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REMOVAL OF PHYTOESTROGENS FROM WATER SOLUTIONS USING TUBULAR NANOFILTRATION MEMBRANES

USUWANIE FITOESTROGENÓW Z ROZTWORÓW WODNYCH ZA POMOCĄ RUROWYCH MEMBRAN NANOFILTRACYJNYCH

Abstract: The research focused on the effectiveness of phytoestrogens (daidzein and coumestrol) removal from different water solutions using a tubular nanofiltration membrane (AFC-30). The micropollutants (concentration of 5 μg/dm^3) were added to different matrices (deionized and tap water – with and without humic acid). The retention coefficient of phytoestrogens and volumetric permeate flux were determined during membrane filtration. The membrane was characterized in terms of the removal of salts representing mono- and divalent ions ie NaCl and $MgSO_4$. The highest retention coefficient was found for coumestrol during the filtration of tap water with humic acid added, however, the volumetric permeate flux for this filtration was the lowest. The removal of inorganic and organic matter (measured as electric conductivity of water and UV absorbance at λ = 254 nm) from the waters was high. Thanks to those properties, nanofiltration can be used to remove simultaneously organic micropollutants, excessive hardness and precursors of disinfection by-products formation, and also partially desalt water.

Keywords: nanofiltration, water matrix, phytoestrogens, water treatment

The compounds of estrogenic activity identified in the aqueous environment include xenoestrogens, mycoestrogens and plant hormones, the so-called phytoestrogens [1]. In the human body, phytoestrogens act like estrogens and their strength ranges from 1/500 to 1/1000 of that typical of 17 β-estradiol [2]. In surface waters, the most frequently identified phytoestrogens include biochanin A, daidzein, genistein and coumestrol [3–7]. The level of phytoestrogens concentrations assayed in the river water in Australia, Switzerland, Germany and Italy fell within 1–12 ng/dm^3 [3–6], although daidzein and genistein assayed in Japan displayed 43 μg/dm^3 and 143 μg/dm^3 respectively [7].

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Pressure-driven membrane operations, notably reverse osmosis (RO) and nanofiltration (NF), are regarded as possible technique for removing organic micropollutants from water [8]. The first investigations date back to the 1990s and dealt with the removal of pesticides by nanofiltration, which led to the launch of several installations operating on a pilot and industrial scale [9]. However, the identification of new compounds in waters makes us continue the research to acquire a better knowledge of membrane operations with respect to organic micropollutants removal.

This works was aimed at assessing the efficiency of phytoestrogens (daidzein and coumestrol) removal by nanofiltration. The filtration was carried out on waters of different matrices containing standard solutions of micropollutants, using a tubular nanofiltration membrane (AFC-30). The membrane was also characterized in terms of organic and inorganic matter removal.

Materials and methods

Nanofiltration was conducted on a TMI 14 installation manufactured by J.A.M. INOX Produkt equipped with a laboratory testing module operating in the cross-flow mode. The tubular AFC-30 membrane employed was produced by ITI PCI Membranes (Poland). Table 1 shows its characteristics. The research took the following steps:

– initial filtration that covered the conditioning of the membrane, using deionized water at a transmembrane pressure of 1.0–2.0 MPa for 3 hours (with and without 1 g/dm^3 NaCl and $MgSO_4$ solutions added),

– 5-hour specific filtration of model water made of deionized and tap water (with and without 10 mgC/dm^3 humic acid added) and 5 mg/dm^3 micropollutants standard solutions.

Table 1

Characteristics of membrane (manufacturer data)

Membrane type	Material	Max pH range	Max pressure [MPa]	Max temp. [°C]	Removal of $CaCl_2$ [%]
AFC-30	composite (active layer-polyamide)	1.5–9.5	6.0	60	75

The effectiveness of the filtration was assessed by determining the volumetric and relative permeate fluxes (J_w – for deionized water, J_v – for the water with micropollutants standard solutions added (1) and α – relative permeability of membrane (2), Table 2). The concentrations of the micropollutants were assayed in the treated water (feed) and that purified with the membrane techniques (permeate), which then formed the basis for calculating their retention coefficients R (3).

Table 2

Equations used to evaluate membrane properties and removal efficiencies

Parameter	Equation
Volumetric permeate flux, J_v (J_w)/(m^3 m^{-2} · s^{-1})	$J_v(J_w) = \frac{V}{F \cdot t}$ (1)
Relative permeability of 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 [$\mu g\ dm^{-3}$], f – feed, p – permeate.

