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Photocatalytic oxidation of natural organic matter enhanced with microfiltration and nanofiltration

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ABSTRACT

In the article, the results of the study on the effectiveness of removal of natural organic matter from simulated water containing fulvic (FA) and humic (HA) acids as well as natural water contaminated with a mixture of organic compounds are presented. The treatment process comprises a photocatalytic microfiltration reactor (PhMFR), the operation of which was supported with nanofiltration (NF). The photocatalysis process was performed with the use of TiO_2 P25 catalyst and immersed UV low-pressure lamps. Microfiltration was carried out with the use of a capillary membrane module—MICROZA, while NF with a flat-sheet composite membrane. It was found that such a configuration of the water treatment process, which resulted in a highly effective removal of natural organic compounds, could be successfully applied in practice.

Keywords: Natural organic matter; Humic and fulvic acids; Photocatalysis; Microfiltration; Nanofiltration

1. Introduction

A photocatalytic oxidation process relies on a degradation of contaminants using highly reactive hydroxyl compounds generated during photocatalytic radiation. It should result in a complete decomposition of a wide range of contaminants, including natural organic matter, which is usually present in natural surface and groundwaters. Those compounds, after being exposed to photocatalysis, are mineralized to carbon dioxide and water. Thus, the problem of transport contaminants from one phase to another, which is typical for conventional water treatment methods such as coagulation or activated carbon adsorption, is eliminated. Another advantage of the photocatalysis process is the preservation of catalytic properties of the catalyst after each treatment cycle, which enables a continuous process performance with any side streams generation [1,2].

Photocatalysis with the use of semiconductors (TiO_2, ZnO, CdS, SnO, and other), next to other advanced oxidation processes such as the phenton process ($Fe^{2+} + H_2O_2$), hydrogen peroxide, ozon, or photochemical methods, is still in the study phase, and it has been intensively investigated at laboratory scale conditions [3].

The increasing interest in the methods of advanced oxidation of natural organic matter (NOM) present in water resulted in the development of laboratory scale

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photocatalytic membrane reactors [4–6]. There are many configurations of such devices. However, in the study, the operation of the photocatalytic reactor with the catalyst suspended in water is discussed. In the literature, one can find many papers on improvement of the photocatalytic membrane reactors' operation. The authors of [7], for example, applied modified titanium dioxide in the form of nanowires (TNW_{10}), which was found to be more effective than commercial P25 titanium dioxide. Other researchers [8] combined the action of TiO_2 with ferrihydrite and obtained higher TOC retention rates than the one with the use of only TiO_2.

The study was focused on the removal of NOM components (fulvic and humic acids) from simulated and SW. The effectiveness of removal of those contaminants using a two-stage treatment system comprised of a photocatalytic membrane reactor equipped with microfiltration module proceeded with a NF polishing being an environmentally friendly water treatment method was investigated.

2. Materials and methods

2.1. Characteristics of examined waters

The study concerned simulated waters containing organic compounds (fulvic or humic acids) as well as surface water (SW) collected at one of the Silesian (Southern Poland) water treatment plants. Tap water, in which fulvic (FA) or humic (HA) acids were dissolved in a defined amount, was used as a matrix for particular simulated solutions. In Table 1, the characteristics of waters exposed to the treatment process are presented.

2.2. Photocatalysis

The photocatalysis process was run in a photocatalytic reactor of volume 20 L (a volume of water in the reactor—17 L). Immersed low-pressure UV lamps of power 15 W emitting radiation of the wavelength 254 nm were used as the light source. As the catalyst commercial titanium dioxide P25 by Degussa, a dose of which was equal to 0.1 g/L was used.

2.3. Microfiltration and nanofiltration

The role of the microfiltration module (MF) was to separate catalyst particles from the treated water and to enable its recycling to the photoreactor. In the study, the capillary microfiltration module MICROZA combined with the photocatalytic reactor and operated in the cross-flow mode was used. The scheme of the photocatalysis–microfiltration installation is shown in Fig. 1. The effective separation area of the

