Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27878

244 (2021) 194–200
December

Ozone assisted photolysis process in reduction of selected micropollutants from nanofiltration retentate

Izabela Zimoch[a,*], Dominik Mroczko[b]

[a]*Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering,*
Silesian University of Technology, Konarskiego St. 18, 44-100 Gliwice, Poland, email: izabela.zimoch@polsl.pl
[b]*Technical Services Enterprise DEMPOL – ECO, Składowa St. 9, 45-125 Opole, Poland, email: dominik.mroczko@dempol.com.pl*

Received 2 August 2021; Accepted 28 September 2021

ABSTRACT

In the presented study, the efficiency of the ozone-assisted photocatalysis (UV/O_3) in the reduction of 7 organic micropollutants (MPs) concentrated in the retentate after nanofiltration (NF) was investigated. The following micropollutants were investigated: 4-nonylphenol (4-NP), 4-tert-octylphenol (4-OP), alachlor (AC), anthracene (ANT), bis(2-ethylhexyl) phthalate (DEHP), heptachlor (HC) and heptachlor epoxide (HCE). The membrane process was carried out in a nanofiltration pilot system using a FilmTec NF90 membrane. The NF concentrate was collected in a batch reactor where the UV/O_3 process was carried out. NF process leads to complete permeate purification. On the other hand, three MPs (AC, HCE and DEHP) were 10-fold concentrated in the retentate. UV/O_3 process effectiveness was in the range of 16% to 98%. Only DEHP and phenolic compounds derivatives were determined during photocatalysis.

Keywords: Nanofiltration; Photocatalysis; Micropollutants; Retentate; Ozone

1. Introduction

The nanofiltration process (NF) is one of the most effective methods for purification water containing organic micropollutants (MPs) [1–6]. As in all conventional membrane processes, reduction of pollutants during NF does not consist in destroying them, but in transferring to the concentrated phase. Concentrated NF retentate is considered as undesirable post-process waste, for management of which is the responsibility of the treatment facilities operator. Despite great potential, the fact that post-process concentrate is created, hence the necessity of its disposal, makes NF a niche technique in the water treatment industry.

Advanced oxidation processes (AOP) are considered effective solutions in the context of micropollutants reduction. AOP includes those processes in which highly reactive species such as O_3 or free radicals are formed and introduced to the treated medium. Under proper conditions, AOP allows for complete mineralization and neutralization of organic pollutants decomposing them into CO_2 and H_2O [7–18]. AOPs classification based on the use of UV radiation is presented in Table 1.

Photochemical AOPs such as photocatalysis or induced photolysis result in the formation of free hydroxyl radicals $^\bullet OH$, which are considered particularly reactive (Table 2). Heterogeneous photolysis is one of the AOPs with proven high effectiveness in organic micropollutants reduction [19–21]. In this process semiconductors such as TiO_2, ZnO, Fe_2O_3 or CdS are used as $^\bullet OH$ radicals formation catalysts. However, despite its high effectiveness, the use of this process raises the problem of the necessity to separate and regenerate the catalyst, which entails a reduction in the economic efficiency of the treatment. Ozone-assisted photolysis (UV/O_3) is a technique that allows the production of $^\bullet OH$ radicals, while eliminating the nuisance caused by the use of solid catalysts.

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[*] Corresponding author.

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Table 1
Advanced oxidation processes classification

Non-photochemical	Photochemical
Ozonation	Direct photolysis
O_3/H_2O_2	Photocatalytic oxidation, UV/Catalyst
Fenton	UV/H_2O_2
Wet air oxidation	UV/O_3
Electrochemical oxidation	$UV/O_3/H_2O_2$
Physical AOP (sonochemical, microwave)	Photo-Fenton

Table 2
Oxidation potentials of some oxidation agents [22]

Oxidant	Oxidation potential (eV)
Fluorine	3.1
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Chlorine dioxide	1.5

Table 3
Target water parameters

pH	8.07
Conductivity (µS/cm)	417
Dissolved organic carbon (mg/L)	2.79
MPs concentration (µg/L)	0.2

