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Effectiveness of ultra-, nanofiltration and selected photolytic processes in removing of selected priority substances from water

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ABSTRACT

This paper presents the results of a study on the effectiveness of ultrafiltration (UF) and nanofiltration (NF) membrane processes and selected photolytic processes in the context of reducing the concentration of organic micropollutants. Studies on the removal of organic matter (dissolved organic carbon) were carried out on a laboratory scale in order to select optimal parameters for the processes. Analysis of micropollutant reduction was carried out on a semi-technical scale. The micropollutants analyzed were: 4-octylphenol, 4-nonylphenol, anthracene, alachlor, di(2-ethylhexyl)phthalate, heptachlor and heptachlor epoxide. In the initial phase of the study, the most effective ultra- and nanofiltration membranes in terms of natural organic matter removal were selected. Among the tested advanced oxidation processes viz: UV, UV/O_3, UV/TiO_2 and UV/H_2O_2, the process using simultaneous UV and ozone was selected as the most effective. In semi-technical scale tests, the following values of micropollutant removal were achieved: UF 63%–100%, NF 100%, UV/O_3 32%–100%.

Keywords: Ultrafiltration; Nanofiltration; Advanced oxidation processes; Ozone; Water; Micropollutants

1. Introduction

High level of vulnerability of natural water resources to the climate change and anthropogenic pollution leads to deterioration of the quality of water intended for human consumption. A crucial problem is the increasing pollution level of groundwater and surface water resources with a large nitrates load and micropollutants, including herbicides, fungicides, and insecticides from agricultural activity. It is necessary to remove these compounds from drinking water because they can penetrate the human body, accumulate in tissues and have a negative and multi-directional effect on its functioning [1–3]. Therefore, coherent and sustainable European Policy is necessary to achieve rational protection and control of natural resources. Such activity would lead to decrease of pollutants introduced into waters, which are taken for water treatment plants for municipal services. The Water Framework Directive 2000/60/EC (WFD) is a fundamental European Policy act that establishes a framework for community action in the field of water policy [4]. In addition to general guidelines intended to bring tangible environmental benefits, the directive introduced the concepts of priority substances and priority hazardous substances, which include organic micropollutants. A consequence of the WFD was the establishment of a list of priority substances for the first time in 2001, which now, after the 2013 amendment, includes as many as 45 compounds. These compounds, despite their relatively low concentrations in the aquatic environment, are characterized by high susceptibility to bioaccumulation, low biodegradability and high toxicity. For this reason, the new directive on the quality of water intended for human consumption 2020/2184 has made risk assessment mandatory along the entire chain from the supply areas to the tap at the consumer [5].

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Thus, the identification and monitoring in the water environment of substances harmful to human health and the development of effective processes to remove them from water are key steps to ensure the health safety of water consumers.

Water treatment plants implement techniques that enable them to provide end users with legally standardized water. These techniques are designed based on the characteristics of local raw water intakes, and are most often directed at treating raw water from the following fractions in general: inorganic, organic and pathogens. Surface water treatment in conventional water treatment plants usually involves the following processes: coagulation/flocculation, filtration and disinfection [6]. These techniques do not allow selective removal of contaminants, and the reduction of micropollutants is mainly dependent on the properties of specific substances [7,8]. The processes that determine the mechanism and efficiency of reduction include adsorption, evaporation, biotransformation and abiotic degradation. Adsorption and volatilization belong to physical processes and can be predicted using physicochemical data. The adsorption potential can be described using the octanol-water partition ($\log P_{o/w}$), which is defined as the ratio of equilibrium concentrations of solute in a two-phase system consisting octanol and water. The higher the $\log P_{o/w}$ value of a compound, the greater its affinity to octanol phase-hydrophobicity, and thus the greater the probability that the compound will undergo adsorption on the solid phase. Rogers [7] proposes the following breakdown:

$\log P_{o/w} < 2.5$	Low sorption potential
$\log P_{o/w} > 2.5$ and <4.0	Moderate sorption potential
$\log P_{o/w} > 4.0$	High sorption potential

Other important properties of micropollutants that have a key impact on their reduction efficiency are volatility, half-life (DT50), water solubility, acid dissociation constant and molar mass [9].

The effectiveness of conventional methods for the elimination of micropollutants varies widely and is highly dependent on the above-mentioned properties of specific compounds, as well as the characteristics of the medium being purified [10–13]. The highest efficiency of the classical water treatment techniques is characterized by sorption on activated carbon, both in the form of filtration on granular carbon and sorption using pulverized carbon, achieving, depending on the conditions of the process, average reduction values exceeding 50% [8,11,14]. In a comparative study, García-Vaquero et al. [15] determined the average effectiveness of conventional treatment technology consisting of coagulation, sedimentation, filtration and disinfection processes, in terms of reducing selected micropollutants, to be about 35%. The effectiveness of only the nanofiltration process in reducing the same substances was determined to be about 72%. Another study by Petrovic [16] put the efficiency of nonylphenols reduction in the coagulation and sand filtration processes at only slightly more than 7%, in the disinfection process at less than 43%. The use of the ozonation process, which is an unconventional method of oxidation of organic pollutants in the context of water treatment, resulted in more than 86% reduction.

Unsatisfactory results in the reduction of micropollutants and an increasingly stringent approach to the assessment of water quality have for many years attracted the attention of scientists around the world to the need to improve water treatment technology-as a method of directly securing the quality of water intended for drinking, and wastewater treatment that allows for the overall improvement of the aquatic ecosystem.

