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Purification of water containing mycoestrogens using ozonation and nanofiltration

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ABSTRACT

This study investigated the efficiency of mycoestrogens removal from water using the sequential combinations of two processes: ozonation and nanofiltration. The results were compared with ones obtained for water treatment via ozonation and nanofiltration performed as single-stage operations. The removal of mycoestrogens was improved using the combination of ozonation–nanofiltration processes in comparison to single-stage ozonation system, while a negligible difference was observed with nanofiltration. However, the analyzed system improved the nanofiltration membrane capacity. Ozonation before membrane filtration limited the intensity of the membrane blocking, which adjusted the use of the complex systems in water treatment.

Keywords: Ozonation; Nanofiltration; Combined treatment; Mycoestrogens removal

1. Introduction

Ozone is applied in water treatment processes to disinfect and to remove taste, smell and color [1]. Considering its high redox potential (2.07 V in an acidic environment and 1.27 V in a basic one), ozone can also be used for the oxidation of natural and anthropogenic organic compounds, including low-molecular-weight micropollutants [1–7]. Increasing the ozone dose and the duration of the oxidation process usually improves the efficiency of organic compound removal [4]. However, considering the technical conditions, it is not always possible to apply exact oxidation parameters, especially if the duration of the contact time is limited. If the ozone doses are too small or the oxidation time is too short, the process does not reach the final mineralization and oxidation byproducts form [4–6]. For living organisms, those compounds can be even more harmful than the original compounds [3–6]. Furthermore, a significant concentration of high-molecular-weight compounds (e.g., humic acids, HA) in water increases ozonation costs [8].

The efficient removal of organic compounds can also occur during nanofiltration [9–12]. The process effectiveness depends on the operation conditions, membrane type and raw water quality [9–11]. Usually, the process is limited by a decrease in permeate flux that in time comes out of deposition from high-molecular-weight organic compounds on membrane surfaces (fouling phenomenon) [12–16].

Membrane fouling can be limited by combining the membrane processes with the other unit operations: the combined system (when processes are run one after another) or the hybrid system (when two or more processes are performed simultaneously) [17–19]. The combined system includes unit operations (subsystems) that can work together as one system. The aim

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of those subsystems is to improve the overall process effectiveness compared to single-stage unit operations. One study [19] shows that combining ozonation with nanofiltration has a significant impact on the formation of disinfectant byproducts as the concentration of dissolved organic compounds in water is decreased.

The aim of the study was to evaluate the efficiency of the sequential combinations of two processes: ozonation and nanofiltration—for removing chosen mycoestrogens from water. The results were compared with results obtained for the single-stage ozonation and nanofiltration treatment processes. Two water types, differing in organic and inorganic compound concentrations, were used in the treatment, which tested four commercial nanofiltration membranes. The severity of membrane fouling was also investigated during the study.

2. Materials and methods

2.1. Reagents and solutions

The process used water solutions prepared on tap-water matrices with the addition of HA and the chosen mycoestrogens (ZON) and α-zearalenol (α-Zol). The concentration of mycoestrogens in the water was 500 μg/dm^3. Typically, in natural waters, the concentration of mycoestrogens is lower, but the addition of the contaminants increased the concentration, the analytical procedure performance and the accuracy of measurements. The HA were used as substitutes for high-molecular-weight organic compounds present in natural water in a wide concentration range [20]. Natural surface water was also introduced to the treatment. The pH ratio of the treated water was equal to 7.0 and was modified using either 0.1 mol/dm^3 HCl or 0.2 mol/dm^3 NaOH solutions. The physiochemical characteristics of the investigated waters are shown in Table 1. The standards for HA, ZON and α-Zol were supplied by Sigma–Aldrich (Poland).

2.2. Ozonation

The ozonation process operated at a temperature of 20 °C in a cylindrical reactor (volume 1000 cm^3) equipped with a magnetic stirrer for constant mixing. The ozone was produced in an Ozoner FM 500 generator (WRC Multiozon, Poland) and was introduced to the reactor using a ceramic diffuser. A constant ozone dose (1 mg/dm^3) was applied. The concentration of ozone in the reactor was determined via the iodometric method. To remove traces of ozone from post-reaction mixtures, the amount of a 24 mmol/dm^3 Na_2SO_3 solution (p.a. grade, P.P.H. Stanlab, Poland) was added. Next, samples were filtered using a 0.45 μm cellulose acetate filter (Millipore, Poland). The contact time (1–10 min), solution pH (4–8) and water matrix composition were investigated for their impacts on the removal rates of organic substances and investigated mycoestrogens.