${}^{\bullet}OH$ radicals formation mechanism in an alkaline environment, in the UV/O_3 process, occurs according to the equations [23]:

$$O_3 + OH^- \rightarrow \cdot O_3 + {}^{\bullet}OH \tag{1}$$

$$ {}^{\bullet}O_3^- \rightarrow {}^{\bullet}O^- + O_2 \tag{2}$$

$$ {}^{\bullet}O^- + H^+ \rightarrow {}^{\bullet}OH \tag{3}$$

$$H_2O + O_3 + h\nu \rightarrow 2{}^{\bullet}OH + O_2 \tag{4}$$

Destruction of micropollutants also takes place as a result of direct reaction with UV radiation:

$$\text{Compound} + h\nu \rightarrow \text{Byproducts} \tag{5}$$

$$\text{Byproducts} + h\nu \rightarrow CO_2 + H_2O \tag{6}$$

In this study, the NF process effectiveness in reducing selected organic micropollutants from the water was analyzed. Chosen MPs were listed as priority or priority hazardous substances in the 2013/39/EU Directive. The main goal of the research, however, was to evaluate the UV/O_3 process in terms of mineralization substances concentrated in retentate during the NF process. The research was conducted on modular pilot stations. The by-products of selected micropollutants decomposition, which were produced as a result of the UV/O_3 process, were also analyzed.

2. Materials and methods

2.1. Research object

The object of this study was tap water with the characteristics given in Table 3. Micropollutants were added to the matrix so that their initial concentration was 0.2 µg/L, which is close to the maximum annual average concentration (AA-EQS) given by 2013/39/EU Directive (except for HC, HCE and DEHP, for which AA-EQS are lower than the limit of detection or high to represent MPs concentrations occurring in natural water).

2.2. Micropollutants

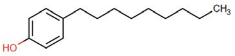
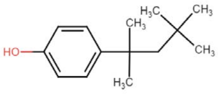
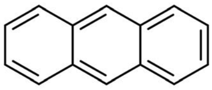
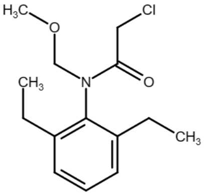
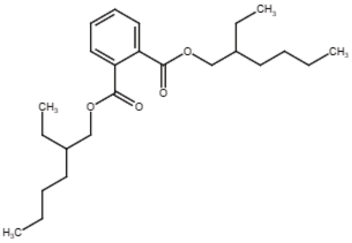
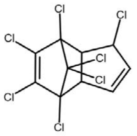
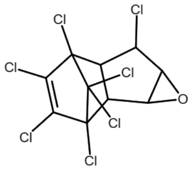
Seven organic MPs were analyzed for the reduction efficiency. Selected MPs are: 4-nonylphenol, 4-tert-octylphenol, anthracene, alachlor, bis(2-ethylhexyl) phthalate, heptachlor and its epoxide. These compounds are included in the list of priority hazardous substances and represent different categories of anthropogenic origin like pesticides (AC, HC, HCE), endocrine disruptors (4-nonylphenol 4-NP, 4-tert-octylphenol 4-OP), polycyclic aromatic hydrocarbons (ANT) and industrial substrates (DEHP) [24]. Substances were supplied by Sigma-Aldrich (Poznań, Poland) and were of purity grade >97%. A standard solution containing compound mix at a concentration of 100 mg/L in methanol was prepared. Substances along with their physicochemical properties are presented in Table 4.

