ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 18, No. 7 2011

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EFFECT OF THE CONTACT ANGEL ON THE EFFECTIVENESS OF MYCOESTROGENS REMOVAL FROM WATER USING NANOFILTRATION MEMBRANES

WPŁYW KĄTA ZWILŻANIA MEMBRAN NANOFILTRACYJNYCH NA EFEKTYWNOŚĆ USUWANIA MYKOESTROGENÓW Z WODY

Abstract: The research addressed the removal of selected mycoestrogens by nanofiltration using membranes different in membrane casting polymers, degree of NaCl removal and efficiency. It also determined the effect of hydrophobicity of a membrane characterized by the measurement of contact angle on micropollutants retention. The tests were carried out on a new membrane and one modified by inorganic and organic matter. The membrane prepared from cellulose acetate CK characterized by a high contact angle and NaCl removal yielded the highest mycoestrogens retention. The presence of inorganic and organic matter in water reduced membrane efficiency and increased hydrophobicity due to the modification of the membrane surface. Those filtration conditions brought about a change in micropollutants retention.

Keywords: nanofiltration, mycoestrogens, water treatment, removal micropollutants, separation mechanism

Normally, a description of transport and separation properties of nanofiltration membranes supplied by a manufacturer gives information on the removal of $MgSO_4$, range of pH tolerance of a treated solution and determination of a typical flux from a unit membrane surface. Sometimes, it also describes a cut-off expressed in Daltons and type of membrane casting polymers. On the other hand, a description of the physical and chemical properties of membrane surface distinguishes only between hydrophilic and hydrophobic membranes. Membrane hydrophobicity is usually determined by contact angle measurements [1]. Papers [2–3] report that membranes of larger contact angles may both remove and adsorb organic micropollutants more than membranes of smaller contact angles. Our research in this field [4–5] revealed that the removal of NaCl (monovalent ions) is an indicator of sorption and separation abilities of membranes to remove micropollutants.

This work focused on the retention of selected mycoestrogens (zearalenone ZON, α-zearalenol α-Zol, β-zearalenol β-Zol and zearalanol ZAN) by nanofiltration using

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membranes that differed in membrane casting polymers, NaCl removal and efficiency. In addition, the membranes were characterized by finding their contact angles with a pocket goniometer. Membrane hydrophobicity and micropollutants retention were determined for a new membrane and one modified by inorganic and organic matter present in filtered water. The tests were aimed at finding the effect of membrane hydrophobicity on micropollutants retention during treatment of aqueous solutions by nanofiltration.

Materials and methods

Four commercial nanofiltration membranes were selected for the tests: CK, DK and HL manufactured by GE Osmonics and NF-27– produced by Dow Filmtec (Table 1). Nanofiltration was carried out in the dead-end mode using a 350 cm^3 steel membrane cell (membrane surface area 38.5 cm^2) equipped with a magnetic stirrer. The tests were conducted under a transmembrane pressure of 2.0 MPa and a temperature of 20 ^oC.

Table 1

Characteristics of membrane (manufacturer data)

Membrane type	Material	Removal of $MgSO_4$ [%]	Max. pH range	Cut off [Da]	Volumetric flux of deionized water $(J_w)^a$, 10^{-6} [m^3/m^2 s]
CK	cellulose acetate	—	2–8	150–300	11.0
DK	polyamide on polysulfone support	98	1–11		21.4
HL		98	3–9		48.3
NF-270		97	2–11	200	58.2

[a] J_w obtained in this work at ΔP = 2.0 MPa.

The transport and separation parameters of the nanofiltration membranes were assessed using the equations given in Table 2.

Table 2

Equations used to evaluate membrane properties and removal efficiencies

Parameter, unit	Equations	Number
Volumetric permeate flux (deionized water), J_v (J_w) [m^3/m^2 s]	$J_V(J_W) = \frac{V}{F \cdot t}$	1
Relative permeability of the membrane α [-]	$\alpha = \frac{J_V}{J_W}$	2
Retention coefficient R [%]	$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100$	3

V – volume [dm^3], F – membrane area [m^2], t – filtration time [s], C – concentrations [μg/dm^3], p – permeate, f – feed.

The determination of nanofiltration effectiveness was based on the measurements of both membrane efficiency (J_v and α) – equations (1 and 2) and selectivity (R) – equation (3). The static contact time was measured with a pocket Fibro System AB PG-1 goniometer.

The tests were conducted on model water prepared from deionized water with and without an addition of inorganic (a mixture of 20 mmol/dm^3 NaCl, 1 mmol/dm^3 $NaHCO_3$ and 1 mmol/dm^3 $CaCl_2$) or organic matter (humic acid HA, 30 mg/dm^3) and 5 μg/dm^3 mycoestrogens standards.

The investigation dealt with the absorbance, conductivity and concentration of particular mycoestrogens. The absorbance (wavelength λ = 254 nm) was measured with a Jena AG VIS Cecil 1000 UV spectrometer while conductivity was determined with a WTW inoLab® Multi 740 laboratory meter. The methodology of mycoestrogens assays covered three steps ie isolation of compounds by SPE (1), derivatization of analytes as a preliminary stage of their determination (2) and quantitative analysis by GC-MS chromatography (3).

