ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 38 no. 2 pp. 103 - 109 2012

PL ISSN 2083-4772
DOI: 10.2478/v10265-012-0022-8

COMBINED OZONATION – NANOFILTRATION FOR MYCOESTROGENS REMOVAL FROM WATER

MARIUSZ DUDZIAK

Institute of Water and Wastewater Engineering, Faculty of Energy
and Environmental Engineering, Silesian University of Technology
ul. Konarskiego 18, 44-100 Gliwice, Poland
Corresponding author's e-mail: mariusz.dudziak@polsl.pl

Keywords: Mycoestrogens, organic micropollutants, ozonation, nanofiltration, integrated system, water treatment.

Abstract: The paper describes the effectiveness of mycoestrogen removal in an integrated ozonation – nanofiltration system for water treatment. The results were compared to those obtained for ozonation and nanofiltration carried out as single processes. It has been found that the effectiveness of mycoestrogen removal in the integrated system was higher than that observed for single ozonation. During ozonation, the removal of micropollutants was affected by the dose of an oxidizing agent and type of treated water. As far as nanofiltration is concerned, its effectiveness both in the integrated system and as a single process was similar. Nevertheless, it is advisable to precede nanofiltration with ozonation because of membrane efficiency.

INTRODUCTION

Ozone is considered to be the most effective oxidizing agent for removing synthetic and natural organic matter, including low-molecular weight micropollutants [8, 10, 14]. Normally, an increase in ozone doses and oxidation time improves the efficiency of organic compounds removal [13]. However, it is hard to meet those requirements under technical conditions, a considerable prolongation of contact time in particular. On the other hand, the presence of high-molecular weight organic compounds at high concentrations makes the use of ozonation more costly [7].

The effective removal of organic matter and micropollutants can also be achieved by nanofiltration [1−6, 11, 12]. Its effectiveness depends on process conditions, membrane type and quality of treated water [5, 6]. Problems occurring during membrane filtration are connected with the low membrane efficiency caused by fouling [4, 9].

The study was aimed at combining ozonation with nanofiltration to reduce limitations occurring when the two processes are carried out separately. The effectiveness of the integrated ozonation-nanofiltration system was assessed on the basis of the removal of low-molecular weight mycoestrogens while treating waters of different concentrations of organic and inorganic matter. The efficiency of the nanofiltration membrane was monitored during the research as well.

EXPERIMENTAL

The tests were carried out on aqueous solutions prepared from tap water containing zearalenone (ZON) and α-zearalenol (α-Zol) at a constant concentration of 500 µg/dm^3 and humic acid (HA). Natural surface water was also treated. Table 1 shows the physico-chemical characteristics of the waters. The standard solutions of the humic acid, zearalenone and α-zearalenol were produced by Sigma-Aldrich. High-molecular weight organic matter was assayed in water by measuring absorbance (wavelength of 254 nm) with a Jena AG UV VIS Cecil 1000 spectrometer, while inorganic matter was assayed by measuring water conductivity with a inoLab® 740 multi-parameter meter (WTW). Mycoestrogens were determined using solid phase extraction (SPE) and HPLC analysis. The extraction was carried out with a Supelclean™ ENVI-18 SPE tube (bed wt. 1 g, volume 6 cm^3). Prior to extraction, the bed was conditioned with acetonitrile (5 cm^3) and then washed with deionized water (5 cm^3). The compound extracted was washed with acetonitrile (4 cm^3). The qualitative and quantitative analysis of zearalenone in the extract was made by HPLC (UV detector, wavelength of 235 nm), using a Microsorb 100 C18 column (25 cm in length, 4.6 mm in diameter, particle size of 5 µm). Methanol produced by POCH was the mobile phase.

Table 1. Physico-chemical characteristics of the water

Waters	Symbols	pH	Conductivity, mS/cm	Absorbance (UV_{254}), 1/cm
Tap water with HA (3 mg/dm^3)	water 1	7.0	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

Ozonation was conducted at 20ºC in a cylindrical reactor, volume 1000 cm^3, where the solution was continuously stirred with a magnetic stirrer. Ozone was generated in an Ozoner FM 500 generator (WRC Multiozon, Poland) and then introduced into the reactor through a ceramic diffuser. The concentration of the ozone was assayed by iodometric titration. Prior to further tests, the samples were filtered through a Millipore 0.45 µm filter made of cellulose acetate.

Nanofiltration was conducted out on a flat composite nanofiltration membrane (Dow Filmtec NF-270, cut-off of 200 Da) at a transmembrane pressure of 2.0 MPa in a steel membrane chamber (volume 350 cm^3, membrane area 38.5 cm^2) which enabled the process to be carried in the dead-end mode.