2.3. Analytical methods

MPs concentration analysis was carried out by gas chromatography (Agilent 7890B, Agilent United States) coupled with mass spectrometry (Agilent 5977A, Agilent United States) (GC-MS). Sample preparation was based on solid-phase extraction. For this purpose, C18 columns (J.T. Baker, 500 mg Octadecyl Phase) were previously conditioned with methanol (Scharlau) and a mixture of dichloromethane/ethyl acetate (DCE) (1:1, v/v) (Chempur/Merck) were used. Extraction was carried out using respectively DCE and acetone (Scharlau). After extraction from the solid phase, solvents were then evaporated (Biotage TurboVap II) and replaced with acetonitrile (VWR). 1,2,3,4-tetrachloronaphthalene was used as an internal standard for SIM (selective ion monitoring) analysis. The analysis was also performed in FS (Full Scan) mode, which operated in the range of mass-to-charge ratio value (m/z) 50–400. The column used for analysis was Agilent J&W DB-5MS and its temperature profile is shown in Table 5. SIM mode recoveries determined for 1.0 µg/L concentration of each micropollutant in target water were (in %): 91 – 4-NP, 85 – 4-OP, 90 – ANT, 104 – AC, 76 – HC, 92 – HCE, 92 – DEHP. All reagents used were of GC-MS grade.

DOC analysis was performed on Multi N/C 3100 organic carbon analyzer (Analytic Jena, Germany).

Table 4
Target micropollutants characteristics [25–27]

No.	Compound	pKa	Structure	Molecular weight	LogP
1	4-Nonylphenol	10.7		220.3	5.76
2	4-Tert-octylphenol	10.3		206.3	5.25
3	Anthracene	4.45		178.2	4.45
4	Alachlor	1.20		269.8	3.52
5	Bis(2-ethylhexyl) phthalate	3.08		390.6	5.03
6	Heptachlor	No data		373.3	4.3
7	Heptachlor epoxide	No data		389.3	4.98

2.4. Methodology

The pilot-scale NF process was carried out on a device with an efficiency of 2 m^3/h. The device consists of a microfiltration section equipped with a 5 μm precision filter which served as a prefilter, and a nanofiltration section consisting of two pairs of FilmTec™ NF90-4040 membranes connected in series. The process was carried out with 90% of permeate production efficiency. Transmembrane pressure during the filtration process was 1.5 MPa. Permeate and retentate was collected in separate tanks, with retentate going directly to the photolysis reactor. Samples for physicochemical analysis were collected from permeate and concentrate streams. NF effectiveness was evaluated based on MPs concentration in the filtrate stream. The process scheme is illustrated in Fig. 1. Membrane characteristics are presented in Table. 6.

The photolysis process was carried out in a batch reactor. NF process retentate was collected in the reactor until the volume of 0.5 m^3 was obtained. The reactor consists of a 1 m^3 tank, a photolytic flow module, a recirculation pump and an ozonizer with its maximum ozone production efficiency

Table 5
Column temperature profile

	Rate (°C/min)	Value (°C)	Hold time (min)	Run time (min)
Initial	n.d.	65	1	1
Ramp 1	30	180	0	4.83
Ramp 2	5	235	0	15.8
Ramp 3	10	300	0	22.3

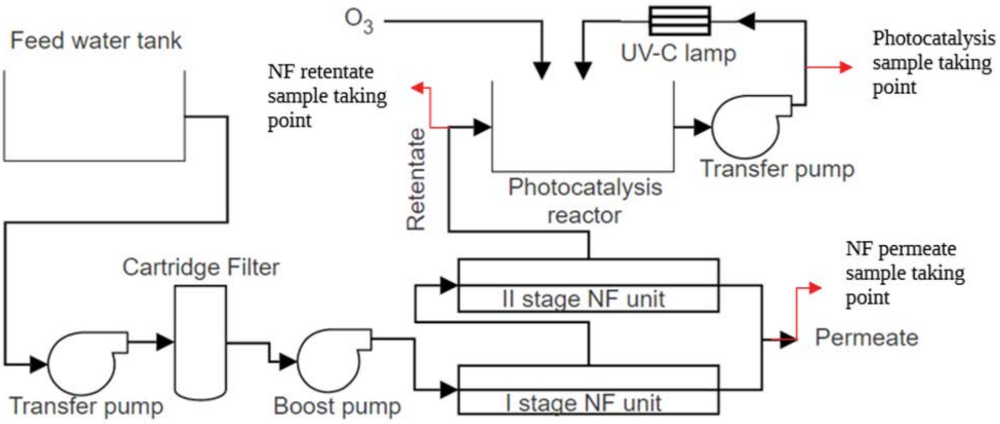


Fig. 1. NF and UV/O_3 processes scheme.

of 5 g O_3/h. The process was based on recirculation of the treated concentrate through a flow, medium-pressure UV-C radiator (VGE LightTech, 75W), while simultaneously dosing O_3. Reaction time was set to 120 min. Samples were taken directly from the reactor tank at 30, 60 and 120 min of the process. Ozone dose was related to the organic matter concentration in form of dissolved organic carbon (DOC) and set to 0.5 gO_3/gDOC.