The micropollutants were separated from the water matrix using Supelco SPE tube (Supelclean™ Envi-18, volume 6 cm^3, 1.0 g of phase), and their concentrations were determined by *gas chromatography-mass spectrometry* (GC-MS Saturn 2100 T manufactured by Varian). Prior to extraction, the tube bed was conditioned with acetonitrile (5 cm^3) and afterwards rinsed with deionized water (5 cm^3). The separated compounds were eluted with acetonitrile (4 cm^3) and then derivatized after the solvent was vaporized to dryness. Mycoestrogens derivatization was carried out with a three component BSTFA/TMCS/DTE mixture for 5 min at a ratio of 1000:10:2 (v/v/w) and a temperature of 90 ^{o}C. A GC-MS quality and quantity analysis of silyl derivatives produced was based on *selected ion monitoring* (SIM), for zearalenone of m/z = 444, 430, 306 and 150, for α-zearalenol and β-zearalenol of m/z = 446, 432, 414 and 306 for zearalanone of m/z = 449, 432, 406 and 308. The temperature of the chromatographic furnace was set at 140–280 ^{o}C (temperature of injector 300 ^{o}C). The chromatographic separation was conducted using a Varian VF-5ms column.

Results and discussion

The retention coefficient for the mycoestrogens largely depends on a removed compound and type of nanofiltration membrane (Fig. 1). The retention of the mycoestrogens fell within 70–97 %. The CK cellulose membrane produced the highest retention. Compared with the other membranes, it was characterized by the highest contact angle of around 54^o and high retention of NaCl removal (Table 3), which makes its properties similar to those of reverse osmosis membranes. The presence of mycoestrogens in deionized water did not affect the transport properties of the nanofiltration membranes. The volume permeate flux was similar to the deionized water flux determined during the conditioning stage (Table 1).

Mycoestrogens retention was also investigated during filtration of deionized water with an addition of a mixture of salt or humic acid. Both the inorganic and organic matter brought about a decrease in membrane efficiency (α < 1, Fig. 2A) accompanied

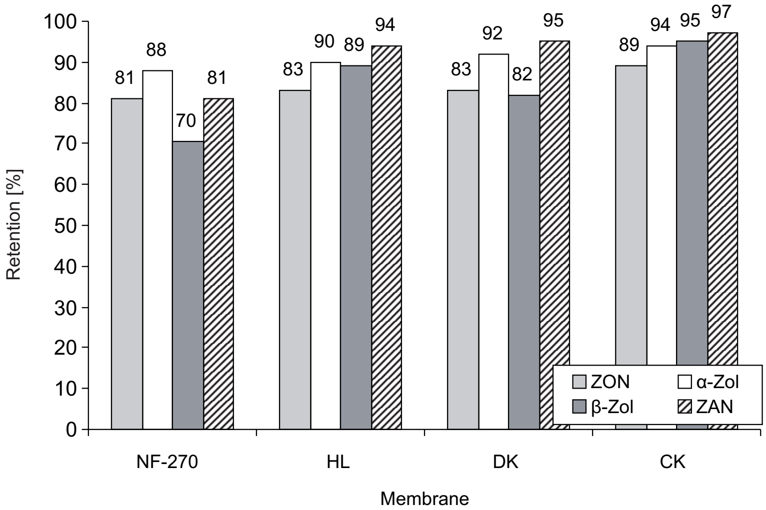

Fig. 1. Retention coefficient of mycoestrogens in nanofiltration

Table 3

Contact angles, NaCl removal and transport properties used membranes

Parameter	Membrane			
	NF-270	HL	DK	CK
Contact angles [^{o}]	17	25	37	54
NaCl removal[a] [%]	41	46	8.0	75
Volumetric permeate flux (J_v), 10^{-6} [m^3/m^2s]	56.0	48.8	21.8	11.2

[a] Determined in experiment during filtration of NaCl solution (1000 mg/dm^3) at ΔP = 2.0 MPa.

by an increase in the contact angle (Table 4). The increase was more significant for the NF-270 membrane which was initially characterized by a low contact angle (17^o, Table 3). In addition, there was an increase in the effectiveness of organic matter removal during nanofiltration, which was determined by measuring absorbance in the permeate (Fig. 2B). The above observations confirm the modification of the membrane surface. Those filtration conditions also revealed a change in the removal of the mycoestrogens. In most cases, the retention of the compounds decreased, although it did not exceed 7 %, except for the filtration of deionized water with an addition of humic acid using the NF-270 membrane which revealed an increase in micropollutants retention from 12 % to 15 %. That filtration also exhibited the lowest relative permeability of the membrane (α = 0.77, Table 4). The presence of humic acid in water intensifies both membrane fouling and formation of HA-mycoestrogens complexes [6] which are more readily retained by the membrane than a single compound due to their larger particles. In the paper [7] it was found that fouling intensifies the adsorption of micropollutants on and in the structure of the membrane, which may also bring about an increase in retention.