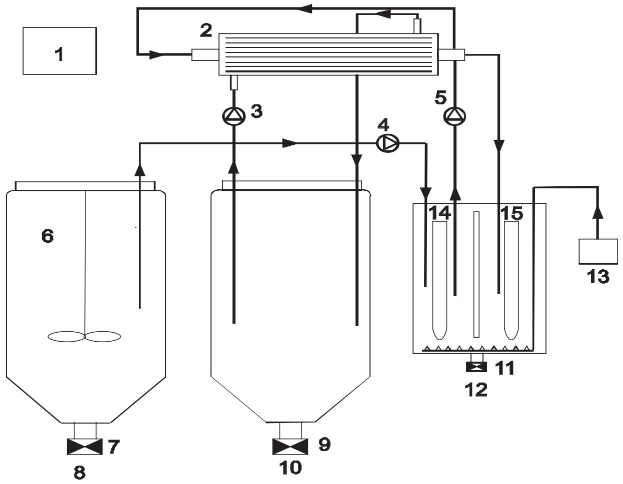

Fig. 1. The scheme of the combined photocatalysis–microfiltration installation (photocatalytic membrane reactor—PhMFR). (1) Control cabinet; (2) capillary microfiltration module; (3) back-flushing pump; (4) and (5) feed pump; (6) stirrer; (7), (9) and (11) valves; (8) raw water tank; (10) permeate pump; (12) reactor; (13) air blower; (14) and (15) UV lamps.

Table 1
Characteristics of examined waters

Parameter	Unit	Water type		
		Water—FA	Water—HA	Surface water—SW
pH	–	6.88	6.66	6.85
Conductivity	mS/cm	0.856	0.769	0.189
DOC[a]	mg/L	12.66	10.05	6.18
UV254[a]	m^{-1}	19.1	24.4	7.8
Color[a]	mgPt/L	26	23	18
Total hardness	$mgCaCO_3/L$	444	432	88
SUVA[b]	L/mg m	1.50	2.32	1.26

[a]Prefiltered samples (0.45 μm).

[b]Specific absorbance in UV, UV254/DOC.

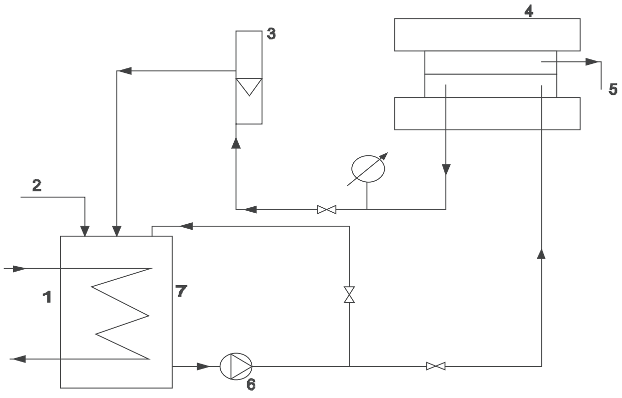

Fig. 2. The scheme of the NF process system. (1) Heat exchanger; (2) raw water inflow; (3) rotameter; (4) membrane cell; (5) permeate outflow; (6) pump; (7) raw water tank.

microfiltration module supplied by Pall Poland was equal to 0.12 m^2. The membrane material was polyvinylidene fluoride, and the nominal pore size was at the level of 0.1 μm.

The water polishing step comprised of nanofiltration (NF) also operated in the cross-flow mode. The composite NF membrane of DK type by GE Infrastructure water & process technologies was used. The effective separation area of the unit was equal to 0.0155 m^2, and the membrane cutoff was 200 Da. The membrane was operated at a constant pressure of 1 MPa. The scheme of the NF system is shown in Fig. 2.

2.4. Methodology

The first step of the treatment was carried out in a continuous photocatalytic membrane reactor with external microfiltration module—PhMFR (Fig. 1). In the photocatalytic reactor, the photocatalysis process with the catalyst (TiO_2) in the suspended form was run. The suspended state of the catalyst, mixing of the reactor content, and reaction mixture aeration were all assured by air diffusors placed at the bottom of the reactor chamber. The radiation of the reaction mixture, necessary to photoactivate the semiconductor (TiO_2), was assured by two immersed low-pressure UV lamps. The temperature of the reaction mixture during the process was relatively stable in the range of 22–28˚C. In order to improve the efficiency of the radiation, the external wall of the reactor was covered with the aluminum foil. The start-up of the operation of the photocatalytic membrane reactor was preceded with 2 h radiation of the feed water in the reactor chamber, which aimed at preventing the negative impact of contaminants present in water on the membrane performance and enabled the system adaptation to the stable flow operation. The treatment of water in the continuous system relied on the constant exploitation of the membrane module and the cyclic radiation of the feed mixture performed after each 1 h of the process run for 30 min. The proper amount of the photocatalyst was introduced to the photoreactor, next, the treated water was directed to the microfiltration module on which the retention of the catalyst particles occurred and the retentate was recycled to the photoreactor chamber. Such a configuration of the system enabled the constant use of the catalyst, even for many hours of the treatment. The flowing arrangement of the system allowed for the constant collection of the purified water, while the inflow of raw water to the photoreactor was made periodically using feed pump and maximum and minimum liquid level probes (operated on the basis of environment conductivity measurements). The automatics of the process were controlled by the controller, which made it possible to set up all the operational parameters of the installation.