The concept of the present study was developed in response to the increasing demands on water quality, including the maintenance of adequate levels of micropollutants constantly still entering the aquatic ecosystem. Given the limitations of typical water treatment plant infrastructure processes in the context of reducing priority substances, a study was undertaken that would ultimately provide data to develop their technological effectiveness.

The purpose of this study was to evaluate the effectiveness of selected advanced water treatment methods in the context of reducing selected micropollutants from water. The micropollutants selected for the study were placed in Annex I of Directive 2013/39/EU [17] and consisted of the following substances: 4-nonylphenol, 4-octylphenol, anthracene, alachlor, heptachlor epoxide, heptachlor and di(2-ethylhexyl)phthalate. The work was carried out in three stages:

I. As part of stage I, methods for reducing micropollutants were selected on the basis of a scientific literature review. Subsequently, the selected methods were analyzed in terms of their effectiveness in ensuring selected general parameters. The research at this stage was carried out on a laboratory scale, and the primary purpose of the work was to obtain data to determine the concept of a modular pilot-scale station that would enable semi-technical scale testing of micropollutant reduction and assurance of general parameters of drinking water.
II. In the second stage, the construction of the research station was carried out.
III. In the third stage, semi-technical scale unit processes of ultrafiltration, nanofiltration and photolysis was conducted, directed primarily at reducing selected micropollutants from water.

2. Materials and methods

2.1. Target compounds

Seven organic micropollutants, which are included in the list of priority substances in the field of water policy, were selected for the study. These substances are: 4-nonylphenol, 4-octylphenol, anthracene, alachlor, heptachlor epoxide, heptachlor and di(2-ethylhexyl)phthalate. These compounds represent different groups of micropollutants:

- alachlor, heptachlor and its epoxide, represent the largest group of priority substances: pesticides,
- 4-nonylphenol and 4-octylphenol represent the surfactant group,
- anthracene represents the polycyclic aromatic hydrocarbons (PAH) group,
- di(2-ethylhexyl)phthalate is a plasticizer.

The characteristics of selected micropollutants are shown in Table 1.

2.2. Matrix

Laboratory scale tests were conducted on natural surface water taken from the Mała Panew River in Opole on the territory of the former village of Czarnowąsy (Opolskie Voivodeship), where the river enters the Odra River. The chosen water was characterized by a high content of natural organic matter expressed by the concentration of total and dissolved organic carbon (TOC and DOC), whose values ranged from, respectively: 12.7–17.5 mg/L and 9.3–13.5 mg/L. Based on the knowledge of the content of DOC and Abs_{254}, the specific ultraviolet absorbance value ($SUVA_{254}$) was determined. This parameter relates the dissolved organic carbon content to the absorbance value and allows for a general estimation of the quality of organic contaminants (Table 2). This indicator is also used to provide a preliminary estimate of the coagulation process efficiency and to determine the reactivity of the organic fraction toward the formation of oxidation and disinfection by-products [18].

To conduct the study water samples were pretreated by subjecting them to coagulation and sedimentation. The characteristics of the waters are shown in Table 3.

The object of the pilot-scale study was groundwater taken in the village of Mańczok (Opole Province). Analysis of selected micropollutants did not reveal their presence in the raw water, hence all studies were conducted on model water, the matrix of which was Mańczok water with seven micropollutants spiked to a level of 5 μg/L for each micropollutant. Its characteristics are shown in Table 4.

2.3. Membranes

Four membranes (Synder Filtration, USA) with different molar mass limits were analyzed: A6 (500 kDa), BX (250 kDa), BY (100 kDa) and BN (50 kDa). These were made of polyvinylidene fluoride (PVDF). The nanofiltration membranes were from FilmTec™ (USA). These were composite membranes with an active layer made of polyamide: NF-270 and NF-90. The parameters of the membranes are shown in Table 5.

2.4. Advanced oxidation processes reagents

In the study, 30% analytical grade hydrogen peroxide from Stanlab (Poland) was used. Commercial titanium dioxide from Degussa (Germany), labeled P25, was used as a solid catalyst.

2.5. Experimental procedures

2.5.1. Laboratory scale

The membrane filtration process was carried out in a dead-end filtration system. The device consisted of a tank (0.4 dm^3) for the medium to be purified, into which an inert gas (nitrogen) was supplied, and a base in which a membrane of 0.00159 m^2 was placed. The transmembrane pressures for the ultra- and nanofiltration processes were 0.3 and 2.0 MPa, respectively. Before the filtration process, the membranes were conditioned with deionized water under nominal operating conditions until the filtration efficiency was stabilized. The filtration process was carried out until 80% permeate recovery, with samples for physical and chemical analysis taken at 20%, 40%, 60% and 80% recovery.

The phenomenon of membrane fouling was determined by determining its relative membrane permeability (α), which is the quotient of demineralized water fluxes determined for the fresh membrane (J_w) and after the process (J_v), calculated from the relationship:

$$J_v\left(J_w\right)=\frac{V}{F\cdot t},\quad \frac{\mathrm{m}^3}{\mathrm{m}^2\times\mathrm{s}}$$

where V - volume; F - membrane area; t - time.