The standard solutions of the phytoestrogens and humic acid were supplied by Sigma-Aldrich (Poznan, Poland). Two phytoestrogenic compounds ie daidzein and coumestrol representing isoflavones and coumestans were chosen for the tests, Fig. 1. Some selected physico-chemical properties of the micropollutnats are given in Table 3. The phytoestrogens were separated from a water sample (200 cm^3), using the solid phase extraction SPE while GC-MS helped carry out quantitative analyses. The detailed methodology of phytoestrogens determination was described in [10].

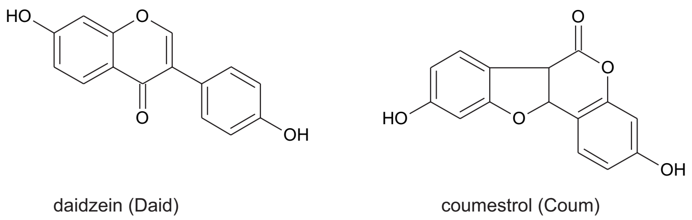

Fig. 1. Chemical structures of phytoestrogens

Table 3

Physico-chemical properties of phytoestrogens

Compounds	Molecular mass [g/mol]	Water solubility [mg/dm^3]	log K_{ow} [1]
Daid	254.24	568.4	2.55
Coum	268.22	281.0	1.57

[1] log K_{ow} values calculated from computer program named "SRC K_{ow} WIN".

Results and discussion

The permeability of the AFC-30 membrane increases with an increasing trans-membrane pressure and the dependence is of linear nature, Fig. 2. The filtration of NaCl

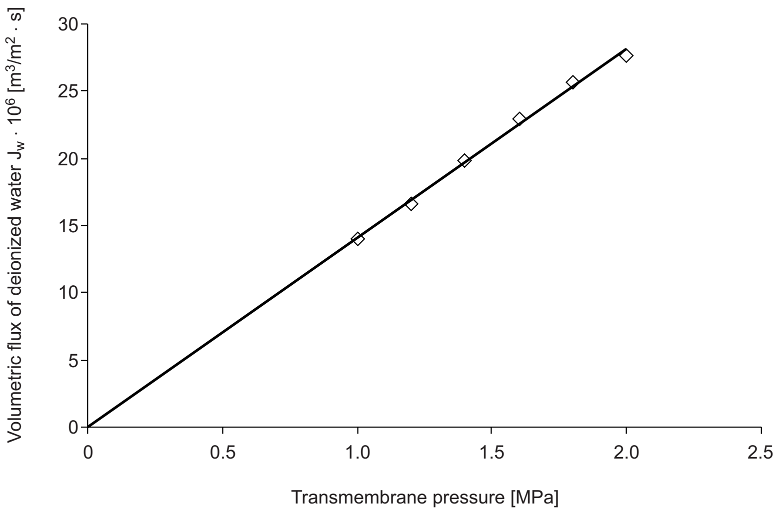

Fig. 2. Relationship between volumetric flux of deionized water and transmembrane pressure

and $MgSO_4$ representing mono- and divalent ions revealed a decrease in the permeability of the membrane during its initial stage, Fig. 3. The relative volume permeate flux was lower than 1, being 0.98 and 0.96 for NaCl and $MgSO_4$ respectively, Table 4. The nanofiltration membrane was very efficient in removing divalent ions (R_{Mg} > 86 %), however, it did not display such efficiency for monovalent ions (R_{Cl} > 58 %). Thus, the AFC-30 membrane can be used to remove the excessive hardness of waters and partially desalt water.