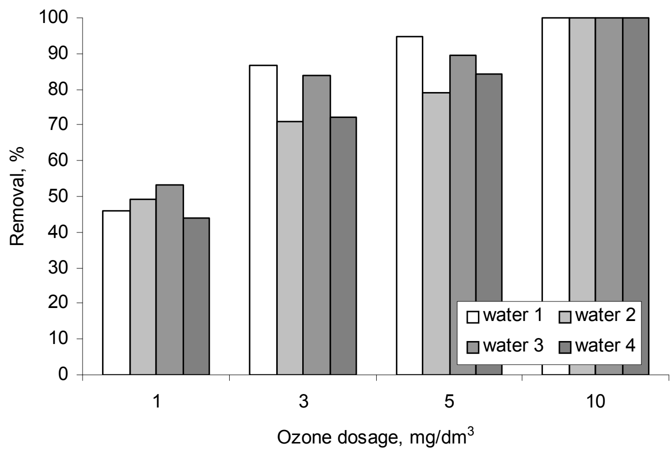
The tests on the effectiveness of mycoestrogens removal from water in the integrated ozonation-nanofiltration system involved the treatment of water by ozonation followed by nanofiltration. The part of the study dealing with ozonation described the effect of ozone doses and composition of water matrix on the removal of organic matter and particular mycoestrogens.

RESULTS

Ozonation

The removal of mycoestrogens by ozonation depended on the ozone dose and water matrix (Figs 1 A and B). An increase in the dose of the oxidizing agent brought about an increase in the effectiveness of micropollutant removal. On the other hand, an increase in the organic and inorganic matter concentration in water brought about a decrease in mycoestrogens removal. The 10 mg/dm^3 dose of ozone enabled a complete removal of mycoestrgoens regardless of water type.

A



B

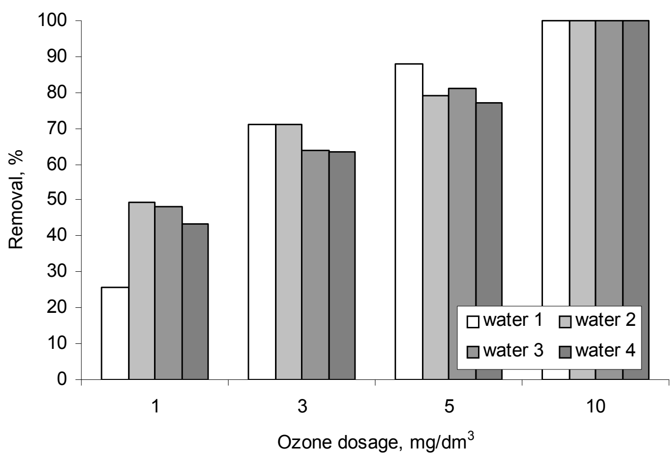


Fig. 1. Effect of ozone dose and water matrix on the removal of zearalenone (A) and α-zearalenol (B)

The increase in the ozone dose also caused an increase in the removal of high-molecular weight compounds (Fig. 2), which was determined by measuring water absorbance.

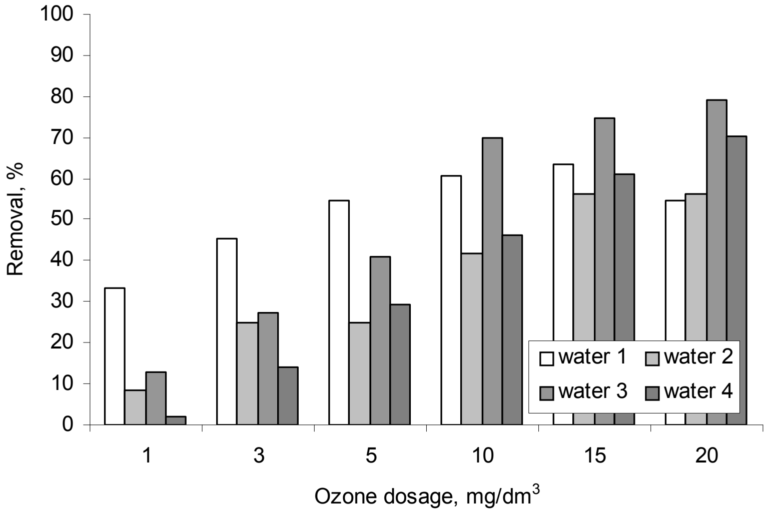


Fig. 2. Removal of high-molecular weight organic compounds during ozonation

Ozonation-nanofiltration

Membrane nanofiltration was tested as an additional treatment of water containing mycoestrgoens after ozonation (ozone dose 1 mg/dm^3, contact time 1 min). It has been found that the addition of nanofiltration to the water treatment system enabled a marked increase in the removal of the micropollutants compared to single ozonation (Fig. 3). Its effectiveness both in the single process and the combination with ozonation was similar. However, considerable differences were found for membrane efficiency by determining a relative volume permeate flux α. The integrated system revealed higher membrane efficiency than single nanofiltration (Fig. 4), with one exception found during the treatment of water which contained the highest concentrations of organic and inorganic matter (water 4).