Photolytic advanced oxidation processes was carried out in a batch reactor with a volume of 0.6 dm^3. The glass reactor made by Heraeus (Germany) was equipped with a magnetic stirrer, and an immersed 150 W medium-pressure UV irradiator cooled by tap water. An O_3 Ozone FM 500 generator from WRC Multiozon (Poland) with a capacity of 250 mg/h was used for ozonation.

The process was carried out in four configurations:

- UV - the exposure time was 60 min. Samples were taken at 15, 30 and 60 min of the process.
- UV/H_2O_2 - the dose of hydrogen peroxide was 30 mg/L. Exposure time and sampling were carried out as for the UV process.
- UV/O_3 - the dose of ozone was 3 mg/L. The irradiation time and sampling were realized as for the UV process.
- UV/TiO_2 - the catalyst dose was 500 mg/L. The exposure time and sampling were realized as for the UV process.

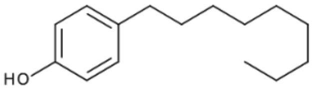
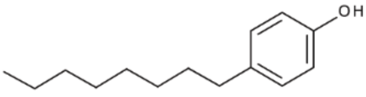
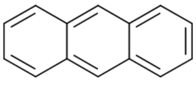
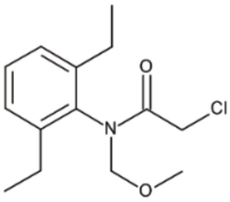
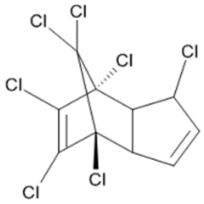
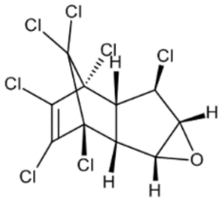
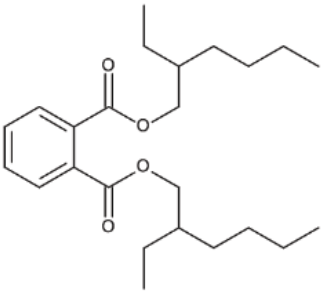
2.5.2. Pilot scale

The ultrafiltration module is driven by an Ebara Pumps (Italy) with a maximum capacity of 9 m^3/h. The system consists of a mechanical filter with a replaceable filter cartridge (a 25 μm filter mesh was installed for this study), acting as a pre-filter. After the pre-filter unit is an ultrafiltration section consisting of two parallel membranes operated in a cross-flow system. The specifics of the membranes corresponded to the membrane selected in the laboratory tests: Synder BY molecular weight cut-off (MWCO = 100 kDa, membrane material: PVDF). The detailed characteristics of the membrane are shown in Table 6.

The nanofiltration section is preceded by a microfiltration module consisting of 5 5 μm pre-filters. Nanofiltration section consists of 4 membranes. Membranes operate in parallel pairs, with pairs connected in series. Membranes used in the study were FilmTec™ (USA) NF-90, detailed specifications of which are shown in Table 7. Filtration process was carried out at a pressure of 1.5 MPa. Membrane operation control is carried out on the basis of transmembrane pressure analysis and with the help of integrated permeate conductivity measurement. Nanofiltration process scheme is shown on Fig. 1.

The UV/O_3 process was carried out in a batch reactor. The reactor consisted of a 1 m^3 tank made of high-density polyethylene (HDPE), recirculation pump and a

Table 1
Characteristics of micropollutants selected for this study

	Structure	Molar mass (g/mol)	log$P_{o/w}$*	pKa**
4-Nonylphenol		220.4	5.7	10.7
4-Octylphenol		206.3	5.5	10.3
Anthracene		178.2	4.5	n.a.
Alachlor		269.8	3.5	n.a.
Heptachlor		373.3	6.1	n.a.
Heptachlor epoxide		389.3	5.4	n.a.
Di(2-ethylhexyl)phthalate		390.6	7.5	n.a.

*log$P_{o/w}$ - octanol-water partition coefficient;
**pKa - acid dissociation constant (logarithmic).

flow-through UV irradiator. The treated water was recirculated through the irradiator and returned to the tank. A medium-pressure UV-C lamp from VGE LightTech (The Netherlands) with a power of 75 W was used as the irradiator. The lamp was placed in a flow-through shield with dimensions L = 100 cm, Ø = 6 cm. The recirculation

Table 2
Estimation of natural organic matter characteristics using $SUVA_{254}$ [18]

$SUVA_{254}$	Natural organic matter characteristics
≥4	Predominance of aromatic, macromolecular, hydrophobic humic substances
2–4	Mix of humic substances, fulvic substances and other NOM forming compounds
<2	Predominance of low-molecular-weight, hydrophilic fulvic substances

Table 3
Laboratory scale water characteristics

	Mała Panew[a]	Mała Panew[b]
pH	7.3–7.9	7.2–7.6
TOC, mg/L	12.7–17.5	6.8–8.2
DOC, mg/L	9.3–13.5	6.3–7.8
Conductivity, µS/cm	455–613	512–773
Abs_{254}	1.23–1.76	0.69–0.88
$SUVA_{254}$	2.60–2.64	2.19–2.26

[a] Raw water;
[b] Pretreated water.