2.3. Nanofiltration

Flat-sheet commercial nanofiltration membranes identified as CK, DK and HL (GE Osmonics, USA) and as NF-270 (Dow Filmtec, USA) were used in the study. The characteristics of the applied membranes are listed in Table 2. The membrane filtration of raw waters was performed at a transmembrane pressure of 2.0 MPa in a stainless steel membrane cell (volume 350 cm^3, membrane surface area 38.5 cm^2), which enabled the performance of the process in the dead-end mode. The efficiency of the filtration was determined by measurements of the volumetric permeate flux, J_v, and the deionized water flux, J_w:

$$J_V(J_W) = \frac{V}{Ft}$$

where V is volume (m^3), F is the membrane area (m^2) and t is the filtration time (s).

The obtained results were used to calculate the relative membrane permeability (a), which was used to determine the extent of the membrane blocking:

$$\alpha = \frac{J_V}{J_W}$$

Table 1
The physiochemical characteristics of the waters

Water	Symbol	Conductivity, mS/cm	Absorbance, UV_{254}, 1/cm
Tap water with HA (3 mg/dm^3)	Water 1	0.199	0.033
Tap water with HA (9 mg/dm^3)	Water 2	0.580	0.048
Tap water with HA (15 mg/dm^3)	Water 3	0.881	0.170
Tap water with HA (30 mg/dm^3)	Water 4	0.905	0.202
Surface water	sw	1.313	0.140

Table 2
Membrane properties (data given by the producer)

Membrane	Manufacturer	Material	Molecular weight cut-off, Da	Contact angle[a], °	Deionized water flux (J_w)[b], 10^{-6} m^3/m^2s	Salts removal rate[c], %	
						$MgSO_4$	NaCl
CK	GE Osmonics	Cellulose acetate	150–300	54	7.60	96.8	75
DK		Polyamide on Polysulfone support		37	19.0	96.3	39
HL				25	56.0	90.7	46
NF-270	Dow Filmtec		200	21	70.6	92.1	41

[a] Experimental determination with a pocket Fibro System AB PG-1 goniometer.
[b] Experimental determination at ΔP =2.0 MPa.
[c] Experimental determination by filtration of $MgSO_4$ or NaCl solution (1000 mg/dm^3) at ΔP =2.0 MPa.

The nanofiltration membranes were characterized by a wide range of volumetric deionized water flux J_w (determined for the process pressure equal to 2.0 MPa): 7.60×10^{-6} m^3/m^2 s for the cellulose CK membrane to 70.6 × 10^{-6} m^3/m^2 s for the composite NF-270 membrane. The differences between membranes were also observed in contact angle values and salt retention rates, expressed as the removal rate of NaCl as a representative of monovalent ions. Nevertheless, the determined retention of bivalent ions (during the filtration of the $MgSO_4$ solution) exceeded 90% in the cases of all tested membranes.

2.4. Combination of ozonation and nanofiltration processes

To determine the effectiveness of mycoestrogen removal from water via the sequential combinations of two processes: ozonation and nanofiltration, the feed water was first introduced to the ozonation, which was followed by nanofiltration.

