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## RETENTION OF MYCOESTROGENS IN NANOFILTRATION. IMPACT OF FEED WATER CHEMISTRY, MEMBRANE PROPERTIES AND OPERATING PROCESS CONDITIONS

The membrane process, i.e. nanofiltration, was considered a method for removal of mycoestrogens, compounds recently identified in aqueous environment, from water. The study was focused on the determination of the separation mechanism and on the possibility of removal of mycoestrogens in the applied process. Retention of zearalenone and  $\alpha$ -zearalenol was investigated depending on the water matrix composition, the membrane applied, filtration mode and operating conditions of the process. As removed mycoestrogens reveal hydrophobic character, the separation mechanisms is based on the adsorption. Retention of those compounds is also dependent on the membrane type and the filtration mode. The highest effectiveness of mycoestrogens removal was obtained for cellulose membrane (CK), which characterized the highest values of the contact angle and the degree of NaCl removal in comparison with other composite membranes applied. Additionally, the CK membrane showed the highest ability to adsorb investigated micropollutants. However, the variation of retention of mycoestrogens was observed as the membrane surface was modified by inorganic and/or organic substances present in filtrated water. The degree of removal of mycoestrogens during nanofiltration exceeded 81% and considering the effectiveness and the capacity of the process, the cross-flow mode should be applied.

### 1. INTRODUCTION

Recently, a group of biologically active environmental micropollutants has been extended with mycotoxins, which despite of toxic effects also posses estrogenic activity [1]. Hence, these compounds are called mycoestrogens. In the literature, the most often discussed toxin is zearalenone (ZON, F-2 toxin), which is produced by *Fusarium* fungi on crops, especially on corn and its products [2]. The increase of threat of the feminization processes among animals has already been observed for the ZON con-

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centration in the feed exceeding 0.06 mg/kg of animal body mass/day [3]. The consumption of toxins with the food and water is a reason for similar threat in humans.

The presence of mycoestrogens in food and feed samples is restrictively controlled [3]. On the other hand, the data about presence of these toxins in the aqueous environment is very limited. Several papers have only been published on appearance of mycotoxins in surface water [1, 2, 4, 5] and wastewater treatment plants influent and effluent [1, 2, 5, 6]. The concentration of these compounds in the aqueous environment varies from 0 to 60 ng/dm<sup>3</sup> [1, 2, 4, 6]. Mycoestrogens the most often identified in aqueous environment are zearalenone and its metabolites, i.e.  $\alpha$ -zearalenol ( $\alpha$ -Zol),  $\alpha$ -zearalanol ( $\alpha$ -Zal) and  $\beta$ -zearalanol ( $\beta$ -Zal) [7, 8].

Table 1

Physicochemical properties of ZON,  $\alpha$ -Zol and 17 $\beta$ -estradiol [8]

Compound	Molecular weight [g/mol]	Solubility in water [mg/dm <sup>3</sup> ]	lgK <sub>ow</sub>	Soil sorption coefficient lgK <sub>oc</sub>	Dissociation constant pK <sub>a</sub>	Half life [day]
ZON	318	5	3.6	3.9	7.6	6–11
$\alpha$ -Zol	320	4–28	3.1–3.5	n.a.	8.4; 11.4	7–30
17 $\beta$ -estradiol	272	13	4.0	3.1–3.7	10.4	3

n.a. – not analyzed

Mycoestrogens are hydrophobic compounds moderately soluble in water (the partition coefficient between n-octanol phase and water i.e.  $\log K_{ow} > 2$ ) hydrophobic. Values of the water solubility and  $\log K_{ow}$  of zearalenone and  $\alpha$ -zearalenol are of the same range as for the follicular hormone 17 $\beta$ -estradiol. The value of  $\log K_{oc}$  of zearalenone indicates its ability to adsorb on organic matter present in water. The accumulation in bottom sediments and remobilization in aqueous environment as well as the introduction of mycoestrogens to the food chain by aqueous flora and fauna are very important transformation steps of those compounds. Even though the relative estrogenic potential of zearalenone is 100 times smaller than one determined for 17 $\beta$ -estradiol the longer biological half-life (in the case of  $\alpha$ -zearalenol ranging from 7 to 30 days) of mycoestrogens in aqueous environment is alarming [9].

