmosis and exceeded 75%. As to nanofiltration, the lowest removal was found for the loose GE membrane characterized by the highest cut-off (Table 4). This definitely proves the impact of the cut-off on the removal of micropollutants. The membranes also differed in the removal of NaCl (45% for DS-5-DK membrane and 9% for GE one), which also affects both their separation properties and micropollutants removal.

The presence of the micropollutants in the treated water did not affect the efficiency of the membranes. The volumetric permeate flux J_v was similar to the one found for deionized water J_w. This was observed for all the membranes.

3.2. Relationship between rejection and the compounds properties

Table 6 shows the statistical analysis results of the correlation between rejection and selected physicochemical parameters that characterize removed compounds. The analysis revealed that the dipole moment of a compound is the most significant parameter affecting retention during reverse osmosis. The correlation coefficient stayed at a level of 0.83

Table 4.
Membrane characteristics

Type	Membrane	Material	Volumetric flux of deionized water $J_W \cdot 10^6$, m^3/m^2·s (ΔP=2.0 MPa)[a]	MWCO[b], Da	NaCl rejection[c], %
RO	DS–3–SE	composite (active layer-polyamide)	3.94	–	95.1
Tight NF	DS–5–DK		23.1	150-300	40.6
Loose NF	GE		17.4	1000	9.40

[a]J_W obtained in this work [b]Molecular weight cut-off [c]Determined in experiment during filtration of NaCl solution (1000 mg/dm^3) with transmembrane pressure 2.0 MPa

Table 5.
Membrane rejection (%) of estrogenic compounds from Milli–Q water

Compound	Membrane		
	RO (DS–3–SE)	Tight NF (DS–5–DK)	Loose NF (GE)
	Rejection ± SD*		
2,4–DCP	87 ± 2.2	74 ± 2.8	55 ± 1.3
2,4,6–TrCP	90 ± 0.8	83 ± 1.4	60 ± 2.6
2,3,4,6–TeCP	91 ± 3.1	85 ± 2.6	64 ± 16
PCP	88 ± 3.8	77 ± 5.4	66 ± 21
BPF	85 ± 0.2	67 ± 3.2	57 ± 21
OP	91 ± 2.3	83 ± 9.4	63 ± 15
NP	94 ± 2.1	80 ± 9.1	68 ± 14
BPA	97 ± 4.4	69 ± 0.2	61 ± 8.7
Daid	75 ± 5.9	68 ± 2.0	61 ± 5.5
Coum	86 ± 2.9	70 ± 3.7	62 ± 6.4
Gen	83 ± 7.3	71 ± 5.2	63 ± 9.6
Bio–A	97 ± 1.2	86 ± 4.2	63 ± 17
Parameter			
Volumetric permeate flux $J_V\cdot 10^6$, $m^3/m^2\cdot s$	3.93	21.7	17.1

*avarge rejection and standard deviation of four replicates are reported

Table 6.
Correlation analysis for estrogenic compounds rejection

Compound property	Membrane					
	RO (DS–3–SE)		Tight NF (DS–5–DK)		Loose NF (GE)	
	Statistical parameters					
	r^a	p^b	r^a	p^b	r^a	p^b
Molecular weight, g/mol	0.07	0.831	0.02	0.958	**0.58**	**0.049**
Stokes radius, nm	0.06	0.841	0.02	0.958	**0.60**	**0.041**
Molecular width, nm	0.19	0.542	0.21	0.516	0.17	0.602
Molecular length, nm	0.01	0.986	0.22	0.489	0.40	0.200
Molecular height, nm	0.26	0.404	0.01	0.986	0.36	0.256
Water solubility, mg/dm^3	0.16	0.623	0.07	0.819	0.05	0.873
LogK_{ow}, –	0.49	0.107	**0.62**	**0.030**	**0.65**	**0.022**
Dipole moment, D	**0.83**	**0.001**	0.50	0.101	0.10	0.765

^{a}coefficient of correlation ^{b}statistical significance of correlation. Correlations in bold are statistically significant (p<0.05, 95% confidence).

($p<0.05$). The retention of the micropollutants decreased with increasing dipole moment, which is demonstrated in Fig. 1 A.

As to nanofiltration, a significant role for both membranes with respect to the removal of micropollutants is attributed to the hydrophobicity of the compound expressed as logK_{ow} (Table 6). Its increasing value brings about an increase in the removal of the compound, Fig. 1 B. This confirms the decisive effect of adsorption on the separation of hydrophobic organic compounds. This is also observed during the removal of hydrophobic micropollutants by ultrafiltration [13] which employs membranes whose cut-off is much higher than the molecular weight of removed compounds.

