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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 I 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. The influence of ozone dose, contact time, pH and water properties on ozonation performance was investigated. 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.

Keywords: zearalenon, 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_3/1 mgDOC [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].

The effectiveness of ozonation and integrated water treatment system ie ozonation/nanofiltration for removal of zearalenone was investigated. Zearalenone (ZON) [6-(10-hydroxy-6-oxo-*trans*-1-undecenyl)-β-resorcylic acid lactone] is a compound from mycotoxins group of estrogenic properties which are produced by fungi of *Fusarium* type [7]. Nowadays, it is found to be present in surface water as a result of environment pollution [7, 8].

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 $\mu g/dm^3$ (Table 1) were used in the study. Humic acids and zearalenone standards were supplied by Sigma-Aldrich. The content of high-molecular weight organic compounds in

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water was determined via absorbance measurements (at wavelength $\lambda = 254$ 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 *high performance liquid chromatography* 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 $\lambda = 235$ 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.

Ozonation process was carried out at 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.

Flat-sheet, composite membrane by Dow Filmtec (USA) of producer symbol NF-270 and molecular weight cut-off 200 Da was used for nanofiltration. 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.

Table 1

Physicochemical 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 humic acids (15 mg/dm^3)	7.0	1112	0.170

*correction of water pH was made by addition of 0.1 M HCl or 0.2 M NaOH

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).

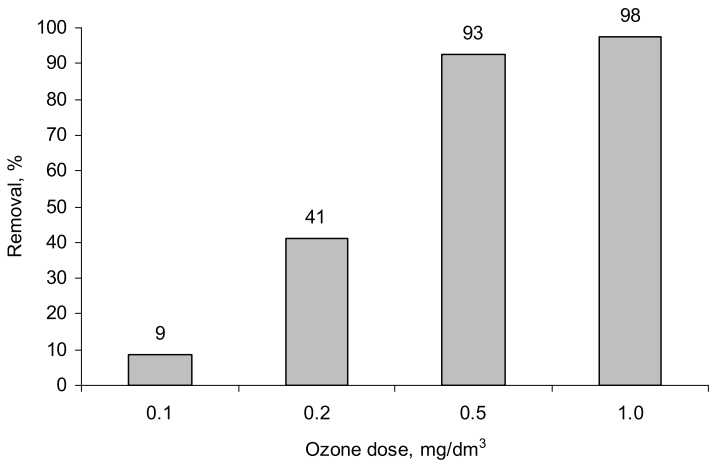

Fig. 1. The influence of ozone dose on degree of zearalenone removal (deionized water, contact time 1 min, pH = 5.3)

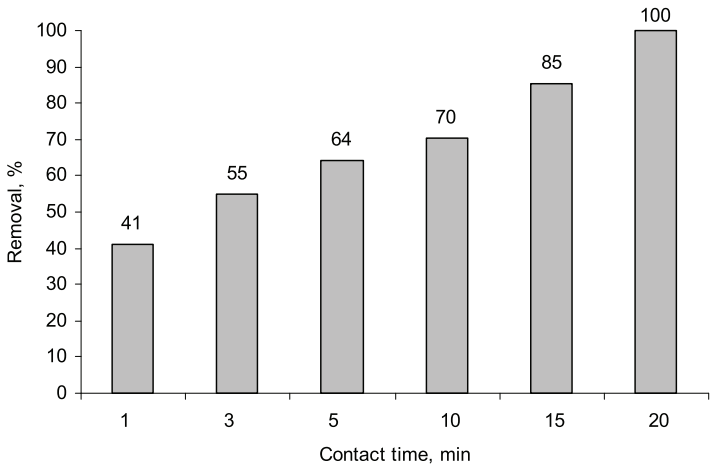

Fig. 2. The influence of contact time on effectiveness of zearalenone removal (deionized water, ozone dose 0.2 mg/dm^3, pH = 5.3)

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.

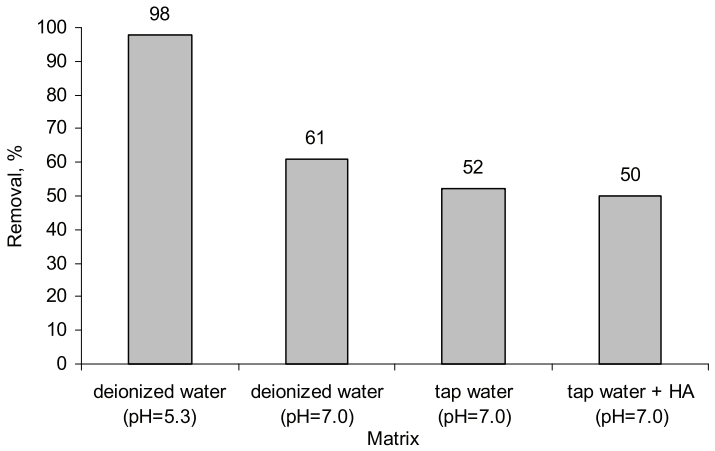

Fig. 3. The influence of water properties on effectiveness of zearalenone removal (ozone dose 1 mg/dm^3, contact time 1 min)

Integrated system ozonation-nanofiltration

Nanofiltration was considered as a method of polishing of water treated via ozonation (tap water with humic acids, ozone dose 1 mg/dm^3). 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). Results of the study are shown in Table 2.

Table 2

The effectiveness and the capacity of nanofiltration performed as a unit process or as a part of integrated system with ozonation used for zearalenone removal from water (tap water with humic acids, pH = 7.0)

	Process/system	
	Nanofiltration (membrane NF-270)	**Ozonation+Nanaofiltration (ozone dose 1 mg/dm^3, time 1 min)**
	Removal (decrease*) [%]	
Zearalenone	85.9	89.7
Conductivity*	51.7	58.4
Absorbance*	100	100
Parameter		
Relative permeability of the membrane α^a, -	0.64	0.80

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

The degree of removal of zearalenone and conductivity decrease in integrated system ozonation - nanofiltration was equal to 89.7 and 58.4%, respectively. Moreover, the total removal of high-molecular weight organic substances determined during absorbance measurements was obtained. Similar results were obtained for water treatment via single nanofiltration, however for such a treatment solution lower membrane capacity was observed ($\alpha = 0.64$).

Conclusions

The study allows 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 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.

Acknowledgements

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USUWANIE ZEARALENONU Z WODY W PROCESIE OZONOWANIA I 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. Wyniki wskazują, że zastosowanie układu zintegrowanego kojarzącego ozonowanie z nanofiltracją jest korzystne pod względem efektywności usuwania zearalenonu oraz innych wskaźników zanieczyszczenia wody, a także biorąc pod uwagę wydajność membrany.

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