Pressure-driven membrane processes, especially reverse osmosis (RO) and nanofiltration (NF) are considered a proper method for removal of organic micropollutants from water [10–22]. Even though the higher retention of low molecular weight organic compounds is observed for reverse osmosis, however complete water desalination obtained during the process makes nanofiltration more suitable for drinking water treatment technology. Nanofiltration is a significant alternative for the classical water treatment method. It is recognized as a method which together with the partial water desalination removes in parallel excessive water hardness, natural organic matter (i.e.

precursors of disinfection by-products), natural and anthropogenic micropollutants, viruses and bacteria as well as nitrates and arsenic [11]. The effective application of nanofiltration for removal of organic micropollutants in water requires knowledge about separation mechanisms and factors which influence on separation. Three most important removal mechanisms of micropollutants in nanofiltration are:

- steric hindrance (a sieving effect: molecules larger than the membrane pores are removed),
- adsorption and hydrophobic-hydrophobic interactions,
- charge interactions (negatively charged molecules are rejected by negatively charged membranes).

The above mentioned mechanisms can be connected with physicochemical properties of removed compounds as well as with the membrane characteristic. The effectiveness of micropollutants removal depends also on filtrated water parameters and operating process conditions.

The aim of the study was to determine the efficiency of removal of chosen mycoestrogens, i.e. zearalenone and  $\alpha$ -zearalenol during nanofiltration. The influence of presence of organic and inorganic substances in water was investigated. Nanofiltration membranes differing in material, capacity, contact angles and NaCl retention degree were applied. The membrane filtration was performed in both, dead-end and cross-flow modes under varying operating conditions.

## 2. EXPERIMENTAL

*Membranes and equipment.* Flat-sheet nanofiltration membranes marked as CK, DK and HL by GE Osmonics and NF-270 by Dow Filmtec were used in the study.

Table 2

Membrane properties

Membrane	Manufacturer	Material	Molecular weight cut-off [Da]	$J_w^a$ [ $10^{-6} \text{ m}^3/(\text{m}^2 \cdot \text{s})$ ] ( $\Delta P = 2.0 \text{ MPa}$ )	Contact angle <sup>a</sup> [deg]	NaCl removal <sup>b</sup> [%]
CK	GE Osmonics	cellulose acetate	150–300	11.0	54	75
DK		polyamide on polysulfone support		21.4	37	8.0
HL				48.3	25	46
NF-270	Dow Filmtec		200	58.2	17	41
AFC-30	PCI Membranes			32.6	31	58

<sup>a</sup>Determined in this work.

<sup>b</sup>Determined in experiment during filtration of NaCl solution ( $1000 \text{ mg/dm}^3$ ) at  $\Delta P = 2.0 \text{ MPa}$ .

Membranes were placed in a steel cell (volume of the feed tank 380 cm<sup>3</sup>, active membrane separation surface 38.5 cm<sup>2</sup>) which enabled one to perform the process in the dead-end mode. The filtration process was carried out until 50% of the initial feed volume was collected.

Comparatively nanofiltration in the cross-flow mode was performed, in which the tubular membrane module equipped with AFC-30 membrane by PCI Membranes System Inc. (active membrane separation surface 240 cm<sup>2</sup>) was used. The process was carried out for 3 h. The characteristics of applied membranes are presented in Table 2. The investigated membranes characterized wide range of the volumetric deionized water flux  $J_w$  (determined under  $\Delta P = 2.0$  MPa) from  $11 \times 10^{-6}$  m<sup>3</sup>/(m<sup>2</sup>·s) in the case of CK cellulose membrane to  $58.2 \times 10^{-6}$  m<sup>3</sup>/(m<sup>2</sup>·s) form NF-270 composite membrane. The molecular weight cut-off of investigated membranes was lower than the molecular weight of removed mycoestrogens, what theoretically indicated the possibility of satisfying retention coefficients of micropollutants.