Table 4
Characteristics of the water used for pilot-scale tests

	Mańczok
pH	7.42
TOC, mg/L	5.04
DOC, mg/L	4.79
Conductivity, µS/cm	404
Abs_{254}	0.253
$SUVA_{254}$	1.06

Table 6
Characteristics of the membrane used in the ultrafiltration process (manufacturers data)

Manufacturer	Motian	
Symbol	UF_3OB160	
Material	Polyvinylidene fluoride	
Flux (deionized water 20°C, 0.1 MPa), L/m²·h	60~120	
MWCO, Da	100,000	
Transmembrane pressure, MPa	Max.	0.30
	Opt.	0.15

Table 7
Characteristics of the membrane used in the nanofiltration process (manufacturers data)

Manufacturer	FilmTec™, USA
Symbol	NF-90-4040
Material	Polyamide (active layer)
Salt retention $MgSO_4$, %	98.7
MWCO, Da	150–200
Max. transmembrane pressure, MPa	4.0

capacity was 2 m³/h. The radiation dose for one recirculation cycle estimated by the manufacturer was ~240 mJ/cm². An ozone generator with a maximum O_3 production capacity of 5 g·O_3/h was used for ozone production. Ozone was introduced into the tank throughout the photolysis process at a dose related to the level of dissolved organic matter in the treated water. The process was conducted for 120 min and samples were taken at: 30, 60 and 120 min of the process. The volume of water subjected to photolysis was 0.4 m³. The ozone dose was set at 0.5 g·O_3/g·DOC, which for water with DOC = 4.79 mg/L corresponded to an ozone production rate of 0.48 g·O_3/h. With the maximum recirculation capacity and the assumed reaction volume, 10 recirculation cycles were performed in 120 min, which translates into a radiation dose of ~2,400 mJ/cm². Process scheme is shown in Fig. 2.

2.6. Analytical procedures

Analysis of micropollutant concentrations was carried out by gas chromatography coupled to mass spectrometry (GC-MS).

Table 5
Membrane characteristics (manufacturers data)

	Manufacturer	Material	Symbol	Cut-off, Da	Salt retention, % $MgSO_4$
Ultrafiltration	Synder Filtration, USA	Polyvinylidene fluoride	A6	500,000	–
			BX	250,000	–
			BY	100,000	–
			BN	50,000	–
Nanofiltration	FilmTec™, USA	Polyamide/ composite	NF-90	100–200	98.7
			NF-270	150–300	97.0

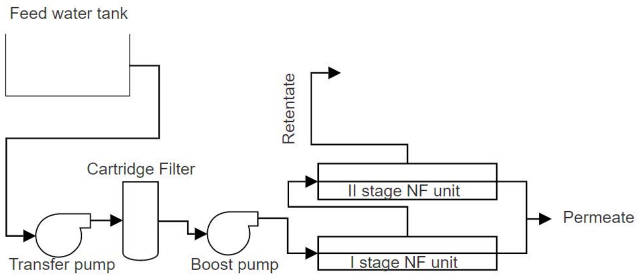


Fig. 1. Nanofiltration device scheme.

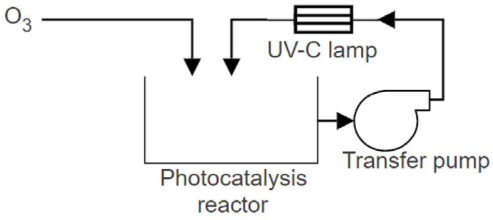


Fig. 2. UV/O_3 process scheme.

Samples for GC-MS analyses were fixed by the addition of methanol at 1% (v/v) of the sample volume. Sample preparation for GC-MS analysis was done with solid phase extraction (SPE). SPE C18 columns (J.T. Baker, Poland, 500 mg octadecyl phase) previously conditioned with methanol (5 mL), a mixture of dichloromethane/ethyl acetate (DCE; 1:1, v/v) (5 mL) and deionized water (5 mL) were used for extraction. The columns were dried under nitrogen after the extraction process, and then subjected to elution. Elution was carried out using DCE and acetone sequentially. The eluate was then evaporated at 30°C, under a nitrogen atmosphere Biotage (Sweden) TurboVap II and the solvent was changed to acetonitrile. 1,2,3,4-tetrachloronaphthalene was used as an internal standard in SIM (selective ion monitoring) analysis.

Samples were analyzed using an Agilent 7890B Gas Chromatograph coupled with Agilent 5977A single quadrupole mass spectrometry detector (Agilent, USA). The gas chromatograph was equipped with an Agilent J&W DB-5ms capillary column (20 m length × 0.25 mm diameter × 0.25 μm phase; Agilent USA) and an Agilent 5190-2293 Liner (900 μL, Agilent USA). The injector temperature was set to 250°C. The sample was injected onto the column in splitless mode for 0.3 min at a pressure of 344.7 kPa (50 psi). The source temperature was 230°C, the quadrupole temperature: 150°C, and the ionization energy was 70 eV. The temperature program is shown in Table 8. Helium with a constant flow rate of 1 mL/min was used as the carrier gas.

The efficiencies of the laboratory-scale processes were evaluated on the basis of general parameters analysis, that is, DOC, absorbance $\lambda = 254$ nm, and conductivity. The pH of the samples was also controlled.

DOC was measured using an Analytik Jena (Germany) Multi N/C 3100 organic carbon analyzer. Absorbance values were measured using a Merck (USA) Spectroquant® Prove 300 UV/Vis Spectrophotometer. Absorbance was measured in quartz cuvettes with an optical path length of 50 mm. WTW (Poland) pH/Ion/Cond 750 meter was used to measure pH and conductivity.