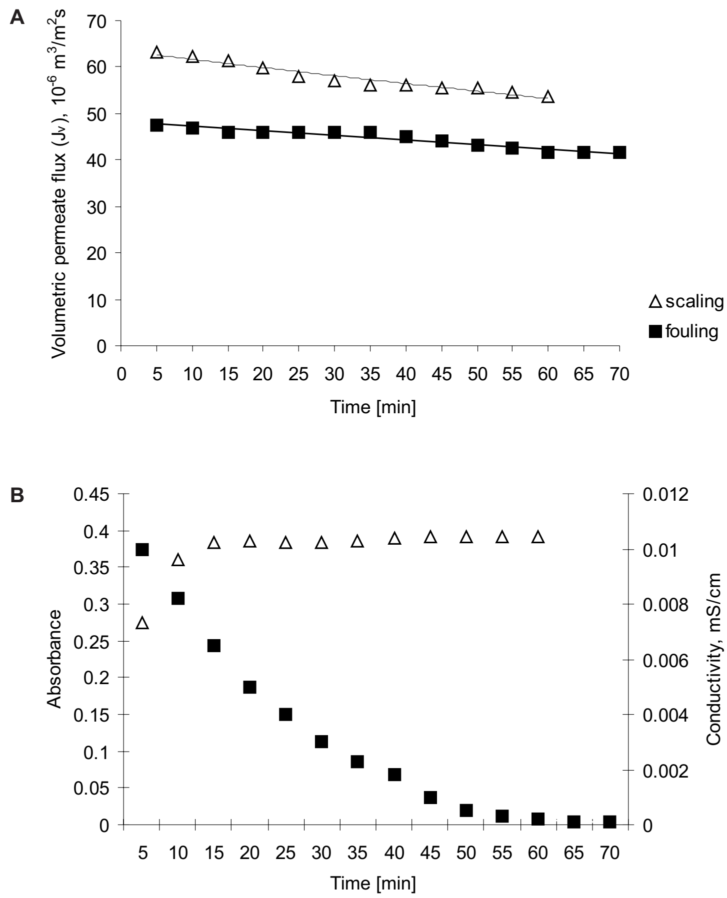

Fig. 2. Volumetric permeate flux and concentration of organic and inorganic susbstances in permeate under conditions of scaling/fouling experiments (membrane NF-270)

Table 4

Change in retention of mycoestrogens due to inorganic and organic substances occurences in water

Compound[a]	Membrane			
	NF-270		CK	
	Matrix			
	Deionized water + salts	Deionized water + HA	Deionized water + salts	Deionized water + HA
	Retention (change in retention[b])			
ZON	78 (–3)	96 (+15)	82 (–7)	88 (–1)
α-Zol	86 (–2)	100 (+12)	92 (–2)	92 (–2)

Table 4 contd.

Compound[a]	Membrane			
	NF-270		CK	
	Matrix			
	Deionized water + salts	Deionized water + HA	Deionized water + salts	Deionized water + HA
	Retention (change in retention[b])			
Parameter				
Relative permeability of the membrane, α	0.99	0.77	0.79	0.82
Contact angles[c] [°]	48	51	57	58

[a] Mycoestrogens concentration 5 μg/dm^3; [b] positive (negative) sign indicates an increase (decrease) in retention; [c] determined after filtration salts or humic acid solutions.

Conclusions

The removal of mycoestrogens during nanofiltration exceeded 70 % and was dependent on the membrane type and composition of the water matrix. The highest retention was found for the cellulose membrane characterized by high contact angles and NaCl removal. The presence of inorganic and organic matter in the treated water may modify the membrane surface and its physical and chemical properties, changing the retention coefficient of micropollutants. The mechanism described herein forms the basis for the differences in micropollutants retention produced both on a bench and technical scale.

Acknowledgement

This work was performed with the financial support from the Polish Ministry of Education and Science under grant no. N N523 5533 38.

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WPŁYW KĄTA ZWILŻANIA MEMBRAN NANOFILTRACYJNYCH NA EFEKTYWNOŚĆ USUWANIA MYKOESTROGENÓW Z WODY

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Abstrakt: Badano efektywność usuwania wybranych mykoestrogenów w procesie nanofiltracji z użyciem membran różniących się polimerem membranotwórczym, stopniem usunięcia soli NaCl i wydajnością. Określono wpływ hydrofobowości membrany scharakteryzowanej przez pomiar kąta zwilżania na retencję mikrozanieczyszczeń. Badania prowadzono dla membrany nowej i zmodyfikowanej przez substancję nieorganiczną i organiczną. Najwyższą retencję mykoestrogenów odnotowano w przypadku membrany wykonanej z octanu celulozy CK charakteryzującej się dużymi wartościami kąta zwilżania oraz stopnia usuwania soli NaCl. Obecność w wodzie substancji nieorganicznej i organicznej powodowała zmniejszenie wydajności membran oraz wzrost hydrofobowości na skutek modyfikacji powierzchni. W tych warunkach filtracji odnotowano zmianę w retencji mikrozanieczyszczeń.

Słowa kluczowe: nanofiltracja, mykoestrogeny, oczyszczanie wody, usuwanie mikrozanieczyszczeń, mechanizm separacji