2.5. Analytical methods

The content of the HA was determined by absorbance measurements (at wavelength 254 nm) using a UV VIS Cecil 1000 spectrometer (Jena AG, Poland). The concentrations of the inorganic substances were determined by water conductivity measurements using the laboratory multiparameter instrument inoLab® 740 (WTW, Poland). The concentrations of mycoestrogens were determined using solid-phase extraction (SPE) and gas chromatography-mass spectrometry (GC-MS Saturn 2100 T; manufactured by Varian). Supelclean™ ENVI-18 tubes (volume 6.0 cm^3, phase mass 1.0 g) (Supelco, Poland) were used. The extraction was preceded by tube phase conditioning with acetonitrile (5.0 cm^3) followed by deionized water (5.0 cm^3). The extracted compound was washed out with acetonitrile (4.0 cm^3). A ternary reaction using a mixture of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA)/trimethylchlorosilane (TMCS)/dithioerythritol (DTE) (v/v/w ratio 1000:10:2) was used to derive the mycoestrogens. The derivation time was 5 min, and the temperature was 90 °C. The qualitative and quantitative GC-MS analyses of the obtained silyl derivatives of mycoestrogens were performed using the selected ion monitoring (SIM) method (ZON m/z = 444, 430, 306 and 150; α-Zol m/z = 446, 432, 414 and 306). The temperature program of the chromatographic oven ranged from 140 to 280 °C (temperature of injector equal to 300 °C). The chromatographic separation was performed using a VF-5ms column (Varian, Poland). A detailed description of the method was discussed in a previous study [21].

The presented results are average values obtained from four experiments. The determined method error was less than 5%, so its range was omitted in the results presentation.

3. Results and discussion

3.1. Ozonation

The efficiency of mycoestrogen removal via ozonation did not exceed 53%, and it depended on the water matrix composition (Fig. 1). The micropollutant removal rate was smallest for surface water. The removal of HA (determined on the basis of absorbance measurements and ranging from 2% to 33%) was significantly less than the removal of mycoestrogens. Similarly, as in the case of the mycoestrogens, the effectiveness of the removal of HA depended on the water matrix composition (Fig. 2).

It was also found that prolonged ozone contact with water resulted in the increase in mycoestrogen removal rates (Fig. 3A); for example, the removal rate of ZON was 50% at a contact time of 1 min, while it exceeded

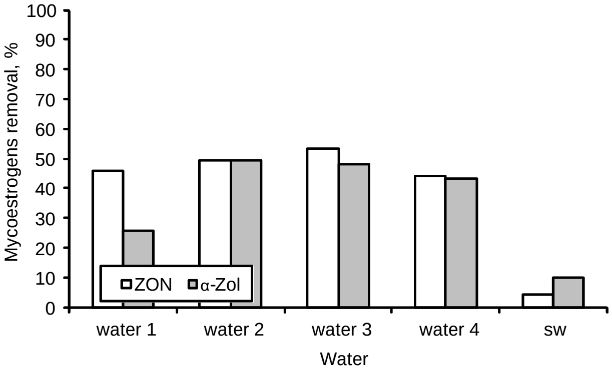

Fig. 1. The influence of the water matrix on the efficiency of mycoestrogen removal (ozone dose 1 mg/dm^3, contact time 1 min).

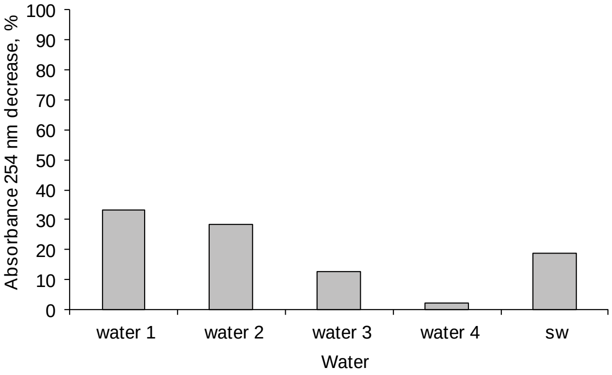

Fig. 2. The efficiency of HA removal during ozonation (determined on the basis of absorbance measurements).

60% at a contact time of 10 min. The mycoestrogen removal rate increase was also caused by the increase in water pH (Fig. 3B). Such a phenomenon is explained by the intensification of hydroxyl $OH^{\cdot}$ radical activity under increased solution pH conditions [4].

3.2. Ozonation with nanofiltration

The membrane nanofiltration process was considered the polishing step in the treatment of water containing mycoestrogens after ozonation (ozone dose 1 mg/dm^3, contact time 1 min). It was shown that the additional application of nanofiltration to the water treatment enabled the increase of removal effectiveness of investigated compounds in comparison with the single-stage ozonation process (Fig. 4). On the other hand, the effectiveness of mycoestrogens removal via nanofiltration performed as a single-stage process was comparable to that performed as a part of combination of those two processes. The micropollutant retention rate exceeded 85% regardless of membrane type (unpublished results). However, the evaluation of relative permeability showed significant differences in the transport properties of the applied membranes (Fig. 5).

