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Retention of mycoestrogens with industrial nanofiltration modules

Mariusz Dudziak

Faculty of Energy and Environmental Engineering, Silesian University of Technology,
Konarskiego 18, 44-100 Gliwice, Poland
Tel./Fax: +48 32 237 10 47; email: mariusz.dudziak@polsl.pl

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ABSTRACT

This study addressed nanofiltration of waters of contrasting organic and inorganic matter concentrations, which contained low-molecular-weight mycoestrogens, using an industrial membrane module. The investigation focused on the effect of water recovery at a range of 10 to 90% vol. on the efficiency and effectiveness of the process. An increase in permeate recovery caused a decrease in both efficiency and removal of inorganic matter and mycoestrogens. The removal of organic matter was high irrespective of water recovery. It has been found that the effect of water recovery on the separation of micro-pollutants was the main cause of the decrease in the removal of the compounds in industrial installations against the results obtained on a bench scale.

Keywords: Organic micro-pollutants; Nanofiltration; Water treatment; Retention; Separation mechanism

1. Introduction

During nanofiltration, the effectiveness of organic micro-pollutant removal depends on a number of factors and phenomena occurring in membrane filtration [1,2]. The most important mechanisms of micro-pollutant separation include the following:

- steric hindrance (a sieving effect: molecules larger than the membrane pores are removed),
- hydrophobic effect causing compound adsorption onto a membrane,
- electrostatic effect (mainly electrostatic repulsion between a negatively charged particle of the membrane and membrane surface).

The three mechanisms can be connected to both the physico-chemical properties of the compounds removed and the characteristics of a membrane used [1,3]. The effectiveness of micro-pollutant removal also depends on the parameters of purified water and operating conditions [1–3]. Articles [4–6] also revealed the influence of other adverse phenomena concomitant with membrane filtration, that is, membrane fouling and scaling on micro-pollutant retention. However, industrial membrane installations usually produce a decrease in the removal of micro-pollutants compared with the results obtained on a bench scale. This study was aimed at finding the causes of that phenomenon.

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The study assessed the effectiveness of mycoestrogen removal (zearalenone, α-zearalenole, β-zearalenole, and zearalanone) during nanofiltration, using a membrane installation equipped with an industrial membrane module. It examined the effect of permeate recovery on mycoestrogen removal during filtration of water containing contrasting concentrations of organic and inorganic matter.

2. Experimental

2.1. Nanofiltration experiments

Nanofiltration was carried out using a cross-flow mode membrane installation equipped with a Dow Filmtec spiral industrial membrane module (NF270–2,540), active membrane area of 2.6 m^2 (cut-off 200–400 Da). The transmembrane pressure was 2.0 MPa and temperature reached 20℃ (linear velocity of fluid flow over the membrane surface = 3.4 m/s). In the assumed operating conditions, the average volume deionized water flux was $58.3 \cdot 10^{-6}\, m^3/m^2 s$. The volume deionized water flux (J_w) and permeate flux (J_v) examined during the water treatment were calculated as follows Eq. (1):

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

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

The efficiency of the membrane process was also assessed on the basis of the relative permeability of the membrane α (Eq. (2)):

$$\alpha = \frac{J_v}{J_w} \tag{2}$$

The effect of water recovery on the retention of mycoestrogens was investigated over a range of 10 to 90% of initial volume of the feed (20 dm^3). The retention (R) of compounds was determined using Eq. (3):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3}$$

where: C-concentration, p-permeate, and f-feed.

The filtered water (deionized, tap, and surface) of different concentrations of organic and inorganic matter contained mycoestrogens of a constant concentration of 5 μg/dm^3. Table 1 gives its physico-chemical characteristics.

Table 1
Physico-chemical characteristic of the water

Parameters	Tap water	Surface water
pH	7.42	7.33
Total organic carbon, mg/dm^3	2.01	7.07
Conductivity, mS/cm	0.744	0.626

2.2. Mycoestrogens

Mycoestrogens are mycotoxins that, apart from toxic effects, exhibit estrogenic activity [7]. They have been included in the group of biologically active organic micro-pollutants of the aqueous environment. The concentration of mycoestrogens in surface water ranges from 0 to 44 ng/dm^3 and is dependent on a season, which is connected to fungi activity [8–11]. The study employed high mycoestrogen concentrations in water which exceeded their environmental levels, because the assumed order of magnitude facilitated the analytical procedure and thus improved the accuracy of the measurements.