*Filtration protocol.* The preliminary study of nanofiltration covered filtration of simulated waters prepared from deionized water with and without addition of inorganic (mixture of salts, i.e. 20 mmol/dm<sup>3</sup> NaCl, 1 mmol/dm<sup>3</sup> NaHCO<sub>3</sub> and 1 mmol/dm<sup>3</sup> CaCl<sub>2</sub>) or organic (30 mg/dm<sup>3</sup> of humic acid HA) substances and standards of mycoestrogens (1 or 5 µg/dm<sup>3</sup>) under 2.0 MPa transmembrane pressure in the dead-end mode,

The flow was examined in the cross-flow mode depending on temperature (10–25 °C), transmembrane pressure (1.0–2.0 MPa) as well as on linear feed velocity (0.5–3.4 m/s).

The basic investigation was filtration of tap water and surface water containing mycoestrogens under constant operating process conditions. Physicochemical characteristics of investigated waters is given in Table 3.

Table 3

Physicochemical characteristics of the water

Waters	pH	Temperature [°C]	Conductivity [mS/cm]	Absorbance [1/cm]
Tap water	7.42	20	0.744	0.035
Surface water	7.33		0.626	0.277

The determination of transport and separation as well as adsorption properties of applied membranes was performed based on equations shown in Table 4. The determination of the effectiveness of the membrane process was enabled by capacity measurements (for deionized water –  $J_w$  and for simulated water  $J_v$ ), relative volumetric permeate flux ( $\alpha$ ) as well as by membranes selectivity ( $R$ ) (Eqs. (1)–(3), while Eqs. (4)

and (5) were used to determine the degree of adsorption ( $A$ ) of mycoestrogens on the surface and in the membrane structures.

Table 4

Equations used to evaluate membrane properties and removal efficiencies

Parameter	Equation	No.
Volumetric permeate flux $J_v$ ( $J_w$ ), $\text{m}^3/(\text{m}^2 \cdot \text{s})$	$J_v (J_w) = \frac{V}{Ft}$	(1)
Relative permeability of the membrane $\alpha$	$\alpha = \frac{J_v}{J_w}$	(2)
Retention coefficient $R$ , %	$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$	(3)
Adsorption $A$ , %	$\text{Recovery} = \left(\frac{C_r V_r + C_p V_p}{C_n V_n}\right) \times 100$	(4)
	$A = 100 - \text{recovery}$	(5)

$V$  – volume,  $\text{dm}^3$ ,  $F$  – membrane surface area,  $\text{m}^2$ ,  $t$  – filtration time,  $\text{s}$ ,  
 $C$  – concentration,  $\mu\text{g}/\text{dm}^3$ ,  $f$  – feed,  $p$  – permeate,  $r$  – retentate

*Analytical methods.* The physicochemical analysis of filtrated waters covered: determination of absorption at 254 nm with the use of UV VIS Cecil 1000 spectrometer, measurements of pH and conductivity using multiparameter inoLab<sup>®</sup> 740 meter by WTW (Poland). The static contact angle was measured using pocket goniometer PG-1 by the Fibro System AB (Sweden).

The presence of mycoestrogens in water was determined by means of the solid phase extraction (SPE) and gas chromatography-mass spectrometry analysis (GC-MS). As a preparatory step before the chromatographic analysis the derivatization of compounds was performed. The extraction was carried out in SPE C<sub>18</sub> tubes (Supelclean<sup>™</sup> ENVI-18, 6  $\text{cm}^3$  and 1.0 g of the phase by Supelco) and was preceded by tubes washing with acetonitrile (5  $\text{cm}^3$ ) and conditioning with water (5  $\text{cm}^3$ ). The volume of the sample introduced on the tube was equal 100  $\text{cm}^3$  or 500  $\text{cm}^3$  in the case of lower concentration of compounds in water (1  $\mu\text{g}/\text{dm}^3$ ). The extract was eluted with 4  $\text{cm}^3$  acetonitrile. The solvent was stripped from the eluate with nitrogen and the derivatization reaction was performed. The silylation reaction of mycoestrogens was made with the use of ternary mixture of *N*, *O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA)/trimethylchlorosilane (TMCS)/ dithioerythritol (DTE) in the proportion 1000:10:2 (v/v/w). The derivatization took 5 min under temperature equal to 90 °C.