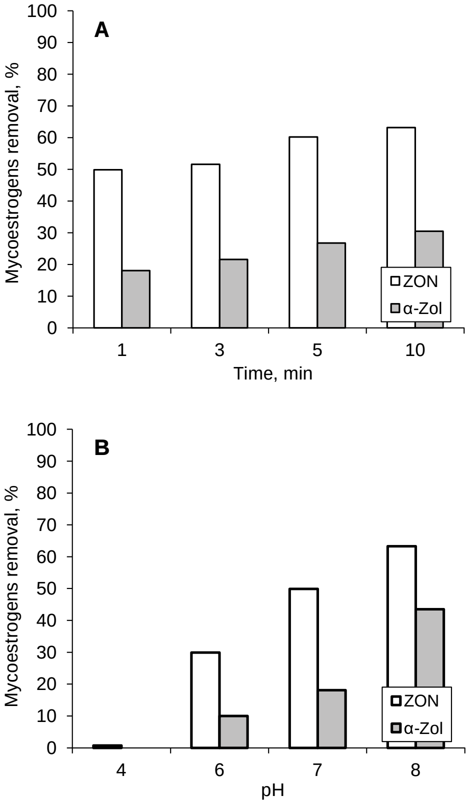

Fig. 3. The influence of contact time (A) and water pH (B) on the mycoestrogen removal (Water 3).

In the case of the sequential combinations of two processes: ozonation and nanofiltration, the permeability of the NF-270 membrane was much higher relative to the permeability observed for the single-stage nanofiltration. The only exception was observed during the treatment of water with the greatest concentration of organic and inorganic compounds (Water 4). A similar tendency was observed in the cases of the other nanofiltration membranes, and the intensity of the membrane blocking depended on the membrane type (Fig. 6).

The smallest difference in relative membrane permeability obtained for the single-stage process and the combined process was observed for the CK cellulose membrane and the NF-270 composite membrane. Considering the membrane properties shown in Table 2, it can be concluded that such dependence is the result of the membrane material properties and/or the values of the contact angle. However, the impacts of other

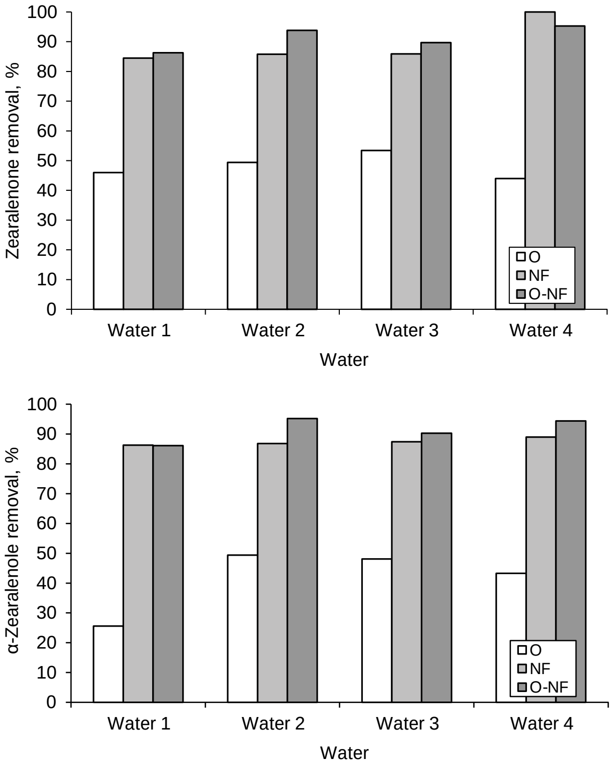

Fig. 4. The removal of ZON and α-Zol via ozonation and nanofiltration (NF-270 membrane) performed as a single-stage process and the combined system; impact of water matrix composition.