The standard solutions of the mycoestrogens selected for the tests, that is, zearalenone (ZON) and its metabolites α-zearalenole (α-Zol), β-zearalenole (β-Zol), and zearalanone (ZAN) were produced by Sigma-Aldrich (Fig. 1). The 1.0 mg/cm^3 stock solution and 100 ng/μl working solution were prepared in methanol.

2.3. Analytical methods

Mycoestrogens were separated from water in Supelco SPE columns (Supelclean™ ENVI-18, volume 6 cm^3, and 1.0 g phase) and their concentrations were assayed by gas chromatography–mass spectrometry (GC–MS Saturn 2,100 T produced by Varian). Prior to extraction, the phase of the column was conditioned with acetonitrile (5 cm^3) and then rinsed with deionized water (5 cm^3). The separated compounds were eluted with acetonitrile (4 cm^3), and when the solvent evaporated to dryness, they were derivatized using a three-component mixture BSTFA/TMCS/DTE at a ratio of 1,000:10:2 (v/v/w). The derivatization time and temperature were 5 min and 90℃, respectively. The GC–MS qualitative and quantitative analysis employed to assess the derivative silyl compounds produced was based selected ion monitoring (SIM), m/z = 444, 430, 306, and 150 for ZON, m/z = 446, 432, 414, and 305 for α-Zol and β-Zol and m/z 449, 432,

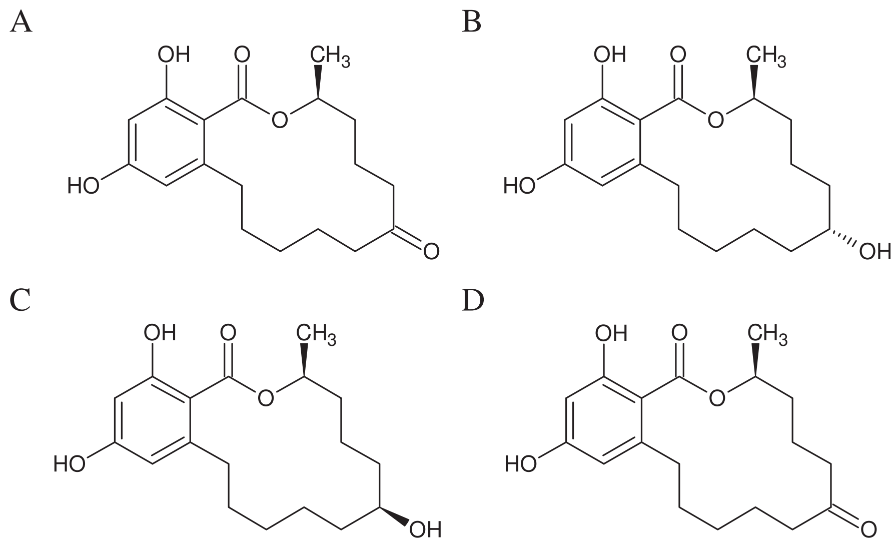

Fig. 1. Structures of zearalenone (A), α-zearalenole (B), β-zearalenole (C) and zearalanone (D).

406, and 308 for ZAN. The temperature of the chromatographic furnace was set at 140–280°C (temperature of injector 300°C). The chromatographic separation was conducted using a Varian VF-5 ms column. The other details of the analytical procedure are given in Dudziak [12].

The total organic carbon was measured with a HiPerTOC analyzer, while pH and conductivity were determined with a WTW inoLab® Multi 740 laboratory meter.

3. Results and discussion

3.1. Influence of water recovery on membrane permeability

The filtration of tap and surface water revealed that the higher the water recovery was assumed, the lower relative permeability of the membrane α was obtained (Fig. 2). This phenomenon originated from membrane blocking by organic and inorganic matter present in water causing membrane fouling and/or scaling. Normally, the phenomena are concomitant with membrane filtration and their intensity depends on the physico–chemical composition of treated water [4,5]. Surface water, compared with the tap one, had a higher concentration of organic matter (found by measuring total organic carbon), and therefore, the α-parameter determined during filtration was lower.