The second stage of the treatment was based on the polishing of the permeate obtained in the PhMFR. The process was carried out using a NF membrane operated in the cross-flow mode (Fig. 2). The NF was run for 3 h in the continuous system, i.e. the level of water in the feed tank was kept at the constant level equal to 10 L and was continuously supplied with the feed in the amount corresponding to the volume of the collected NF permeate.

The effectiveness of the process was evaluated on the basis of measurements of both dissolved organic carbon performed using a HiPerTOC analyzer by Thermo Elektron corporation and absorbance at 254 nm made with a spectrophotometer UV–vis Cecil 1000 by Analytical. All analyses were carried out for raw water and filtered water, i.e. MF and NF permeates.

The molecular mass distribution of NOM was made using high-performance size exclusion chromatography (HP-SEC) with DIONEX ICS-2500 chromatograph equipped with UV/VIS AD25 detector (Dionex, USA), TosoHaas TSK gel G 3000 SW_{XL} analytical column, and TosoHaas TSK gel SW protective column (by Tosoh Corporation, Japan). Chromatograms were registered at the wavelength of 254 nm. Analyses were carried out at the temperature of 30˚C and 0.01 M phosphate buffer of the flow rate 1 mL/min was used as the eluent, while the injected sample volume was equal to 75 μL.

Trihalomethanes (THM) analysis was made using a gas chromatograph Trace Ultra DSQH GC–MS by ThermoScientific. Helium was used as a carrier gas. The separation of compounds was made on the capillary column Rxi™-5 ms by Restek (the film thickness 0.5 μm; column length 30 m; internal column diameter 0.25 mm). The GC–MS analysis of volatile compounds THMs was preceded by their extraction from water samples using methyl tert-butyl ether. The temperature program set for the analysis was as follows: the initial temperature—35˚C hold for 9.5 min, the temperature jump—40˚C/min, and the final temperature—200˚C hold for 0 min.

3. Results

The basis for the evaluation of the oxidation of natural organic substances which appear in water is measurements of absorbance at 254 nm and dissolved organic carbon. The ratio of those parameters has been provided by the parameter known as SUVA, which more specifically defines changes of hydrophilicity/hydrophobicity in waters caused by the presence/absence of humic substances. It is known that when the value of SUVA exceeds 4.0 L/mg m, the main fraction of dissolved organics is of hydrophobic character, when SUVA varies around 2.0 L/mg m or more, the mixture of substances of hydrophobic and hydrophilic character can be assumed, while at SUVA, while below 2.0 L/mg m, non-humic hydrophilic substances are dominant ones.

3.1. The effectiveness of oxidation of natural organic compounds (including FA and HA) in PhMFR

The results of the studies on the treatment of simulated waters containing fulvic or humic acids are shown in Figs. 3 and 4, while in Fig. 5, the effectiveness of the process observed for SW is presented. The evaluation of the results was made on the basis of DOC, UV254, and SUVA measurements performed twice a day for 2 d for simulated water and for 4 d for SW.

The results of the studies shown in Figs. 3–5 indicated on both the efficient photooxidation of natural organic substances in the photoreactor and satisfactory separation of the photocatalyst from purified water by the microfiltration membrane. However, it was observed that the recirculation of the photocatalyst in the system reactor–membrane reactor resulted in the lower degradation rate of organic contaminants than in the case when the system with the immersed capillary module discussed in [9] was used. The analysis of the UV254 measurements indicated on the degradation of dissolved aromatic compounds by means of photocatalytic oxidation, but the rate of the decomposition depended on the character of a compound. Fulvic acids underwent the oxidation with the highest rate (Fig. 3), similarly as organic compounds present in SW (Fig. 5). The concentration of humic acids decreased with the process of elongation, but the observed degradation rate was the lowest in comparison with the ones obtained for fulvic acids and SW organic contaminants. The measurements of the content of dissolved organic carbon in treated water

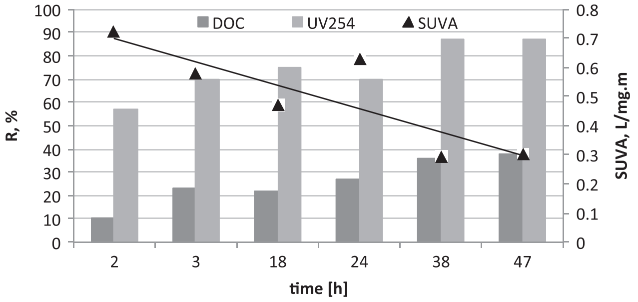

Fig. 3. The effectiveness of removal of fulvic acids, FA, from simulated water in photocatalytic microfiltration reactor, PhMFR.