3. Results and discussion

3.1. Nanofiltration

The NF90 membrane, due to its molecular weight cut-off (MWCO) < 200 Da, is considered "dense". Based only on the mechanism of steric exclusion, for which the retention conditions of analyzed substances are met (compounds MWCO greater or close to the membrane MWCO), also assuming the established 90% efficiency of the NF process, the concentration of MPs in retentate can be predicted. Therefore, concentration values should increase 10 times the initial concentrations of the matrix.

Results of the retentate and filtrate analysis after the NF process are presented in Tables 7, 8 and 9. Overall organic content determined by TOC was decreased under 0.1 mg/L achieving almost 100% retention. Only 3 out of 7 tested compounds: AC, HCE and DEHP were concentrated in relation to the initial amount. The predicted 10-fold concentration was observed for AC and HCE, 1.93 and 1.44 µg/L, respectively. Concentrations of 4-OP, 4-NP, ANT, DEHP and HC in retentate were similar or lower than initial values. Importantly, neither of these substances was observed in filtrate at a concentration greater than 0.002 µg/L. This may mean that these substances were bound to the membrane surface as part of adsorptive interactions [29,30]. Separation mechanisms of NF polyamide membranes strictly depend on membrane properties and contaminants characteristics. Some membrane properties are related to matrix physicochemical, especially its pH value. Studies [31] have shown, that in pH values higher than 5, NF90 surface zeta potential values are negative, which indicates that membrane surface in that conditions is negatively charged. Since AC pKa is relatively low (approx. 1.20), in pH = 8 it most likely de-protonate. Negatively charged AC ions interacted with the negative charge of membrane surface causing electrostatic repulsion (Donnan Exclusion [32]). Compounds with higher pKa values, like 4-NP or 4-OP, are more likely to ionize with cation generation. These may be bound to the membrane surface due to attraction forces. Donnan Exclusion and adsorptive

Table 6
NF membrane characteristics [28]

Manufacturer	FilmTec™
Product	NF90-4040
Type	Thin-film composite
Material	Polyamide (full aromatic)
Molecular weight cut-off (MWCO), Da	180–200
Salt rejection ($MgSO_4$) [%]	98.7

Table 7
Concentrate characteristics (MPs)

4-Nonylphenol	0.05
4-Tert-octylphenol	0.10
Alachlor	1.93
Anthracene (μg/L)	0.10
Bis(2-ethylhexyl) phthalate	0.25
Heptachlor	0.20
Heptachlor epoxide	1.44

Table 8
Concentrate characteristics (physicochemical)

pH	7.07
Conductivity (μS/cm)	2,681
Dissolved organic carbon (mg/L)	27.5

Table 9
Filtrate characteristics

Conductivity (μS/cm)	21
Dissolved organic carbon (mg/L)	<0.1
MPs concentration (μg/L)	<0.002 each

Table 10
Dissolved organic carbon reduction during UV/O_3 process

Dissolved organic carbon (mg/L)			
Concentrate	30 min.	60 min.	120 min.
27.5	26.2	26.1	26.1

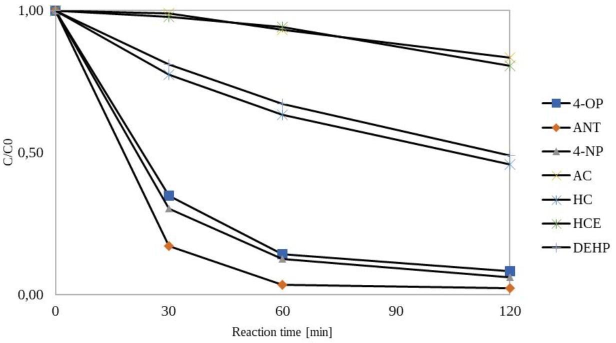


Fig. 2. Changes in MPs concentration during UV/O_3 process.

separation mechanisms are the most probable cause of MPs concentration differences in the obtained retentate.