The qualitative-quantitative analyses were performed with the use of a gas chromatograph coupled with a mass detector GC-MS model Saturn 2100 T (ion trap) by Varian. The extract was separated in the VF-5 ms column of dimensions 30 m×0.25 mm×0.25 μm (the thickness of the film). Helium (5 N) was applied as the carrier gas; its flow rate was equal to 1.4 cm<sup>3</sup>/min. The temperature of the column oven was ranged from 140 °C to 280 °C. Other temperature parameters were as follows: split/splitless injector – 300 °C, ion trap and ion source – 200 °C. The quantitative analysis was performed based on selected ion monitoring (SIM) chromatograms, i.e. for *m/z* equal to 444, 430, 306 and 150 for ZON and 446, 432, 414 and 306 for α-Zol. The method enables one to determine the presence of mycoestrogens in water at the concentration level 0.2–0.5 ng/dm<sup>3</sup>. The recovery of compounds from 500 cm<sup>3</sup> water samples exceeded 60% and the repeatability of analyses was in the range from 2 to 7%.

### 3. RESULTS AND DISCUSSION

#### 3.1. INFLUENCE OF MEMBRANE PROPERTIES, OPERATING MODE AND FEED WATER CHEMISTRY ON MYCOESTROGES REJECTION – MECHANISM OF SEPARATION

The increase of concentration of zearalenone in nanofiltration permeate samples was higher for the dead-end mode in comparison with the cross-flow mode (Fig. 1).

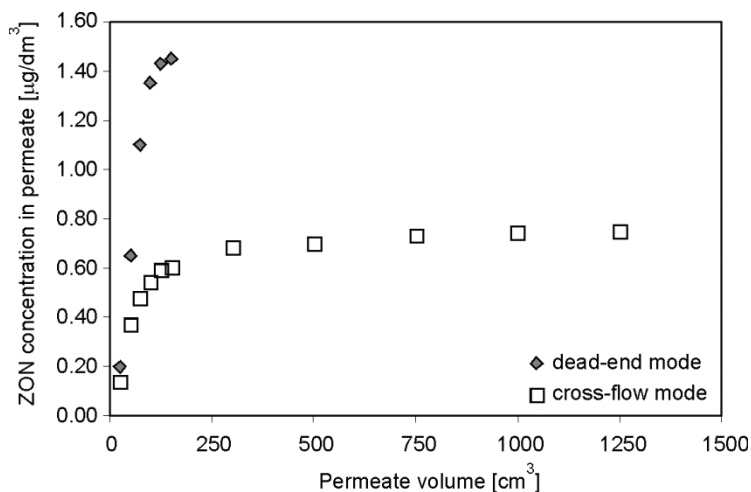


Fig. 1. Dependences of zearalenone (ZON) concentration in the NF permeate in dead-end mode (NF-270 membrane) and cross-flow mode (AFC-30 membrane) ( $\Delta P = 2.0$  MPa)

Under concentration conditions characteristic of the dead-end mode, the concentration of the removed compound in the feed increased, being the reason for the deterioration of permeate quality in time. It was caused by the intensification of the adsorption of hydrophobic micropollutants on the surface and in the membrane structures. A similar dependence was observed by Nghiem et al. [12] during the membrane separation of 17 $\beta$ -estradiol. The retention coefficient of investigated mycoestrogens was clearly dependent on the removed compound as well as on the nanofiltration membrane type (Fig. 2).