Table 8
Temperature profile of the gas chromatography column

	Temp. ramp, °C/min	Temp. value, °C	Hold time, min.	Time min.
(Initial)	n.d.	65	1	1
Phase 1	30	180	0	4.83
Phase 2	5	235	0	15.8
Phase 3	10	300	0	22.3

3. Results and discussion

3.1. Laboratory scale tests

3.1.1. Ultrafiltration

Fig. 3 shows the results of an analysis of the effectiveness of organic matter removal using four commercially available membranes.

The initial efficiency of the ultrafiltration process ranged from 10%–48% and varied depending on membrane morphology. The efficiency of organic carbon concentration reduction increased with decreasing membrane MWCO, so for A6 membrane (500 kDa) was 10%, for BX (250 kDa) 17%, for BY (100 kDa) 39%, and for BN (50 kDa) 48%. The DOC reduction efficiency using the A6 membrane measured in the sample taken at the end of the process was 3% higher compared to the sample taken at the beginning of the experiment. This indicates operational stability of this membrane under set conditions. For the other membranes, a decrease in efficiency was noted as filtration progressed. Decrease in process efficiency compared to the initial value was most noticeable for membrane with the smallest MWCO - BN, and was as high as 33%. For BX and BY membranes, the efficiency reduced by 10% and 11%, respectively.

The analysis of determined α coefficients showed that BN membrane underwent a significant fouling phenomenon during operation, lowering the volumetric flux of deionized water after the process by as much as 84% compared to the fresh membrane. In this regard, the best performance was shown by membrane A6, for which differed in volumetric fluxes by 17%. BY and BX membranes also underwent a noticeable fouling phenomenon. For these membranes, the decrease of streams was 41% and 48%, respectively. The α coefficient may give partial information about the quality of natural organic matter (NOM) in the tested water. Organic substances adsorbing or blocking inside the membrane pores are largely responsible for the fouling phenomenon [19]. Analysis of humic substances conducted by Antonelli et al. [20] showed that the predominant fraction of macromolecular humic substances is that with a molar mass of more than 100 kDa. In the case of low-molecular-weight fulvic compounds, the dominant fraction is that with a molar mass of less than 10 kDa. Such characteristics of NOM coincide with the determined performance of tested membranes. In case of the membrane blocked to the greatest extent, fulvic compounds were most likely responsible for the fouling phenomenon, while in the case of the membrane with MWCO = 250 kDa the dominant, large-molecular fraction of humic compounds.

3.1.2. Nanofiltration

Nanofiltration membranes effectiveness analysis is shown in Fig. 4.

In nanofiltration, the best process results were achieved with the NF-90 membrane. This membrane allowed to achieve 93% DOC removal, compared to "only" 80% achieved with the NF-270 membrane. In addition to greater efficiency, the NF-90 membrane proved to be more fouling-resistant, reaching α = 0.88. For the NF-90 membrane, an increase in efficiency was also observed as the process progressed. This may be caused by the deposition of

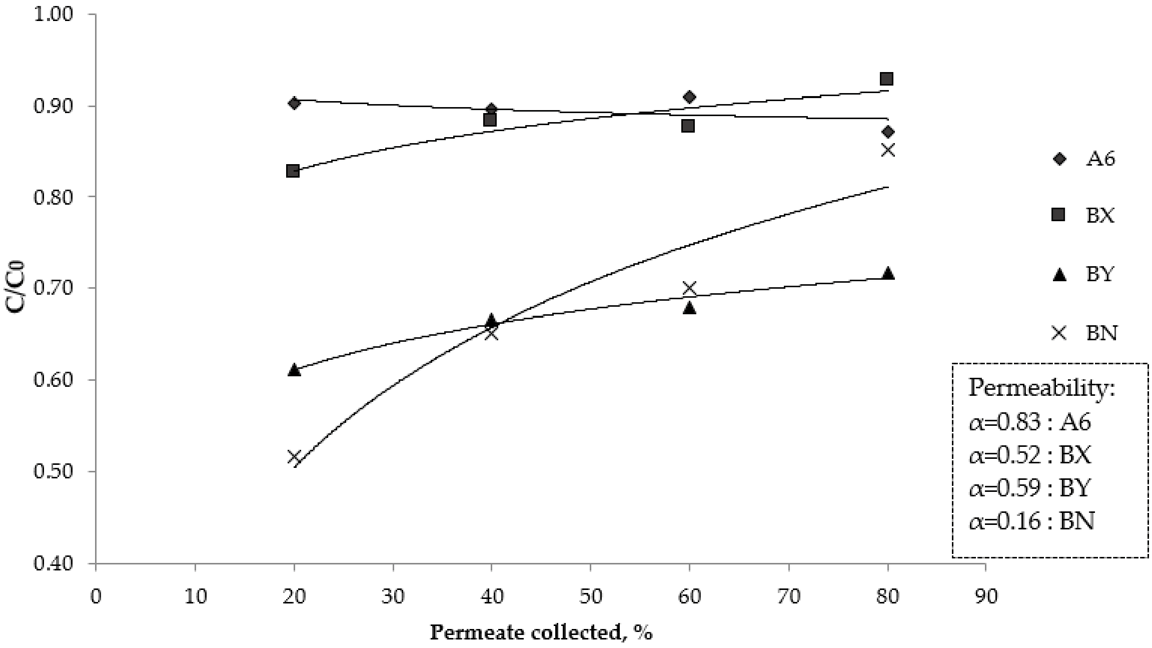


Fig. 3. Dissolved organic carbon removal efficiency of membrane filtration process – ultrafiltration.