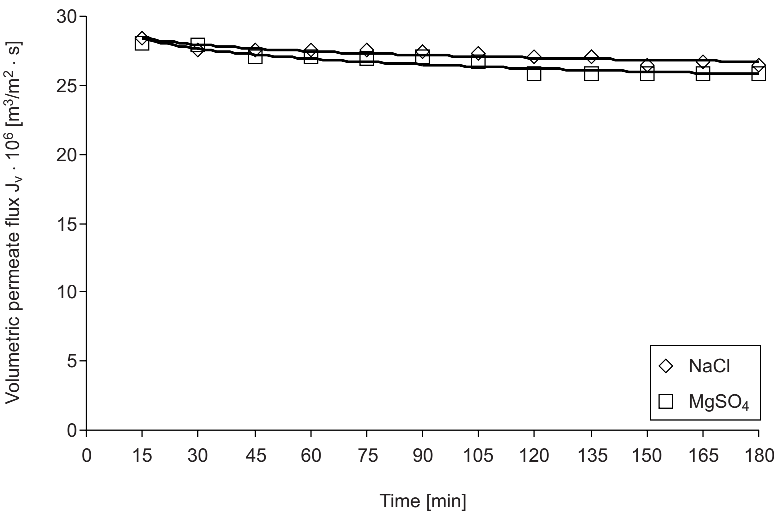

Fig. 3. Volumetric permeate flux on time during filtrations of salt solutions (transmembrane pressure 2.0 MPa, temperature 20 °C and velocity 3.4 m/s)

Table 4

Volumetric permeate flux, relative permeability of the membrane and retention coefficient of NaCl and $MgSO_4$

Salt	Volumetric flux of deionized water, $J_w \cdot 10^6$ [$m^3/m^2 \cdot s$]	Relative permeability of the membrane, α [-]	Salt retention [%]
NaCl	27.6	0.98	58.2
$MgSO_4$		0.96	86.2

The filtration of the model solutions revealed the lowest volume permeate fluxes J_v for tap water with an addition of humic acid and standard solutions of phytoestrogens, Fig. 4A. However, the coefficients of phytoestrogens retention were the highest with reference to the comparative filtration of deionized and tap waters (without humic acid added) containing standard solutions of micropollutants, Fig. 4B and Table 5. A similar trend was shown in paper [11] which investigated the effect of organic matter on the removal of xenoestrogens in the dead-end mode. The increase in the removal of estrogenic micropollutants was caused by the formation of natural organic matter--estrogenic micropollutants complexes and membrane fouling. Coumestrol, characterized by a higher molecular mass (Table 3), turned out to be removed more efficiently than the comparatively tested daidzein. Moreover, the compound displays lower water solubility in water.

Table 5

Retention coefficients of phytoestrogens, membrane transport properties and removal of selected physico-chemical parameters of the waters

Compound	Water solutions		
	Deionized water + phytoestrogens	Tap water + phytoestrogens	Tap water + HA + phytoestrogens
	Retention coefficient [%]		
Daid	70.9	71.0	80.3
Coum	69.9	71.4	92.0
Membrane transport properties	Volume		
Relative permeability of the membrane, α [-]	0.98	0.91	0.78
Physico-chemical parameters	Removal [%]		
Coductivity[1] [μS/cm]	—	66.0	57.5
Absorbance in UV (λ = 254 nm)[2] [cm^{-1}]	—	92.9	96.3

[1] Conductivity in tap water: 782 μS/cm (without HA) and 998 μS/cm (with HA); [2] Tap water absorbance: 0.028 cm^{-1} (without HA) and 0.321 cm^{-1} (with HA).

The membrane also enables an effective removal of organic and inorganic matter from water, depending on the water matrix, Table 5. The conductivity of the model