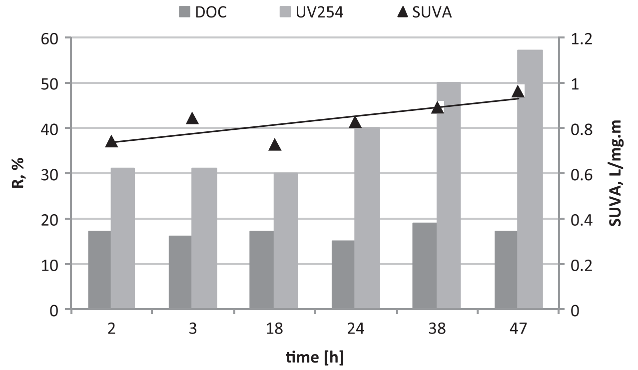

Fig. 4. The effectiveness of removal of humic acids, HA, from simulated water in photocatalytic microfiltration reactor, PhMFR.

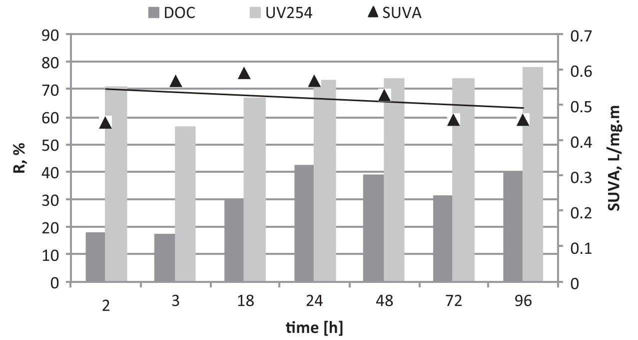

Fig. 5. The effectiveness of removal of natural organic substances from SW in PhMFR.

revealed much lower removal rates than it could be concluded from UV254 absorbance analysis in the case of each investigated water.

It confirmed the formation of by-products during the photocatalytic oxidation process, which was the most intensive in the case of humic acids decomposition. HA degradation analysis resulted in the relatively stable level of DOC in the treated water observed for 47 h with a simultaneous continuous decrease in absorbance. However, an increase in SUVA with time suggested an insufficient decrease in HA oxidation with time. A different tendency was observed for other waters, especially for one with FA, for which the values of SUVA significantly decreased.

3.2. *The effectiveness of two-stage water treatment system PhMFR–NF*

The complete separation of the photocatalyst from purified water was obtained for the membrane PhMFR. On the other hand, the maximum removal rates of compounds determined as DOC reached only 40% and ones as UV254—80% for SW and simulated water contaminated with FA, while in the case of the stream containing FA, the observed removal rates were even lower. Thus, the photocatalytic microfiltration system was combined with NF. The high-pressure-driven membrane filtration was carried out for 3 h, and after each hour, DOC, UV254, and SUVA were measured. In Fig. 6, the mean values of parameters obtained during NF process are presented; however, one must realize that particular values are negligibly differed among each other. The analysis of the obtained results showed that the impact of NF on removal of contaminants determined as DOC and UV254 in the case of HA was more significant than the one of PhMFR, while for FA contaminated simulated water and SW, the action of PhMFR was dominant. Finally, the SUVA value reached zero for the system with NF in the case of SW and the removal rates of investigated organic compounds in surface and FA contaminated water exceeded 90%. HA were the least efficiently removed; nevertheless, the final retention coefficient value reached ca. 90%.

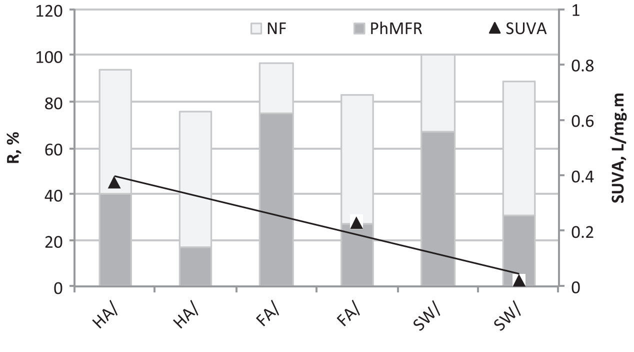

Fig. 6. The effectiveness of removal of organic compounds for investigated waters treated via two-stage system: (1) PhMFR; (2) NF.