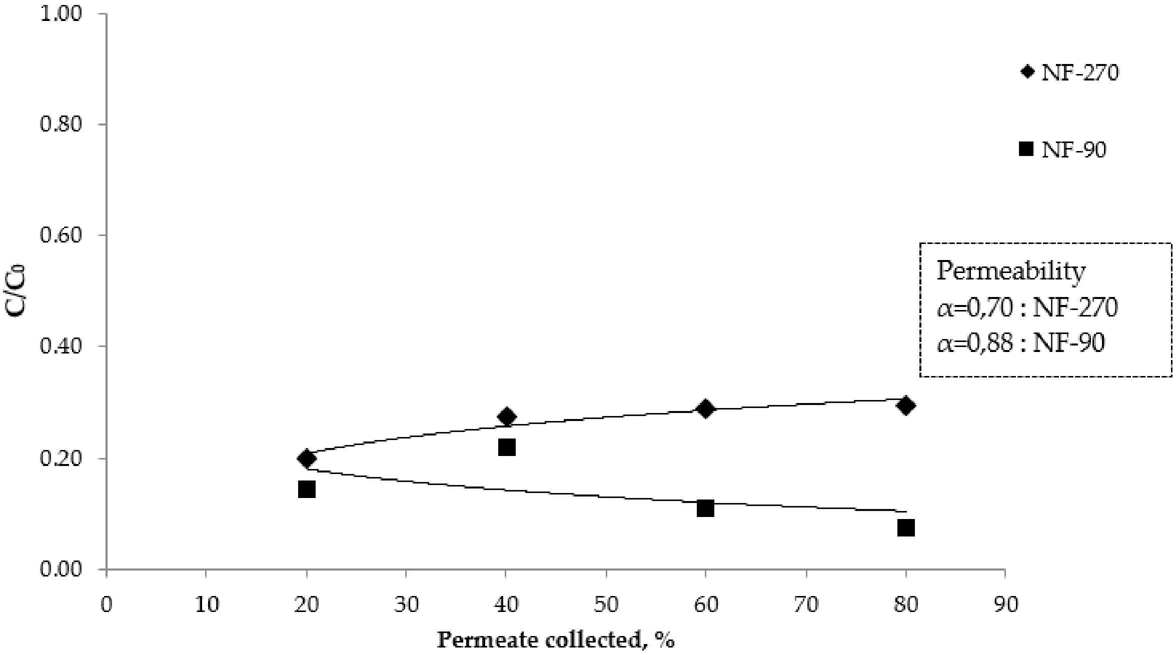


Fig. 4. Dissolved organic carbon removal efficiency of membrane filtration process – nanofiltration.

contaminants on its surface during filtration, and its consequent "fouling". The formation of a film of impurities on the membrane surface may result in interactions between the impurities and the formed layer, thus increasing the retention rate [21].

3.1.3. Advanced oxidation processes

The efficiencies of photolytic advanced oxidation processes are shown in Figs. 5 and 6. Efficiency expressed by Abs_{254} value reduction was at maximum of 71% and was achieved for the photolysis process associated with ozonation. The lowest efficiency of 30% was achieved for the UV process, confirming the benefits of associating UV irradiation with oxidants or catalysts.

Absorbance reduction results are not consistent with the achieved organic-carbon-based substances removal efficiency. Despite the relatively high reduction of Abs_{254}, the degree of DOC reduction was at most 11%. It can be assumed that the NOM-forming substances present in the treated water did not undergo complete mineralization and were only converted to intermediate products.

Nevertheless, it was decided that in the next phase of the study, the UV/O_3 process would be carried out with appropriate modifications to potentially increase its effectiveness, that is, the irradiation time would be extended,

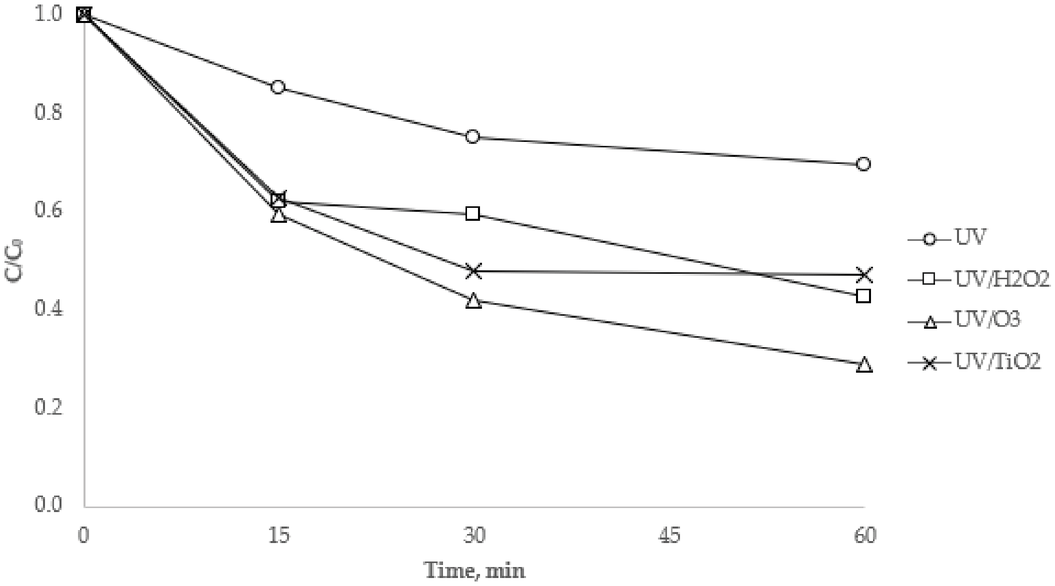


Fig. 5. Abs_{254} reduction efficiency of photolytic advanced oxidation processes.