The final stage of the study involved the treatment of surface water which was enriched with mycoestrogens (500 µg/dm^3). Originally, the water did not contain the micropollutants. The results for the surface water were similar to those observed for the model waters. Mycoestrogens removal was high and exceeded 90% irrespective of both the type of removed compounds and system for water treatment (Table 2). However, the application of nanofiltration to the integrated system after ozonation was more favourable in terms of membrane efficiency. Nanofiltration, regardless of the water treatment system used, enabled both a complete removal of high-molecular weight organic matter and marked decrease in the concentration of inorganic matter to an extent exceeding 55%.

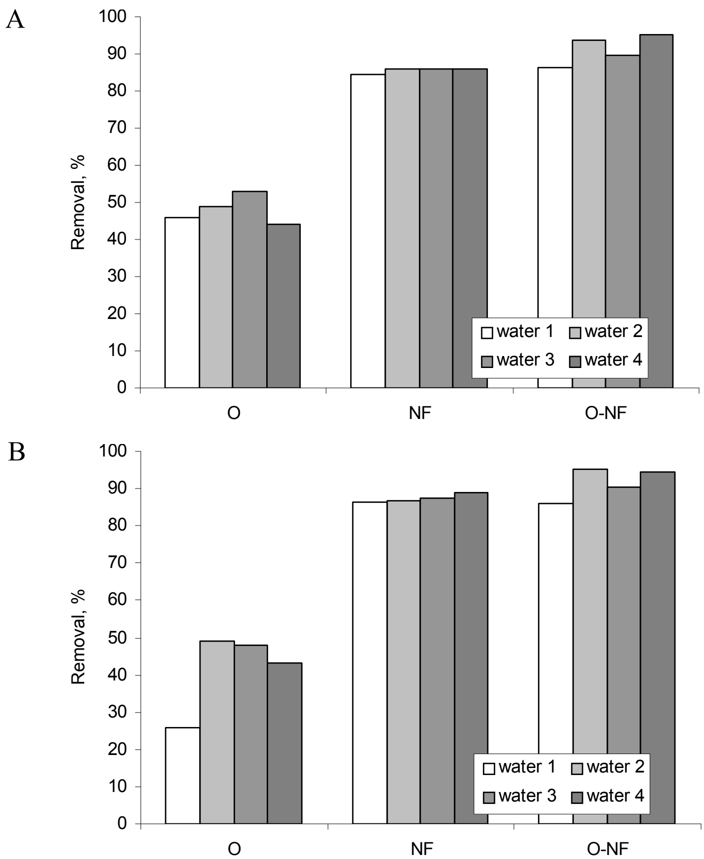


Fig. 3. Comparison of zearalenone (A) and α-zearalenol (B) removal during ozonation (O), nanofiltration (NF) and integrated system (O-NF)

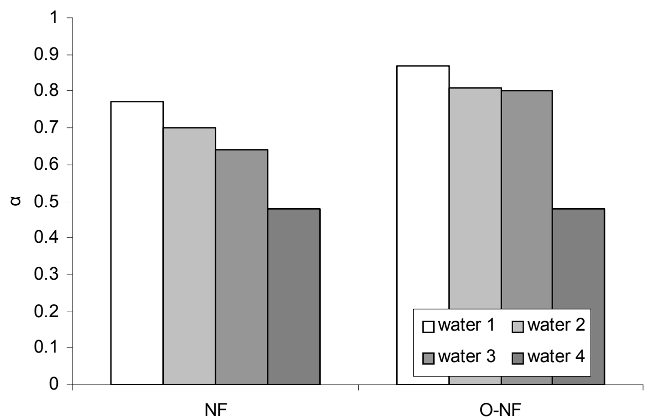


Fig. 4. Relative volume permeate flux α determined during nanofiltration carried out as a single process and in the system integrated with ozonation

Table 2. Effectiveness and efficiency of nanofiltration carried out as a single process and in the integrated system during filtration of surface water