3.2. Photocatalysis

In retentate obtained after NF, MPs concentration were aligned to the value of highest concentrated compound: AC, thus MPs concentrations obtained as a consequence of addition was 2 μg/L for each compound. The retentate sample was then analyzed for DOC and conductivity value.

DOC value in retentate at the level of 27.5 mg/L corresponded to O_3 dose approx. 14 g/m^3. Taking into account process conditions (volume, time) approx. 7 g O_3 during 120 min was introduced into the reactor.

Reduction of the dissolved fraction of organic matter, achieved as a result of the photolysis process, has been realized to a small extent and reached the maximum value of approx. 5% (Table 10). DOC reduction degree, however, does not correspond to the reduction values of the analyzed micropollutants, for which the maximum reduction levels reached the value of almost 98%. It has been observed, that MPs reduction effectiveness raised as the process progressed. As can be seen in Fig. 2, the lowest reduction efficiency was observed for AC and HCE, 16 and 19%, respectively. For 2 micropollutants: DEHP and HC, approx. 50% reduction was observed. For the remaining 3 substances: 4-OP, 4-NP and ANT, the reduction degree was the highest and amounted to 92%, 94% and 98%, respectively. Differences in reduction values may result from ozonolysis reaction parameters. For example, O_3 reacts significantly faster with 4-NP and 4-OP, for which reaction kinetics are respectively 3,8 × 10^4 and 4,3 × 10^4 M^{-1} s^{-1}, than with AC, $k = 3{,}4$ M^{-1} s^{-1} [33].

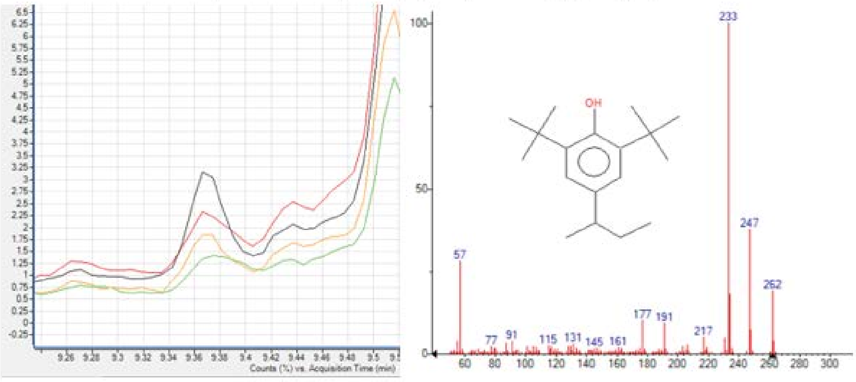
3.3. Full-scan analysis

The FS model GC-MS analysis was performed on the samples obtained during the photolysis process. Chromatograms were superimposed, and then signals for which the intensity increased with photolysis process duration were searched. Thus, 4 signals meeting the given condition were found (Fig. 3). 3 signals came from compounds with benzoic acid in their structure. It can therefore be assumed that these are derivatives of DEHP mineralization. For one signal, a compound with phenolic characteristics was identified, suggesting a 4-NP or 4-OP p derivative. The NIST library was used for substance identification.

