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REMOVAL OF ZEARALENONE FROM WATER BY MEANS OF OZONATION AND INTEGRATED SYSTEM OF OZONATION/NANOFILTRATION

USUWANIE ZEARALENONU Z WODY W PROCESIE OZONOWANIA ORAZ W UKŁADZIE OZONOWANIE/NANOFILTRACJA

Abstract: Results of the study on the effectiveness of zearalenone removal *via* ozonation and integrated ozonation/nanofiltration water treatment are presented in the paper. The influence of ozone dose, contact time, pH and water properties on ozonation performance was investigated. The impact of nanofiltration membrane type on the integrated system effectiveness was tested. The study shows that application of integrated system of ozonation and nanofiltration is advantageous according to the effectiveness of zearalenone and other water contaminants removal as well as membrane capacity. The best performance of the system was observed for cellulose acetate nanofiltration membrane.

Keywords: zearalenone, organic micropollutants, ozonation, nanofiltration, water treatment

Ozone was found to be a very strong oxidizer already at the beginning of XIX century. The redox potential of ozone in the acidic environment is equal to 2.07 V while in basic to 1.27 V. Theoretically, it assures the amount of energy sufficient to oxidize organic and inorganic compounds present in water. Ozone is usually applied for removal of color, taste and smell of water as well as for its disinfection [1].

The elimination of organic micropollutants by means of ozonation is also discussed in the literature [2–4]. The effectiveness of the process depends on ozone dose, contact time, pH and water properties [1–4]. The ozone dose sufficient for total oxidation of organic compounds (determined as *dissolved organic carbon* DOC) is quite high and equal to 8 mgO_3/mg DOC [1]. The decrease of required ozone dose can be obtained by integration of ozonation with other unit operations *eg* activated carbon adsorption [5]. The application of membrane processes is also possible, and additionally the polishing of water is performed [6, 7].

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It was shown in [7] that combination of eg ozonation and nanofiltration had significantly limited the formation of disinfection by-products as the amount of dissolved organic compounds in water was decreased.

The effectiveness of ozonation and integrated water treatment system *ie* ozonation/nanofiltration for removal of zearalenone was investigated. Zearalenone is a compound from mycotoxins group of estrogenic properties which are produced by fungi of *Fusarium* type [8]. Nowadays, it is found to be present in surface water as a result of environment pollution [8, 9].

Materials and methods

Simulated solutions prepared on two water matrices *ie* deionized water and tap water with and without addition of humic acids and constant zearalenone concentration equal to 500 μg/dm^3 were used in the study (Table 1). *Humic acids* (HA) and zearalenone standards were supplied by Sigma-Aldrich. The content of humic acids in water was determined *via* absorbance measurements (at wavelength λ = 254 nm) using UV VIS Cecil 1000 spectrophotometer by Jena AG, while inorganic substances concentration *via* conductivity measurements with laboratory multiparameter analyzer inoLab® 740 by WTW. The determination of zearalenone concentration was made by solid phase extraction SPE and HPLC analysis. Supelclean™ ENVI-18 tubes (volume – 6 cm^3, phase – 1.0 g) by Supelco were used. The tube phase was firstly conditioned with acetonitrile (5 cm^3) and next washed with distilled water (5 cm^3). The separated compound was washed out with acetonitrile (4 cm^3). Quantitative and qualitative analyses of zearalenone in obtained extract were performed by means of HPLC (UV detector, wavelength λ = 235 nm). Microsorb 100 C18 column of length 25 cm, diameter – 4.6 mm and granulation – 5 μm. Methanol by POCH was used as a mobile phase.

Table 1

Physico-chemical characteristics of the waters

Waters	pH	Conductivity [μS/cm]	Absorbance, UV_{254} [1/cm]
Deionized water	5.4 and 7.0*	5.180	0.000
Tap water	7.0	1064	0.004
Tap water with HA [15 mg/dm^3]	7.0	1112	0.170

* Correction of water pH was made by addition of 0.1 M/dm^3 HCl or 0.2 M/dm^3 NaOH.