A surprising observation for the loose nanofiltration membrane is that the molecular weight and Stokes radius of the compound affected its rejection, despite the fact that the molecular weight of removed micropollutants was much lower than the cut–off of the GE membrane. This was probably caused by the effect of membrane porosity (pores distribution) and irregular shapes of the pores in its structure. The dependence of the compounds rejection for GE membrane as a function of Stokes radius is shown in Fig. 1 C.

Paper [14], which deals with investigations similar to those described herein, confirmed the correlation between the rejection of micropollutants during nanofiltration and water solubility of compounds. It describes the separation of 22 compounds of different hydrophilicity/hydrophobicity which might explain the above observation. On the other hand, the authors of paper [15] present evidence to support the effect of the geometry of a compound on rejection (molecular width and length) during separation of a pharmaceutical in the form of electrically neutral particles. The research covered RO and NF. The authors point to the electrostatic interactions as the main separation mechanism of ionic compounds (usually a negative charge).

The rejection of micropollutants is the outcome of a number of factors and phenomena concomitant with membrane filtration. However, it is possible to find some key factors that determine rejection, depending on the group of compounds removed or by describing the properties of micropollutants (e.g. hydrophobicity/hydrophilicity). When the GE membrane is used, the dependence of rejection on factors that characterize a given compound suggests that an analysis of the dependence of rejection on group parameters (function of multiple regression) should be made. This will be considered in later papers in this scope of research.

A promising approach to the mechanism of organic micropollutants rejection by membrane operations covers the use of methods for mathematical modeling of separation. In the future, this will aim at enabling an easier design of membrane installations and forecasting rejection coefficients for little known micropollutants. It cuts down the costs and time of laboratory tests. This is topical nowadays when a wide range of micropollutants of high biological activity are identified in surface waters.

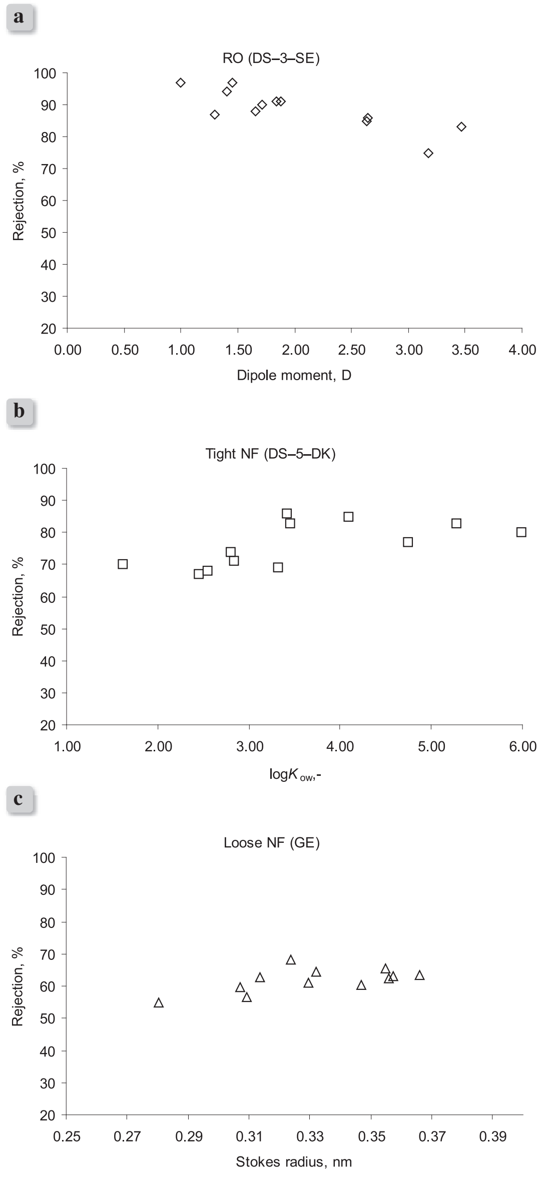


Figure 1.
Relationship between rejection by RO/NF membranes vs. selected properties of the tested compounds

4. CONCLUSIONS

The removal of hydrophobic and moderately hydrophobic micropollutants depends on both membrane processes and membrane types. This is caused by the differences in the properties of the membranes i.e. cut-off, degree of NaCl removal and selected physico-chemical characteristics of removed micropollutants. The statistical analysis revealed:

- the effect of the dipole moment of a compound on its removal by reverse osmosis,
- the predominant role of compound hydrophobicity expressed as $\log K_{ow}$ on rejection during nanofiltration, irrespective of the cut-off,
- dependence of rejection on the molecular weight and Stokes radius of a compound for loose nanofiltration membranes.

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