3.2. Mycoestrogens retention

The removal of the mycoestrogens by nanofiltration depended on a given compound, feed composition, and water recovery (Fig. 3). The increase

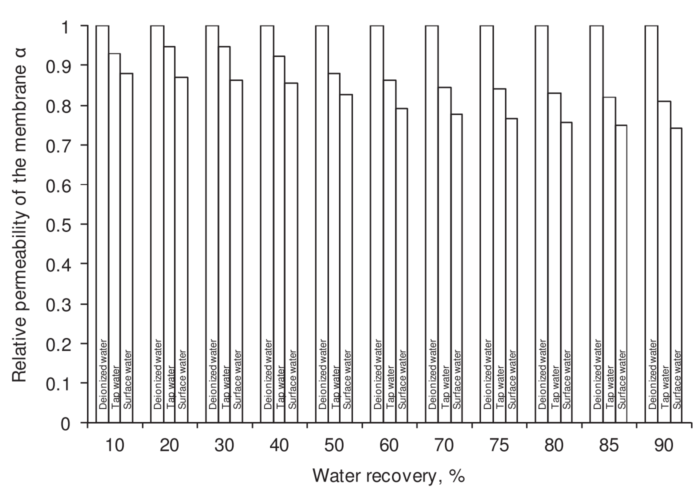

Fig. 2. Effect of water recovery on the relative permeability of the membrane α during filtration of the water.