Ozonation process was carried out under 20 °C in cylindrical reactor of volume 1000 cm^3 in which treated solution was constantly mixed with the use of magnetic stirrer. Ozone was generated in Ozoner FM 500 (by WRC Multiozon, Poland) and introduced to reactor *via* ceramic diffuser. The concentration of ozone was determined by iodometric method. In order to remove ozone from post-reaction mixtures 24 mM/dm^3

Na_2SO_3 (analytical grade, P.P.H. Stanlab) was added. Next, samples were filtered through 0.45 μm membrane made from cellulose acetate by Millipore.

Two commercial nanofiltration membranes differ in the polymer material were used in the study ie composite NF-270 membrane with polyamide skin layer by Dow Filmtec (USA) and cellulose membrane CK by Osmonics Inc. (USA). The characteristic of applied membranes is shown in Table 2.

Table 2

Characteristic of the membrane

Membrane	Molecular weight cut-off [Da]	Deionized water flux $(J_w)^a$, 10^{-6} [$m^3/m^2 \cdot s$]	Removal of salts[b] [%]	
			$MgSO_4$	NaCl
NF-270	200	70.6	92.1	41
CK	150–300	7.60	96.8	75

[a] Determined in this work at ΔP = 2.0 MPa; [b] determined in experiment during filtration of $MgSO_4$ or NaCl solution (1000 mg/dm^3) at ΔP = 2.0 MPa.

The transport and separation parameters of the nanofiltration membranes were assessed using the equations given in Table 3. The determination of nanofiltration effectiveness was based on the measurements of both membrane efficiency (J_v and α) – equations (1 and 2) and selectivity (R) – equation (3).

Table 3

Equations used to evaluate membrane properties and removal efficiencies

Parameter, unit	Equations	Number
Volumetric permeate flux (deionized water) J_v (J_w) [$m^3/m^2 \cdot s$]	$J_v(J_w) = \frac{V}{F \cdot t}$	1
Relative permeability of the membrane α [-]	$\alpha = \frac{J_v}{J_w}$	2
Removal degree 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 [μg/dm^3], p – permeate, f – feed.

The process was carried out under transmembrane pressure 2.0 MPa in steel membrane cell (volume – 350 cm^3, membrane area 38.5 cm^2) enabling dead-end process configuration.

The study determining effectiveness of zearalenone removal from water using integrated system ozonation/nanofiltration comprised of water treatment in ozonation process after which nanofiltration was performed. In the part of study discussing ozonation, the influence of ozone dose, contact time, pH and water matrix properties on the degree of zearalenone removal was investigated.

Results

Ozonation

The degree of zearalenone removal depended on ozone dose and as the dose increased the degree of compound removal also increased (Fig. 1). Moreover, the elongation of ozone contact time with treated water also improved the effectiveness of zearalenone removal (Fig. 2).

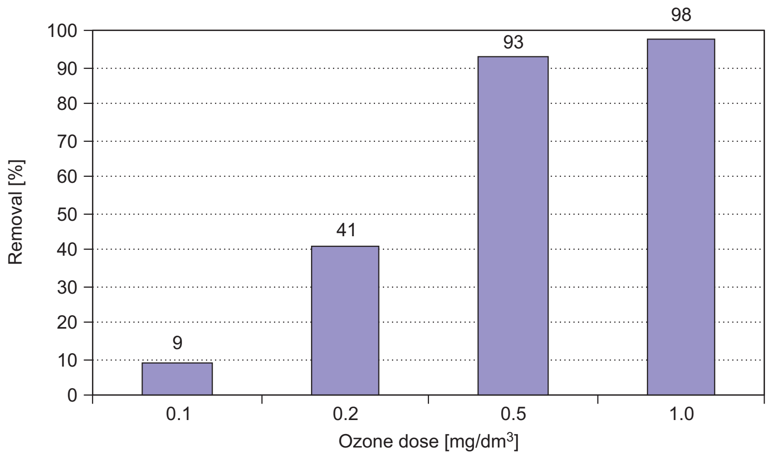

Fig. 1. The influence of ozone dose on degree of zearalenone removal (deionized water, contact time 1 min, pH = 5.3)