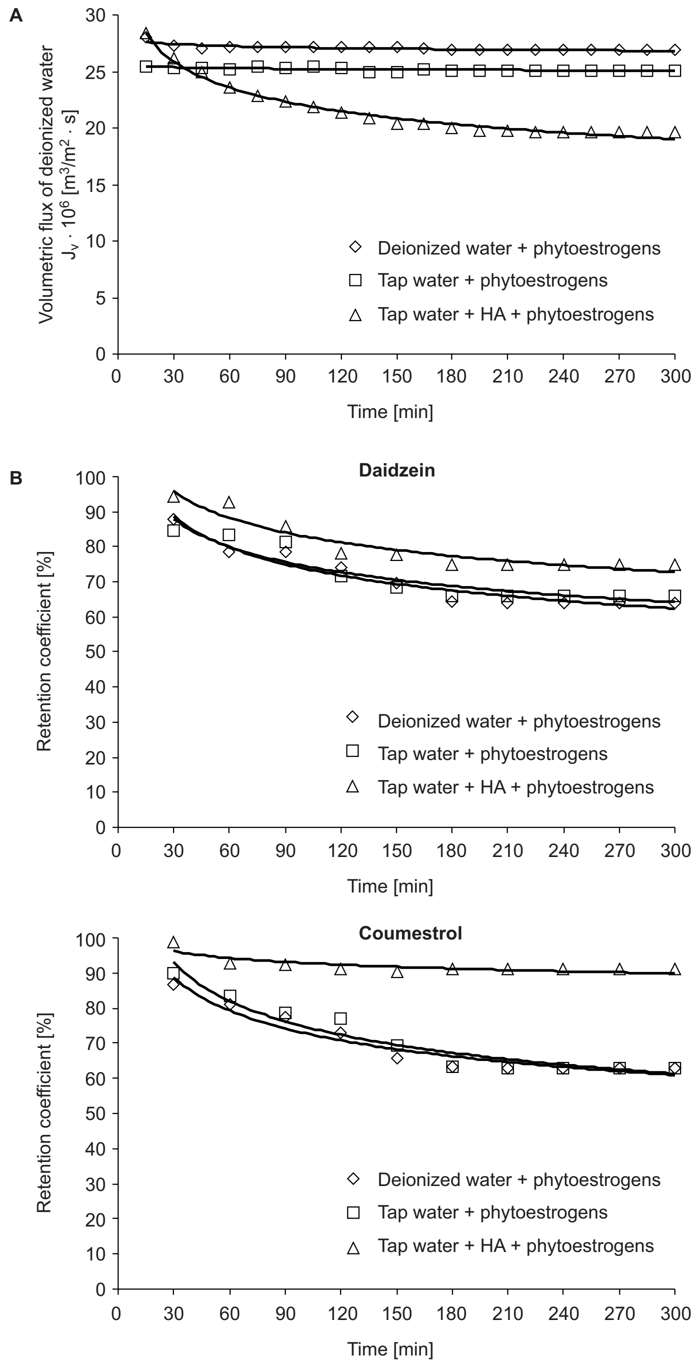

Fig. 4. Volumetric permeate flux (A) and retention coefficient of phytoestrogens (B) during filtrations of water solutions

solution made of tap water with and without an addition of 10 mgC/dm^3 humic acid was 782 μS/cm and 998 μS/cm, respectively. As to its removal by nanofiltration, it reached 66 % and 57.5 % for tap water without and with humic acid added, respectively. The removal of organic matter for both waters tested was high and exceeded 92 %.

Conclusions

1. The removal of phytoestrogens from water solutions by the tubular nanofiltration membrane depends on a water matrix and type of a compound. The highest retention was found for coumestrol (R = 92 %) during filtration of tap water with humic acid added. However, the volumetric permeate flux for that type of filtration was the lowest.
2. The AFC-30 nanofiltration membrane sufficiently removes mono- and divalent ions, which makes it feasible to use it in the removal of excessive hardness and partial desalination of waters.
3. The high removal of organic matter by nanofiltration enables a considerable reduction in the formation of by-products in water disinfection during the technological process of its treatment.

Acknowledgement

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USUWANIE FITOESTROGENÓW Z ROZTWORÓW WODNYCH ZA POMOCĄ RUROWYCH MEMBRAN NANOFILTRACYJNYCH

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Abstrakt: Badania dotyczyły efektywności usuwania dwóch fitoestrogenów (daidzeina i kumestrol) z różnych roztworów wodnych przy użyciu rurowej membrany nanofiltracyjnej (AFC-30). Mikrozanieczyszczenia dodawano do różnych matryc (woda dejonizowana i woda wodociągowa – bez i z dodatkiem kwasu humusowego) w stężeniu 5 μg/dm^3. W trakcie filtracji membranowej wyznaczano współczynniki retencji fitoestrogenów oraz objętościowy strumień permeatu. Membranę scharakteryzowano pod kątem usuwania soli reprezentujących jony jedno- i dwuwartościowych, mianowicie NaCl i $MgSO_4$. Największy współczynnik retencji uzyskano dla kumestrolu podczas filtracji wody wodociągowej z dodatkiem kwasu humusowego, ale objętościowy strumień permeatu dla tej filtracji był najmniejszy. Usunięcie substancji nieorganicznej i organicznej (mierzone jako przewodność elektryczna właściwa wody i absorbancja UV dla λ = 254 nm) z badanych wód było duże. Z uwagi na te własności proces nanofiltracji może być stosowany do równoczesnego usuwania mikrozanieczyszczeń organicznych, nadmiernej twardości, prekursorów tworzenia ubocznych produktów dezynfekcji oraz do częściowego odsalania wody.

Słowa kluczowe: nanofiltracja, matryca wody, fitoestrogeny, oczyszczanie wody