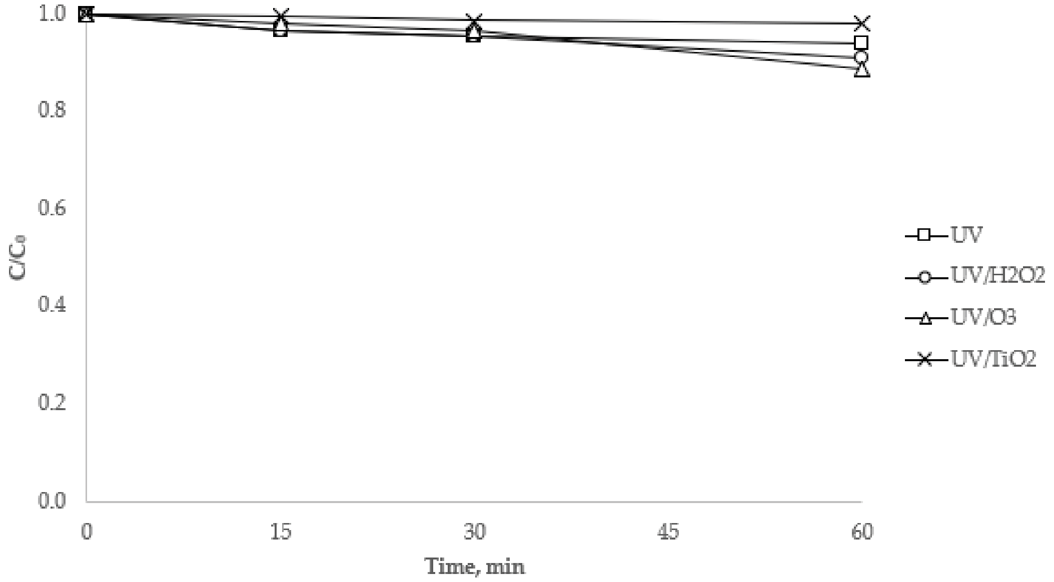


Fig. 6. Dissolved organic carbon reduction efficiency of photolytic advanced oxidation processes.

the O_3 dose would be related to the organic carbon content in the ratio of 0.5 g·O_3/1 g·DOC.

3.2. Pilot scale tests

3.2.1. Ultrafiltration

The effectiveness of the ultrafiltration process in removal of selected micropollutants is shown in Fig. 7.

The ultrafiltration process showed satisfactory reduction efficiency for the analyzed compounds. For 6 of the 7 analyzed compounds, a reduction rate in the range of 95%–100% was achieved, of which 3 compounds (4-Op, Ant and Hcl-e) were able to be eliminated completely. The lowest efficiency was achieved for alachlor (Acl), with concentration reduction value of 63%. The membranes MWCO of 100 kDa significantly exceeds the molecular masses of the compounds analyzed, which means that their retention takes place through interactions with the surface of the membrane material. Membranes made of PVDF are characterized by high hydrophobicity [22], which allows adsorption of hydrophobic micropollutants on their surface. As observed during laboratory scale studies, a membrane with a given MWCO is effective in terms of NOM retention. Preferential adsorption of micropollutants on organic matter components may also account for the high removal rate of these compounds. The mechanism of adsorption on the membrane surface, as well as interactions with NOM, may explain the results of the process efficiency, which was noticeably lower for substances with the lowest value of the partition coefficient $\log P_{o/w}$.

3.2.2. Nanofiltration

In nanofiltration process, 100% retention of each analyzed micropollutant was achieved. Separate tests [23] conducted on tap water, into which the analyzed micropollutants were introduced to a level of 0.2 μg/L for each compound, which was also subjected to the nanofiltration process using an NF-90 membrane, also showed 100% retention of micropollutants. However, retentate tests showed compound concentrations corresponding to the process

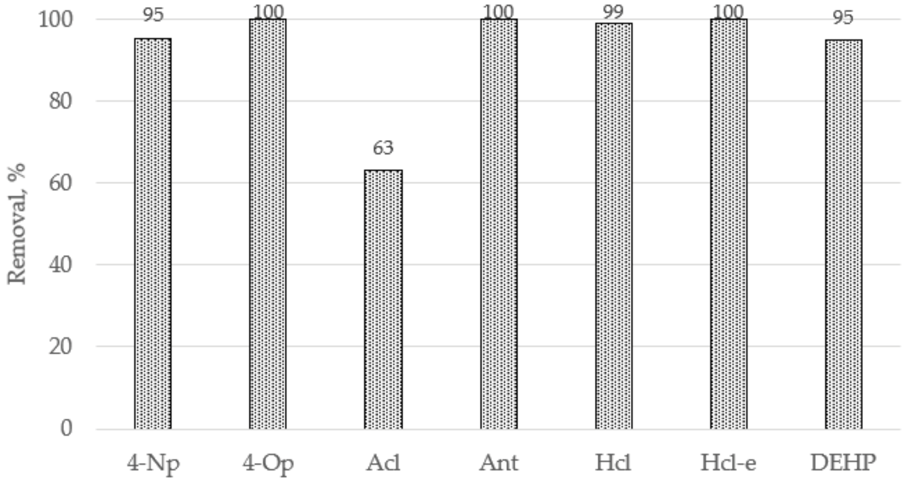


Fig. 7. Removal efficiency of selected micropollutants in ultrafiltration process.