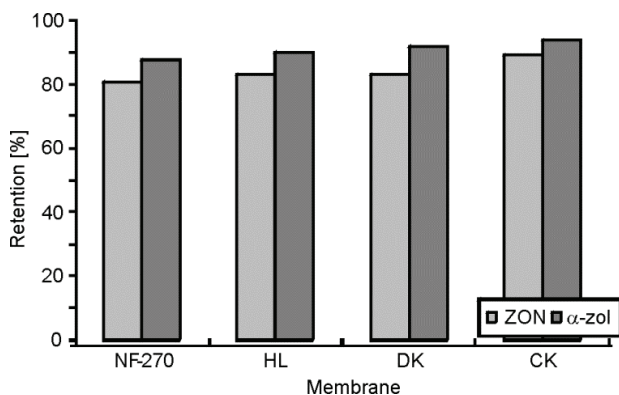


Fig. 2. Retention of ZON and  $\alpha$ -Zol for nanofiltration membranes (concentration 5  $\mu\text{g}/\text{dm}^3$ ,  $\Delta P = 2.0$  MPa)

The average value of the mycoestrogens retention for the investigated membranes was in the range from 81% to 94%. The highest retention of zearalenone and  $\alpha$ -zearalenol equal to 89% and 94%, respectively, was obtained for CK cellulose membrane. The membrane characterizes a high degree of retention of NaCl (Table 2), making it similar to the membranes applied in the reverse osmosis process. Jung et al. [13] found that the degree of retention of NaCl could be a determinant of the separation properties of nanofiltration membranes during nanofiltration of organic micropollutants. The CK cellulose membrane also characterized the highest value of the contact angle equal to 54 $^\circ$  in comparison with other investigated membranes. The parameter is the measure of membrane hydrophobicity and indicates that in the case of the CK membrane, the phenomena accompanying filtration and appearing on the membrane surface are crucial for micropollutants removal. Among those phenomena, membrane scaling and fouling should be mentioned. It was already discussed in the literature [14, 15] that those phenomena resulted in the modification of the membrane surface and according to the membrane pores blocking could contribute to the increase of the retention of organic micropollutants.

The retention of  $\alpha$ -zearalenol was determined for its water concentration equal to 1  $\mu\text{g}/\text{dm}^3$ . Additionally, the degree of adsorption of  $\alpha$ -zearalenol on the surface and in

nanofiltration membranes structure was determined. The results of the study are shown in Fig. 3. It was found that the concentration of the compound did not influence the retention degree as values of the parameter were similar to those obtained for higher compound concentration in water ( $5 \mu\text{g}/\text{dm}^3$ ). The nanofiltration separation of  $\alpha$ -zearalenol was accompanied by the adsorption of the compound on the membrane surface absorption in its structures. In the case of composite nanofiltration membranes, i.e. NF-270, HL and DK, the degree of  $\alpha$ -Zol adsorption was in the range from 29% to 41%. A significantly higher value of the parameter equal to 54% was obtained for CK cellulose membrane. The results confirm the participation of the adsorption in the mechanism of removal of organic micropollutants ( $\log K_{ow} > 2$ ). Such dependence was already discussed in the literature [10, 12–17]. The adsorption is also mentioned to be the reason of surprisingly high retention of compounds observed during ultrafiltration despite the fact that the cut-off of applied membrane in the ultrafiltration process is much higher than molecular weight of removed micropollutants [17].

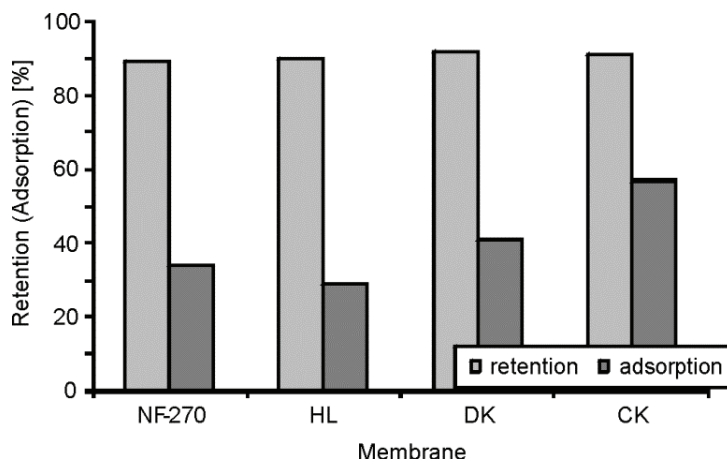


Fig. 3. Retention and adsorption of  $\alpha$ -Zol for nanofiltration membranes (concentration  $1 \mu\text{g}/\text{dm}^3$ ,  $\Delta P = 2.0 \text{ MPa}$ )