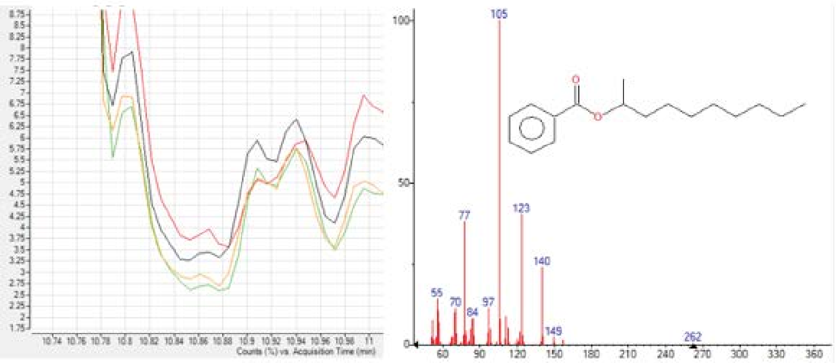
4. Conclusions

The nanofiltration process allowed for the reduction of micropollutants in the filtrate below the quantification limit. Part of the compounds was concentrated in the retentate, some remained in the system, most likely bound to the membrane surface. From the treated water recipient point of view, the NF process is 100% effective. However, from the treatment plant operator's point of view, due to the necessity to dispose of the retentate, the problem was only partially solved. The ozone-assisted photocatalysis process showed a relatively high destruction efficiency of the tested substances. In the assumed time of 2h, the reduction value for individual micropollutants ranged from 16 (AC) – 98% (ANT). As a result of GC-MS (FS) analysis, DEHP derivatives and phenolic compounds (4-OP, 4-NP) were found. The remaining 4 compounds underwent complete destruction (CO_2 and H_2O), their derivatives were not subject to the sample preparation proposed for

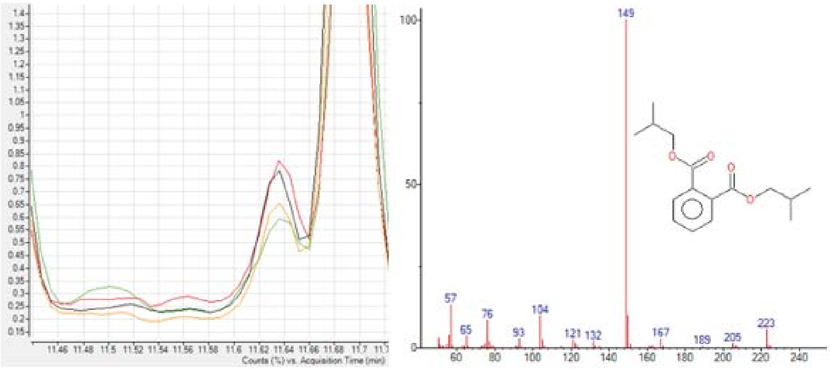
a) 2,6 bis(1,1-dimethylethyl)-4-(1-methylpropyl)-Phenol



b) Benzoic acid, dec-2-yl ester



c) Phtalic acid, diisobutyl ester



d) Dibutyl phthalate

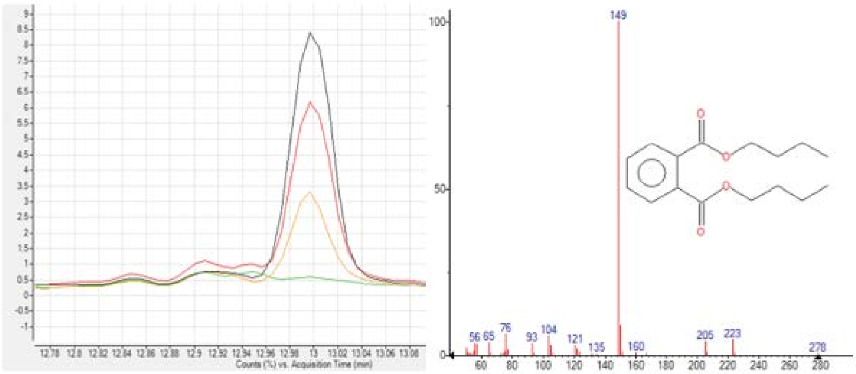


Fig. 3. MPs derivatives signals found after UV/O_3. Legend: green line – represents sample before treatment; orange line – results after 30 min into the process; red line – results after 60 min; black line – results after 120 min.

the original compounds, or initial concentrations of MPs were too low for further derivative determination.

Acknowledgments

This study was supported by the Ministry of Science and Higher Education of Poland within statutory funds no BK-261/RIE4/2021 and the program of Ministry of Science and Higher Education "Implementation Doctorate".

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