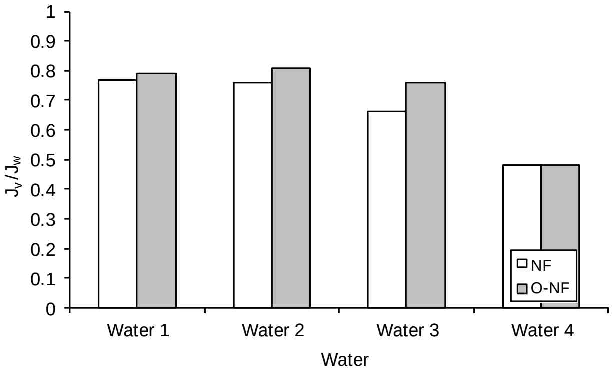

Fig. 5. The influence of the water matrix on the relative permeability of the NF-270 membrane.

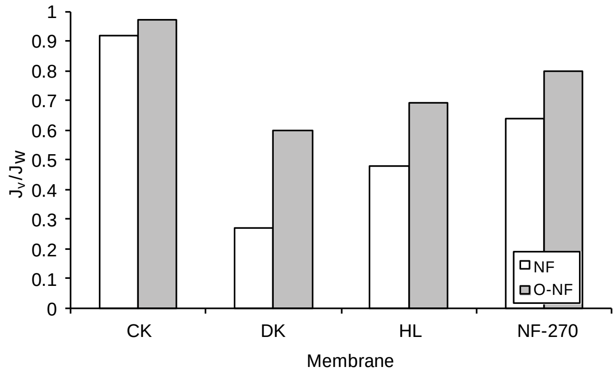

Fig. 6. The relative permeability of the membranes during the simulated water treatment (Water 3).

membrane properties, as well as the complexity of the membrane blocking phenomenon, cannot be completely ignored [12–16].

In the final step of the study, natural surface water, to which 500 μg/dm^3 mycoestrogen was added, was introduced to the treatment process. The original surface water did not contain the investigated micropollutants. The NF-270 membrane was used in that step for its transport properties. The results obtained for the surface water were similar to the results observed for the simulated waters. The removal of mycoestrogens was significant and exceeded 90% regardless of the type of removed compound or the type of water treatment system (Table 3). However, the application of nanofiltration in combination with ozonation was more advantageous according to the membrane's relative permeability. Regardless of the water treatment system, the nanofiltration process enabled the high retention of high-molecular-weight organic compounds as well as the significant decrease of inorganic compound concentrations at a level exceeding 55%.

Table 3
The effectiveness and transport properties of the nanofiltration performed as a single-stage process or as a part of a combinated system with ozonation during the treatment of surface water (NF-270 membrane).

	Process/system	
	NF (NF-270 membrane)	O+NF (ozone dose 1 mg/dm^3, contact time 1 min)
	Removal (decrease*), %	
ZON	90.7	90.1
α-Zol	93.1	91.7
Conductivity*	56.4	55.3
Absorbance*	100	98.1
Parameter		
Relative permeability of the membrane α, –	0.77	0.87

4. Conclusion

The efficiency of mycoestrogen removal during ozonation depends on the quality and the pH of the treated water and on the contact time. The increase in the micropollutant removal rate can be explained by the prolonged contact time or the increase in the treated water pH.

The development of the treatment by nanofiltration introduced to the treatment after ozonation enables the highly effective removal of mycoestrogens at a rate greater than 85%, despite the application of a low ozone dose (1 mg/dm^3) and a short contact time (1 min). The efficiency of mycoestrogens removal in the combinated system was much higher in comparison to that obtained for single-stage ozonation. This result was observed for both the simulated and the natural water treatments.

The performance comparison between the single-stage and sequential combination of nanofiltration and ozonation processes revealed that the mycoestrogens removal rate was independent of the system configuration. However, a significant difference was observed in the membrane transport properties. The relative membrane permeability was greater when the process was preceded by water ozonation. The sequential combination of two analyzed processes improves the water quality according to high-molecular-weight organic compound concentration (expressed as absorbance) and inorganic compound content (expressed as specific conductivity).

The nanofiltration membranes investigated in this study have similar separation properties according to mycoestrogens retention, but the membranes differ in their affinity for blocking. This phenomenon is related to the membrane material properties and/or the contact angle of those membranes.

Acknowledgements

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