The retention of mycoestrogens was investigated during filtration of deionized water with the addition of salts mixture or humic acid (HA). Both, inorganic and organic substances caused the decrease of the membrane capacity ( $\alpha < 1$ ) accompanied by the increase of the contact angles (Table 5). The increase of the contact angles was greater in the case of NF-270 membrane, for which the initial value of the parameter was equal to  $17^\circ$ . This confirms the modification of the membrane surface by inorganic or organic substances. The change of the degree of retention of investigated mycoestrogens was also observed under such process conditions. In most cases, the retention of compounds decreased, however the change level did not exceed 7% excluding the filtration of deionized water with addition of humic acid with NF-270 membrane. In



this case, the retention of micropollutants increased in the range from 12% to 15%. The lowest value of the relative membrane permeability ( $\alpha = 0.77$ ) was also observed for this filtration. However, there are several hypotheses explaining such a phenomenon. The presence of the humic acid in water intensify both, the membrane fouling as well as the formation of HA-mycoestrogens complexes. The retention of complex molecules during nanofiltration is greater according to their bigger size what also results in higher retention of micropollutants. The scheme of formation of discussed complexes was shown by Jin et al. [18]. According to Xu et al. [19] the increase of the retention of micropollutants is also caused by the increase of the hydrophobicity of the membrane which is the result of adsorption of organic substances on the membrane surface (humic acid).

Table 5

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

Compound <sup>a</sup>	Membrane			
	NF-270		CK	
	Water matrix			
	Deionized water + salts	Deionized water + HA	Deionized water + salts	Deionized water + HA
	Retention (change in retention) <sup>b</sup>			
ZON	78 (-3)	96 (+15)	82 (-7)	88 (-1)
A-Zol	86 (-2)	100 (+12)	92 (-2)	92 (-2)
Parameter				
Relative permeability of the membrane $\alpha$	0.99	0.77	0.79	0.82
Contact angle <sup>c</sup> , deg	48	51	57	58

<sup>a</sup>Mycoestrogens concentration – 5  $\mu\text{g}/\text{dm}^3$ .

<sup>b</sup>Positive (negative) sign indicates an increase (decrease) in rejection.

<sup>c</sup>Determined after filtration of solutins containing salts or HA.

### 3.2. EFFECT OF OPERATING PROCESS CONDITIONS ON MYCOESTROGENS RETENTION

The influence of temperature, transmembrane pressure and linear feed velocity on the mycoestrogens retention and process capacity was investigated in the cross-flow mode with the use of AFC-30 membrane. The results are shown in Fig. 4. It was observed that the capacity of the process increased with the temperature and pressure increase, however increase of temperature decreased the retention of  $\alpha$ -zearalenol. It was explained by the change of the dynamic viscosity coefficient of feed water. The increase of the feed linear velocity did not influence neither the process capacity nor

the  $\alpha$ -zearalenol retention. Similar dependences were also observed in case of zearalenone.