3.3. *The analysis of reactivity and molecular mass distribution of natural organic compounds in investigated waters*

In Table 2, the results of the studies on the potential of THM formation in raw and treated waters are presented. The obtained THM levels for raw waters were in the range of 84–751 μg/L. The highest potential of THM formation was revealed by simulated water contaminated with HA, while the lowest for the stream with FA. THM potential is slightly lower than the one of simulated water with FA. The treatment process carried out in PhMFR resulted in a significant decrease in the THM content in both SW and HA water at the level of 66–69%, respectively. The use of the second treatment stage, i.e. NF caused some further decrease in THM formation potential for all investigated waters, and the observed THM removal rates were in the case of SW—56%, HA—79%, and for FA—85%.

In Table 3, the characteristics of FA containing water and SW due to the molecular mass distribution of natural organic compounds are given. The analyzed waters characterized with the similar SUVA level (Table 1), which also corresponded to similar molecular weights of organic compounds present in those waters in the range of 250–3,000 Da. The application of photocatalytic oxidation resulted in complete degradation of compounds with higher molecular weight

Table 2
Concentrations of THM in raw and treated waters

Sample\parameter		∑THM (μg/L)
Raw water	FA	84
	HA	751
	SW	127
Treated water	FA–PhMFR	n/a[a]
	HA–PhMFR	234
	SW–PhMFR	43
	FA–PhMFR–NF	15
	HA–PhMFR–NF	50
	SW–PhMFR–NF	19

[a] Below detection level.

Table 3
Molecular weight distribution ranges (MW) in raw and treated water

Sample/parameter		MW (Da)
Raw water	FA	300–3,000
	SW	250–2,000
Treated water	FA-Ph	300–700
	SW-Ph	250–840

(above 900 Da) and only 840 Da, and less particles could be found in the stream after the process.

4. Discussion

4.1. The impact of NOM photocatalytic oxidation on membrane process effectiveness

The results of the presented study show that the combination of photocatalysis and membrane separation leads to the production of stable quality pure water and prevents the formation of disinfection byproducts, especially after NF. Such a configuration of the technological water treatment system enables also the limitation of membrane fouling caused by NOM, which has already been discussed in many scientific papers [8,10,11]. The photocatalysis can be successfully applied as a preliminary water treatment method before its further purification, but it can also be placed after a conventional water treatment, e.g. after coagulation. Uyguner et al. [12] have performed the studies on photocatalytic water treatment before and after coagulation. They found out that the system with photocatalytic pretreatment was less efficient by 15% in comparison with one with preliminary coagulation. The discussed studies also showed that the use of preliminary treatment before the photocatalysis was advantageous. Nevertheless, the use of NF as a polishing step was found to be more favored as the obtained retention coefficients of contaminants were very high (above 90%). Moreover, the capacity of both membranes, i.e. microfiltration and NF ones, was stable, despite operating long hours in the case of MF. Another benefit of the presented system is that no side stream or waste was generated.

4.2. The change of NOM properties during photocatalysis process

During the photocatalytic oxidation of natural organic compounds, the change of the structure of particular NOM components can be observed. This phenomenon may have a significant impact on the process that is used after the photocatalytic treatment. TiO_2–UV system is very effective for removal of high molecular weight, hydrophobic organic compounds, which is also confirmed in these studies (Table 3). Organic compounds of higher molecular weight are decomposed to structures of lower masses. Thus, at a certain stage of the oxidation, an increase in low molecular weight compounds concentration regarding their initial content in a raw water may be observed. The authors of [13,14] found out that mineralization of NOM and change of their physic-chemical features made it possible to control and limit the phenomenon of membrane fouling. Hence, it is said that the use of the photocatalytic oxidation before membrane filtration is a sufficient method of membrane blockage minimization and its control. Nevertheless, there are some studies, e.g. [15], in which the opposite tendency is suggested.

5. Conclusions

(1) Photocatalytic oxidation of NOM depends on the type of contaminant present in water. Fulvic acids were found to be favorably decomposed, while humic acids were removed to a lower extent. The oxidation rate of the mixture of organic substances present in SW was within the range observed for fulvic and humic acids.
(2) Particular components of NOM are removed during photocatalysis or NF, while microfiltration acts only as a separation method of the photocatalyst from purified water.
(3) The use of combined PhMFR–NF system results in a significant decrease in disinfection by-products formation potential, and it depends on the type of NOM component.
(4) Photocatalysis leads to a change in organic compound structures, during which low molecular weight compounds of hydrophilic properties (SUVA <2.0 L/mg m) remain in water and do not cause membrane fouling.
(5) The use of NF as a polishing step of the stream purified via PhMFR is beneficial as it results in producing water characterized by high quality and purity.

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