	Process/system	
	NF (membrane NF-270)	O+NF (ozone dose 1 mg/dm^3, time 1 min)
	Removal (decrease*), %	
ZON	90.1	90.7
α-Zol	91.7	93.1
Conductivity*	56.4	55.3
Absorbance*	100	100
Parameter		
Relative permeability of the membrane α^a,-	0.66	0.76

[a] calculated as a ratio of simulated water permeate flux to deionized water flux (J_v/J_w) where $J_v(J_w) = V/F{\cdot}t$: V – volume (dm^3), F – membrane area (m^2), t – filtration time (s)

CONCLUSION

1. The integrated system of ozonation and nanofiltration for treating water is favourable in terms of membrane efficiency. Its effectiveness in mycoestrogen removal exceeded 90% and was similar to that observed for single nanofiltration. As to ozonation, the removal of myscoestrogens depends on the dose of an oxidizing agent and type of water.
2. The application of nanofiltration after water ozonation, despite the low ozone dose (1 mg/dm^3), enables the removal of inorganic matter to an extent exceeding 55% and complete removal of organic matter.

ACKNOWLEDGMENTS

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

REFERENCES

[1] Bellona Ch., J.E. Drewes, P. Xu, G. Amy: *Factors affecting the rejection of organic solutes during NF/RO treatment – a literature review*, Water Research, **38**, 2795−2809 (2004).

[2] Bodzek M., K. Konieczny: *Membrane processes in water treatment*, Oficyna Wydawnicza Projprzem-Eko, Bydgoszcz 2005 (in Polish).

[3] Bodzek M., K. Konieczny: *Membrane techniques in the removal of inorganic anionic micropollutants from water environment – state of the art*, Archives of Environmental Protection, **37**, 1529 (2011).

[4] Contreras A.E., A. Kim, Q. Li: *Combined fouling of nanofiltration membranes: mechanisms and effect of organic matter*, Journal of Membrane Science, **327**, 87−95 (2009).

[5] Dudziak M., M. Bodzek: *Selected factors affecting the elimination of hormones from water using nanofiltration*, Desalination, **240**, 236−243 (2009).

[6] Dudziak M., M. Bodzek: *Removal of estrogenic micropollutants from water solutions by high-pressure driven membrane processes*, Ochrona Środowiska, **31**, 33−36 (2009) (in Polish)

[7] Gottschalk C., J.A. Libra, A. Saupe: *Ozonation of drinking water and of wastewater*, Wiley-VCH, 2000.
[8] Kowal A.L., M. Świderska-Bróż: *Water treatment*, PWN, 2009 (in Polish).
[9] Nghiem L.C., P.J. Coleman, C. Espendiller: *Mechanisms underlying the effects of membrane fouling on the nanofiltration of trace organic contaminants*, Desalination, **250**, 682−687 (2010).
[10] Reungoat J., M. Macova, B.I. Escher, S. Carswell, J.F. Mueller, J. Keller: *Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration*, Water Research, **44**, 625−637 (2011).
[11] Van der Bruggen B., C. Vandecasteele: *Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry*, Environ. Poll., **122**, 435−445 (2003).
[12] Verliefde A., E. Cornelissen, G. Amy, B. van der Bruggen, H. van Dijk: *Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration*, Environmental Pollution, **146**, 281−289 (2007).
[13] Von Gunten U.: *Ozonation of drinking water: part I. oxidation kinetics and product formation*, Water Research, **37**, 1443−1467 (2003).
[14] Zimmermann S.G., M. Wittenwiler, J. Hollender, M. Krauss, C. Ort, H. Siegrist, U. von Gunten: *Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection*, Water Research, **45**, 605−617 (2011).

OZONOWANIE-NANOFILTRACJA W USUWANIU MYKOESTROGENÓW Z WODY

W pracy przedstawiono efektywność usuwania mykoestrogenów w zintegrowanym układzie oczyszczania wody ozonowanie – nanofiltracja. Wyniki badań porównano do wyników uzyskanych podczas ozonowania i nanofiltracji, które realizowane były jako procesy pojedyncze. Określono, że efektywność usuwania mykoestrogenów w układzie zintegrowanym jest wyższa niż obserwowana w pojedynczym procesie ozonowania. W przypadku ozonowania na usuwanie mikrozanieczyszczeń ma wpływ dawka utleniacza i rodzaj oczyszczanej wody. Z kolei efektywność nanofiltracji realizowanej jako proces pojedynczy i w układzie zintegrowanym pod kątem usuwania mykoestrogenów była zbliżona. Jednak biorąc pod uwagę wydajność membrany korzystniej jest proces nanofiltracji poprzedzić procesem ozonowania wody.