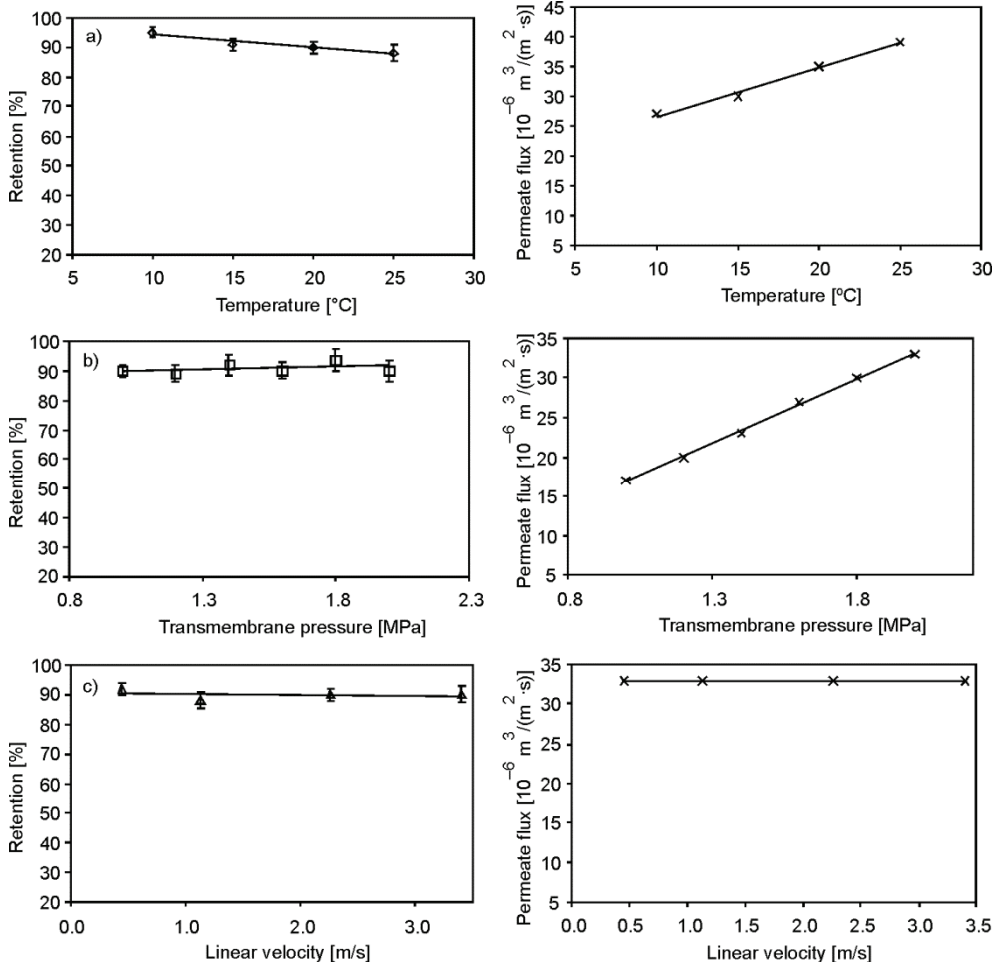


Fig. 4. Retention of  $\alpha$ -Zol and permeate flux related to temperature (a), transmembrane pressure (b) and linear velocity of feed flow (c) (AFC-30 membrane, cross-flow mode, concentration  $5 \mu\text{g}/\text{dm}^3$ )

### 3.3. RETENTION OF MYCOESTROGENS DURING FILTRATION OF TAP WATER AND SURFACE WATER

In the main part of the study, filtrations of tap water and surface water were examined with mycoestrogens introduced to obtain concentration of  $5 \mu\text{g}/\text{dm}^3$ . Operating process conditions were as follows: transmembrane pressure – 2.0 MPa, water temperature – 20 °C and linear feed velocity – 3.4 m/s. During filtration of water without

addition of mycoestrogens, decrease of the volumetric permeate flux in time was observed (Fig. 5a). The relative membrane permeability  $\alpha$  was equal 0.92 for tap water and 0.86 for surface water. During the first hour of the filtration, the increase of the retention of  $\alpha$ -zearalenon was observed (Fig. 5b). As the process continued, its value kept constant and the retention of  $\alpha$ -Zol for tap water and surface water were quite similar. It was due to lower intensity of unfavorable phenomena accompanying membrane filtration in the case of cross-flow mode than in the dead-end mode. Cross-flow mode filtration characterized also less significant membrane surface modification caused by inorganic and/or organic substances present in the feed water. The results of the study presented in Section 3.1 showed that the modification of membrane surface significantly influenced the removal of organic micropollutants by means of nanofiltration.