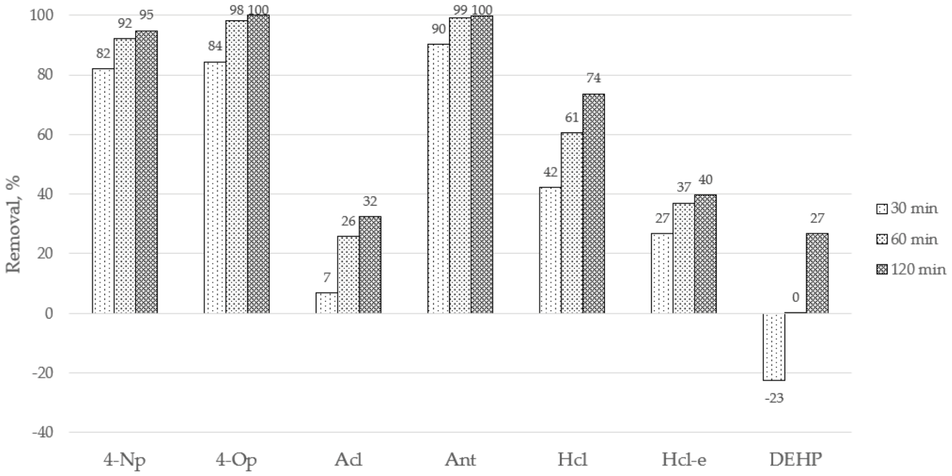


Fig. 8. Removal of micropollutants within UV/O_3 process.

performance for only 2 of the 7 substances: Acl and heptachlor epoxide (Hcl-e). The zeta potential of the NF-90 membrane in aqueous environments with pH values > 5 takes on negative values, indicating its negative surface charge [24]. Concentrated compounds have functional groups in their structure (the ester group of Hcl-e, the amine group of Acl), which can cause their strong polarization, leading to repulsive interactions between the negatively charged membrane and the substance, and thus to their concentration in the post-process concentrate.

3.2.3. UV/O_3 process

The reduction of selected micropollutants in the UV/O_3 process is shown in Fig. 8. The negative reduction rate of di(2-ethylhexyl)phthalate is most likely due to the leaching of this compound from the reaction reactor, so that an evaluation of its reduction efficiency was not carried out.

Of the 6 compounds evaluated, the lowest reduction efficiency was achieved for Acl, for which there was a 32% decrease in concentration after 120 min of running the process. On the other hand, for the substances 4-nonylphenol (4-Np), 4-octylphenol (4-Op) and anthracene (Ant), the reduction exceeded 95%, with complete elimination observed for the latter two. A study conducted by Yao and Haag [25] confirm the difficulties associated with alachlor degradation in ozonation-related reactions. It was shown that the half-time of Acl reduction during ozonation was $t_{1/2}$ = 2.4 h, and the reaction kinetics was only 3.8 M/s. In another study, Maldonado et al. [26] achieved full reduction of Acl after 270 min. Also, compounds with multiple halogen substituents (such as Hcl or Hcl-e) are much more difficult to oxidize than substances with no heteroatoms in their structure or with a high degree of electron delocalization [27,28]. This explains the high degree of reduction of aromatic and unsubstituted 4-Np, 4-Op, and Ant, as well as the better reduction efficiency of Hcl compared to Hcl-e despite significant similarity in structure. A time-dependent increase in process efficiency was observed for all substances.

4. Conclusions

- The results obtained as a result of the laboratory-scale studies proved useful in the design and construction of a pilot research station, ultimately directed at optimizing the technology for the treatment of water intended for consumption in terms of improving the overall parameters of water, and reducing micropollutants.
- The efficiencies of the processes carried out at the laboratory scale largely coincided with the efficiencies of the processes carried out at the semi-technical scale.
- The effectiveness of the processes studied in the context of organic micropollutant reduction largely depends on the composition and characteristics of the water matrix in terms of the presence of natural organic matter. In ultrafiltration the higher content of organic matter positively influenced the overall efficiency of micropollutant reduction, which was due to the adsorption mechanism of the tested substances on NOM-forming compounds, which underwent partial removal or retention.
- It was observed that the highest efficiency of reduction of selected micropollutants was characterized by nanofiltration processes using NF-90 membrane. Nanofiltration process allowed the complete removal of micropollutants from the treated water.
- In process of photolysis associated with ozonation, a high dependence of the process efficiency on the characteristics of the removed compounds was observed. Substances without substituents in the form of heteroatoms were mineralized to a much greater extent than halogen-organic compounds. The aromaticity of the compounds also affected the reduction efficiency, as was observed for the Hcl and Hcl-e pair. In the case of the first compound, the reduction efficiency was visibly higher, despite the structural similarity of these substances. For all analyzed compounds, an increase in reduction efficiency related to the time course of the oxidation process was also observed.

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