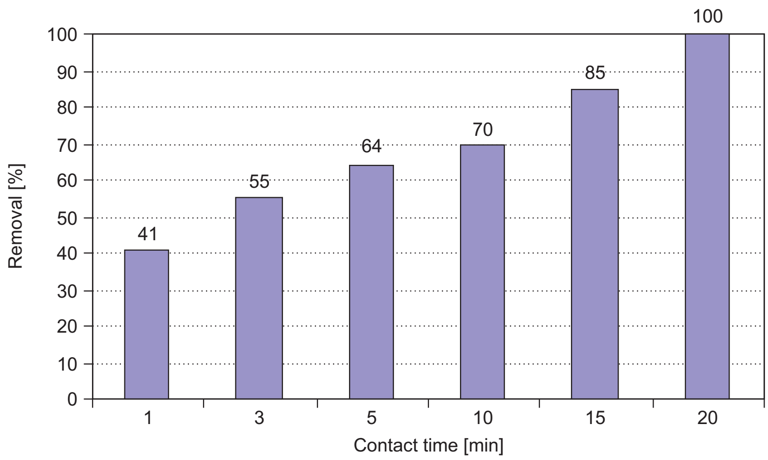

Fig. 2. The influence of contact time on effectiveness of zearalenone removal (deionized water, ozone dose 0.2 mg/dm^3, pH = 5.3)

It was found that the increase of water pH resulted in decrease of zearalenone removal degree (Fig. 3). It proved the greater reactivity of molecular ozone (direct oxidation) in comparison with free radicals $OH^{\bullet}$ formed during ozonation [1]. The lower process effectiveness was also observed in cases when except from zearalenone also other compounds ie inorganic and high-molecular weight organic substances were present in water (tap water with and without humic acids addition). The phenomenon is probably caused by decrease of ozone concentration reacting with low-molecular weight zearalenone, which is used for oxidation of inorganic and organic compounds present in water.

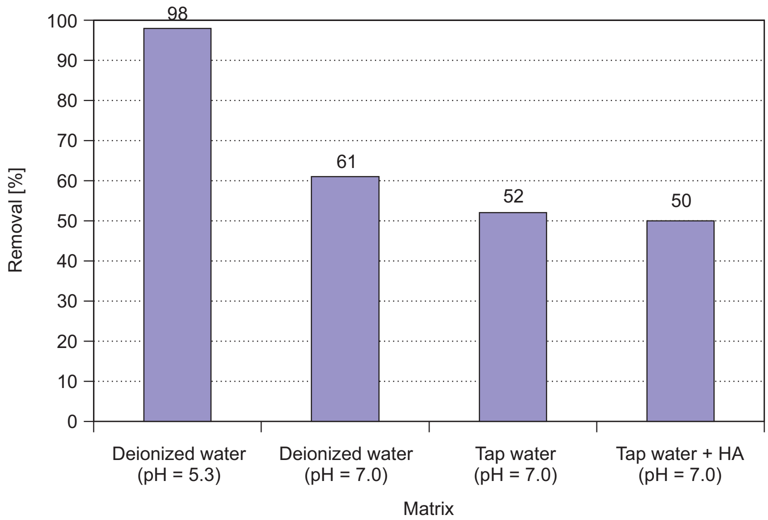

Fig. 3. The influence of water properties on effectiveness of zearalenone removal (ozone dose 1 mg/dm^3, contact time 1 min)

Integrated system ozonation-nanofiltration

Nanofiltration was considered as a method of polishing of water treated *via* ozonation (tap water + HA, ozone dose 1 mg/dm^3 and contact time 1 min). It was found that introduction of nanofiltration to water treatment system improved not only removal of zearalenone, but also other water contaminants (decrease of conductivity and absorbance). However, the effectiveness of the integrated system performance depended on the type of nanofiltration membrane applied (Fig. 4). The highest efficiency of contaminants removal was observed in case of cellulose membrane CK for which the removal rates of conductivity, zearalenone and absorbance were equal to 65, 97 and 100 %, respectively. The membrane characterized also with lower affinity to fouling what was determined by means of membrane relative permeability α (Fig. 5). The phenomenon is probably connected with properties of membrane material including contact angle of the membrane [10–13].