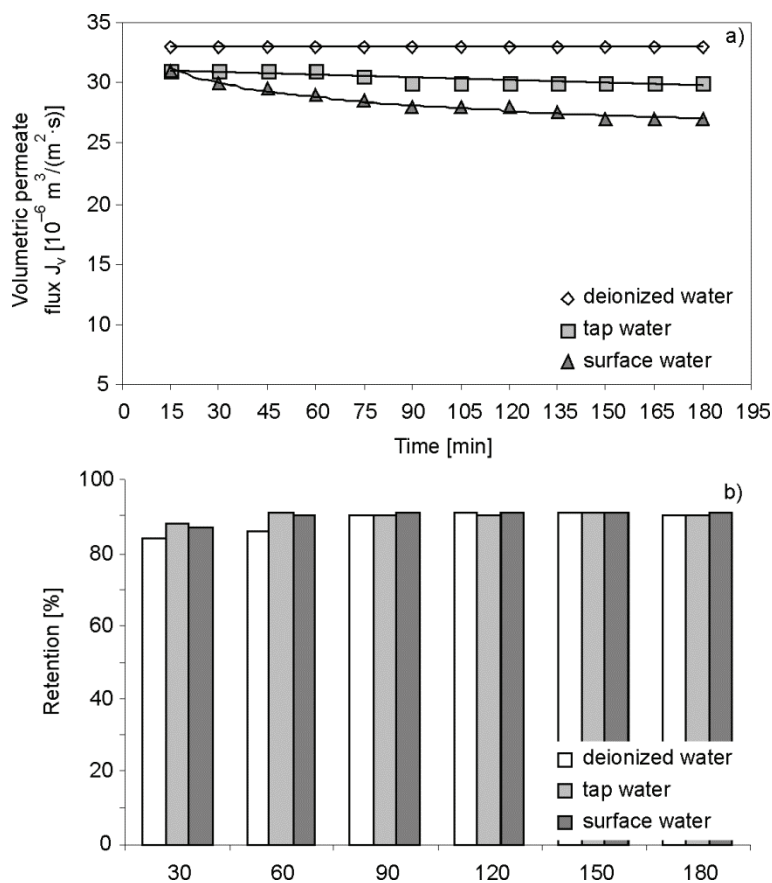


Fig. 5. Effect of water matrix on permeate flux (a) and  $\alpha$ -Zol retention (b) (AFC-30 membrane, cross-flow mode, concentration  $5 \mu\text{g}/\text{dm}^3$ ,  $\Delta P = 2.0 \text{ MPa}$ ,  $v = 3.4 \text{ m/s}$ )

The AFC-30 membrane allowed one to remove effectively inorganic and organic substances present in the feed depending on the water matrix. The conductivity of feed waters which determined the degree of the pollution by inorganic substances was equal to 0.744 mS/cm for tap water and 0.626 mS/cm for surface water. The value of this parameter decreased by 66% in the tap water permeate and by 63% in the surface water permeate. Nevertheless, removal of organic substances (determined by the absorbance measurements) in both cases was high and equal to 96%.

#### 4. CONCLUSION

The study of the separation mechanism of mycoestrogens by means of nanofiltration revealed that the nanofiltration separation of mycoestrogens is accompanied with the adsorption of the compounds on the surface and in structures of the membrane. The adsorption of the compound has the lowest impact on the process in the case of composite membranes (of polyamide separation layer) in comparison with cellulose acetate membranes.

The degree of removal of mycoestrogens during nanofiltration exceeded 81% and depended on the filtration mode, membrane type, operating conditions and water matrix composition. Considering the effectiveness of the micropollutants removal as well as the capacity of the membrane filtration process, it was found that the performance of the process in the cross-flow mode was the best solution. In this system unfavorable phenomena which occurred on the membrane surface and caused the decrease of the retention of the compounds were less intensive in comparison with the dead-end mode. The highest retention of mycoestrogens was observed for cellulose membrane which characterized a high degree of NaCl retention. However, this membrane had the highest ability to adsorb the removed mycoestrogens. The presence of inorganic and organic substances in water could modify the surface of the membrane, resulting in the change of the retention coefficient of micropollutants. The operating conditions of nanofiltration had significant influence on the membrane capacity, but to a smaller extent changed the effectiveness of mycoestrogens removal.

Nanofiltration of tap and surface waters containing mycoestrogens in the cross-flow mode confirmed the possibility of removal of both, inorganic and organic substances as well as low-molecular weight micropollutants. Nanofiltration seems to be an attractive water treatment method, which allows one to solve many problems of modern environmental engineering and protection.

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