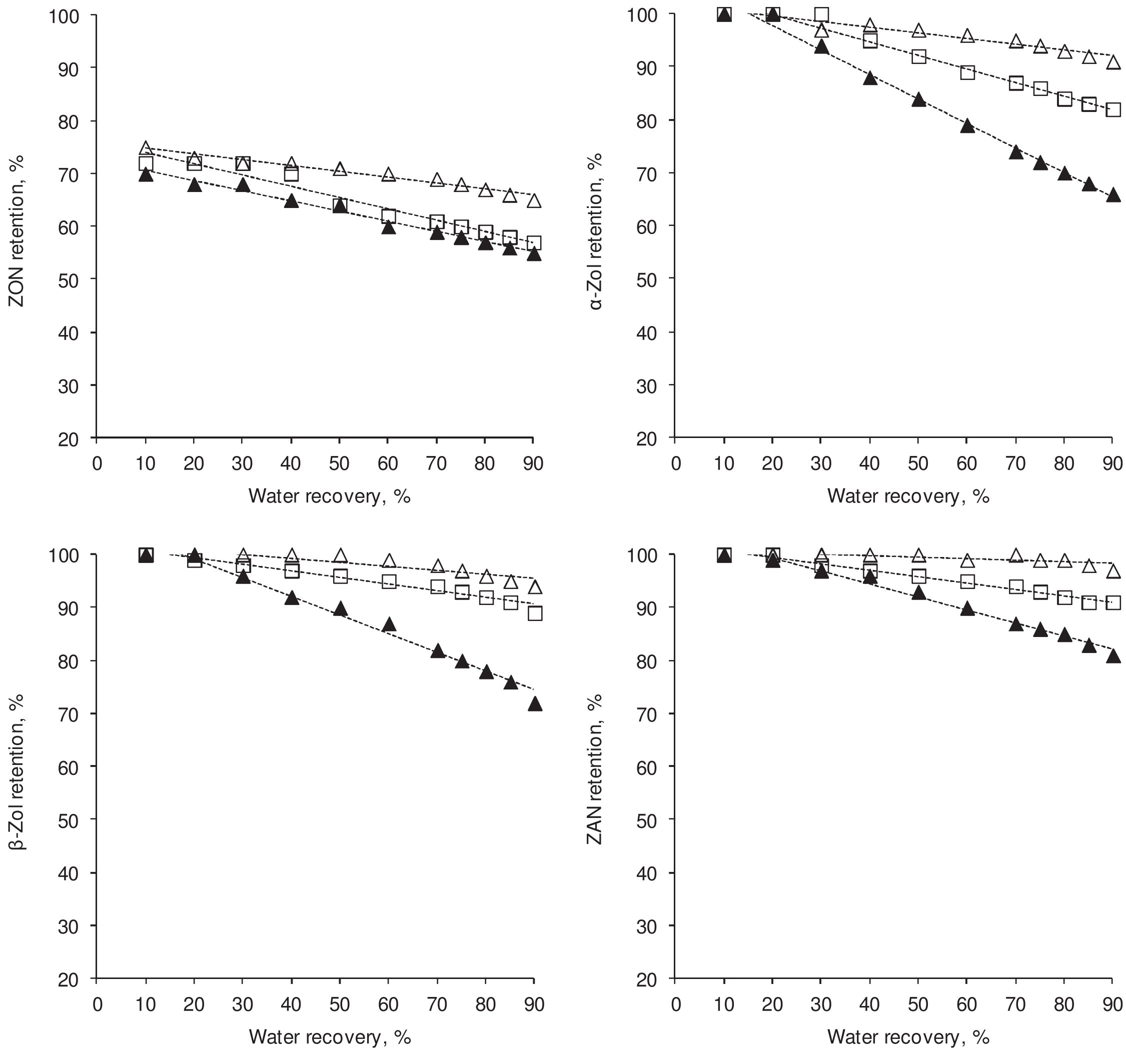

Fig. 3. Correlation of mycoestrogens with water recovery during filtration of deionized (Δ), tap (■) and surface water (▲).

in the water recovery resulted in the decreased efficiency of micro-pollutants removal. The lowest retention of mycoestrogens was observed during filtration of surface water and at higher assumed water recovery rate. At such conditions, the removal of zearalenone, α-zearalenole, β-zearalenole, and zearalanone was at the level of 55, 66, 72, and 81%, respectively. The phenomenon was caused by the increased concentration of micro-pollutants on the membrane surface. However, the impact of high-molecular-weight organic compounds (humic acids and other) on the separation of low-molecular-weight micro-pollutants could not be excluded, as those substances were preferably rejected by the membrane (the phenomenon of high-molecular-weight compounds during the process was discussed at the next paragraph).

It has been found that water recovery exerts a considerable influence on micro-pollutant separation. In industrial installations, nanofiltration is carried out under conditions of high recovery within a range of 75 to 95% [13,14], which might be the main cause of the decrease in micro-pollutant removal against the bench scale. Most of the published laboratory articles do not investigate the effect of permeate recovery on the effectiveness of the membrane process, and membrane filtration is carried out assuming low values of that parameter [1].

3.3. *Impact of water recovery on removal of organic and inorganic matter*

An increase in water recovery caused an increase in the concentration of inorganic matter in the

Table 2
Correlation between water recovery and removal of organic and inorganic matter

Water recovery, %	Waters			
	Tap water	Surface water	Tap water	Surface water
	Parameters			
	Conductivity, mS/cm (Removal, %)		Total organic carbon, mg/dm^3 (Removal, %)	
10	0.365 (51.0)	0.211 (66.3)	0 (100)	0.25 (96.5)
20	0.371 (50.2)	0.213 (65.9)	0 (100)	0.16 (97.8)
30	0.373 (49.8)	0.218 (65.2)	0 (100)	0.07 (99.0)
40	0.377 (49.3)	0.232 (62.9)	0 (100)	0 (100)
50	0.381 (48.8)	0.242 (61.4)	0 (100)	0 (100)
60	0.383 (48.5)	0.248 (60.4)	0 (100)	0 (100)
70	0.386 (48.1)	0.250 (60.0)	0 (100)	0 (100)
75	0.390 (47.6)	0.253 (59.6)	0 (100)	0 (100)
80	0.400 (46.2)	0.255 (59.2)	0 (100)	0 (100)
85	0.410 (44.9)	0.261 (58.3)	0 (100)	0 (100)
90	0.420 (43.5)	0.266 (57.5)	0 (100)	0 (100)

permeate, which was determined by measuring the specific water conductivity (Table 2). This trend was observed for both tap and surface water. On the other hand, the removal of organic matter was high and exceeded 96%, irrespective of recovery.

4. Conclusions

Water recovery exerts a significant influence on the efficiency of the process and removal of inorganic matter and micro-pollutants. An increase in recovery caused a decrease in the efficiency and effectiveness of nanofiltration. In industrial installations, filtration under the conditions of high recovery is the main cause of the decrease in micro-pollutant removal against the bench scale.

Acknowledgements

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