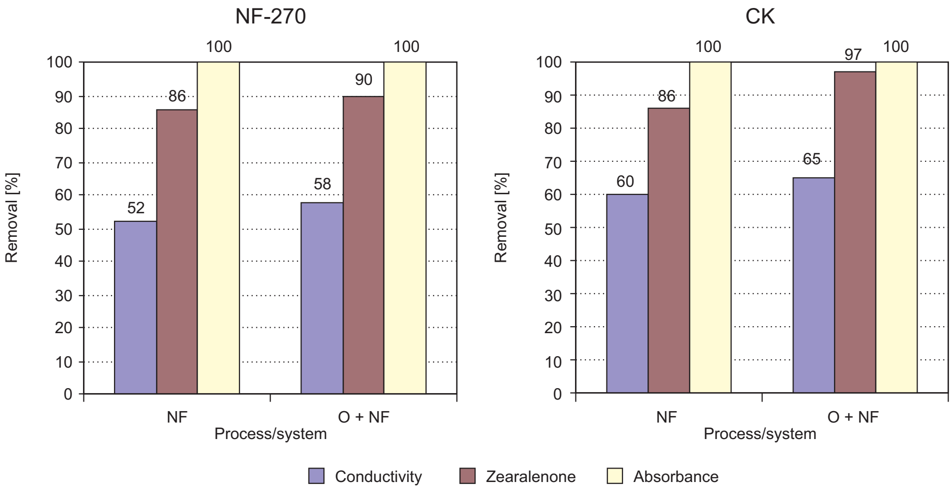

Fig. 4. The effectiveness of nanofiltration performed as a unit process or as a part of integrated system with ozonation

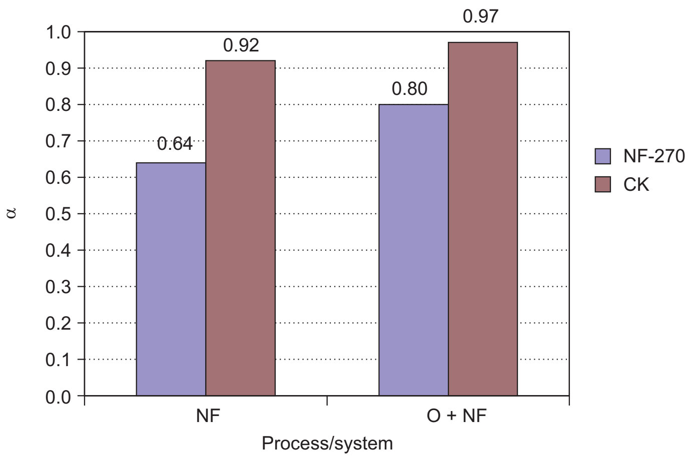

Fig. 5. Relative permeability of the membrane α

Conclusions

The study allow to conclude that the effectiveness of removal of zearalenone in ozonation process depends on ozone dose and contact time. The lower degree of compound removal was observed in case when inorganic and high-molecular weight organic substances (humic acids) were present in water or pH of water increased.

The application of nanofiltration after ozonation (integrated system) improves zearalenone removal in comparison with single ozonation treatment. The total removal of high-molecular weight compound and sufficient decrease of inorganic substances concentration are also obtained for integrated system. The combined solution also improves the capacity of applied membrane.

The higher effectiveness of the integrated system was observed in the combination with cellulose acetate membrane CK, which additionally revealed the lower affinity to fouling.

Acknowledgements

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USUWANIE ZEARALENONU Z WODY W PROCESIE OZONOWANIA ORAZ W UKŁADZIE OZONOWANIE/NANOFILTRACJA

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Abstrakt: Zaprezentowano wyniki badań dotyczące efektywności usuwania zearalenonu w procesie ozonowania i w zintegrowanym układzie oczyszczania wody ozonowanie/nanofiltracja. W trakcie ozonowania badano wpływ dawki ozonu, czasu kontaktu, pH i rodzaju wody na stopień usunięcia zearalenonu. Badano również wpływ rodzaju membrany nanofiltracyjnej na efektywność pracy układu zintegrowanego. Wyniki wskazują, że zastosowanie układu zintegrowanego kojarzącego ozonowanie z nanofiltracją jest korzystne pod względem efektywności usuwania zearalenonu oraz innych wskaźników zanieczyszczenia wody, jak również biorąc pod uwagę wydajność membrany. Wyższą efektywność pracy układu obserwowano w przypadku zastosowania membrany nanofiltracyjnej z octanu celulozy.

Słowa kluczowe: zearalenon, mikrozanieczyszczenia organiczne, ozonowanie, nanofiltracja, oczyszczanie wody