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Removal of halogenated by-products precursors in photocatalysis process enhanced with membrane filtration

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ABSTRACT

In the article, the results of the research on removal of halogenated by-products precursors in a photocatalysis (PC) process enhanced with membrane filtration have been presented. In the research, the following by-products were analyzed as follows: trihalomethanes (trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane), haloacetic acids (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, bromochloroacetic acid, dibromoacetic acid, trichloroacetic acid), haloacetonitriles (bromochloroacetonitrile, dibromoacetonitrile, dichloroacetonitrile, trichloroacetonitrile), haloketones (1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone), chloropicrin, and chloral hydrate. The analyses were conducted on the model solutions of humic and fulvic acids and also on the samples of surface water taken from the Goczalkowice Reservoir. These water samples were treated in a sequence of PC and membrane filtration. The PC process was conducted using TiO_2 and low-pressure monochromatic UV lamps. The samples of untreated water and the one obtained as a result of those processes were chlorinated with sodium hypochlorite in a dose which resulted in 3–5 mg/L of free chlorine after 24 h. After that time, the formed chlorination by-products were analyzed with gas chromatography, and the formation potential was calculated for each considered group of halogenated organic compounds.

Keywords: Photocatalysis; Membrane filtration; Halogenated by-products; Disinfection by-products formation potential

1. Introduction

Natural organic matter (NOM) is a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, hydroxyl, ketone, and other minor functional groups [1]. NOM is converted from dead animals and plants in the process of decomposition, and its major fraction presented in surface or drinking water is composed of humic substances (humic and fulvic acids) [2,3]. During

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conventional water treatment processes, such as coagulation, sand filtration, activated carbon adsorption, ion exchange, NOM is not completely removed from water. These processes remove mostly hydrophobic fractions of NOM [4,5]. Hydrophilic compounds are much more difficult to remove, and they remain in water after its treatment. During commonly performed chlorination, they can become the precursors of the formation of potentially harmful disinfection by-products (DBPs), among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the major groups [6–12].

Advanced oxidation processes (AOP) can be used to remove NOM from water, and they are an alternative to the conventional treatment technology [13–17]. AOP have been shown to break down a wide range of NOM compounds [4]. One example of AOP is a photocatalysis (PC), using TiO_2 as a catalyst, usually combined with membrane filtration to separate and recover TiO_2 after the main PC reaction [2,3,5,15,17,18]. During AOP, hydroxyl radicals (OH^*) are generated, which are considered to react quickly and non-selectively with NOM compounds [19]. However, several scientific reports have proved that amino acid L-leucine is significantly more reactive with chlorine after PC than other examined compounds (amino acids, carbohydrates, phenolic compounds) [4]. Tercero Espinoza and Frimmel [20] also investigated the selectivity of PC oxidation of NOM and found out that this selectivity is most likely caused by the adsorption onto TiO_2 surface. The large aromatic and long-chain aliphatic molecules are degraded in PC reaction into smaller molecular weight compounds, which are more hydrophilic in nature, but short-chain aldehydes and ketones are identified as degradation products [16,21,22]. After the PC process, low-molecular acids and neutral compounds remain in water [23].

NOM is a complex mixture, with a complicated structure, composition and chemical characteristics. Most photocatalytic studies of NOM focus on measuring dissolved organic carbon (DOC) concentration and UV absorbance at 254 nm (UV_{254}) or specific absorbance at 254 nm ($SUVA_{254}$). Assessing removal of DBPs precursors, the most suitable method to characterize NOM seems to be the normalized (per DOC) DBPs formation potential (FP). There are only a few publications on the changes of DBPs FP after the PC process. These publications consider mostly carbonous DBPs (C-DBPs) from THMs and HAAs groups. In some of these publications, the THMs FP decrease after the PC process has been reported [18,21,22,24–26]. In the research conducted by Liu et al. [21], HAAs FP did not change—due to the presence of hydrophilic precursor compounds, which were formed as a result of the PC oxidation process. Mori et al. [18] observed HAAs FP decrease after the PC process of swamp water. In the research conducted on raw surface water, Beckbolet et al. [26] found out that after the PC process, the formation of trichloroacetic acid was enhanced. For other C-DBPs, such as haloketones (HKs) or chloral hydrate (CH), the FP after the PC treatment has not been studied.

The important issue connected with the NOM reactivity after oxidation processes is a change in the share of brominated DBPs (Br-DBPs) in the total concentration of DBPs. Bromide ions are more reactive with hydrophilic and low-molecular-weight organic precursors than their hydrophobic and high-molecular-weight counterparts [27,28]. There are no publications, which would analyze the changes in Br-DBPs concentration after the PC reaction. However, the experiments showed higher concentration of brominated species in water treated with chlorination and UV irradiation in comparison with water, which was only chlorinated [27,28].

There is also a shortage of publications, which would discuss the changes of the FP of DBPs consisting nitrogen (N-DBPs) after the PC process, while organic nitrogen compounds commonly presented in source water, can cause the formation of N-DBPs [29]. This issue was only reported by Bekbolet et al. [26] in the research on Instabul surface water. The investigation showed that the PC process can increase the concentration of some haloacetonitriles (HANs)—dichloroacetonitrile, dibromoacetonitrile, and bromochloroacetonitrile [26]. During UV irradiation, the photolysis of $–NO_3^-$ generates reactive nitrogen species ($-NO_2^*$) and causes the nitration of NOM. Chlorination of nitrated NOM can form N-DBPs, especially trichloronitromethane—chloropicrin (CP) [27,30].

In this paper, the influence of PC-membrane filtration treatment on DBPs formation potential is examined. The experiments were conducted for several water chlorination by-products, such as THMs—trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM); HAAs—monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA); HANs—trichloroacetonitryle (TCA), dichloroacetonitryle (DCA), bromochloroacetonitryle (BCA), dibromoacetonitryle (DBA); HKs—1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP); CH and CP.

2. Materials and methods

2.1. Samples

The experiments were conducted on three kinds of water: (1) a model solution with humic acids (HAs); (2) a model solution with fulvic acids (FAs); (3) surface water taken from the Goczalkowice Reservoir (GR). Their characteristics are presented in Table 1. FAs used in the research were produced by Beijing Multigrass Formulation Co. Ltd. (China) and HAs by Sigma-Aldrich (Germany).

2.2. PC process

The research on the efficiency of photocatalysis-microfiltration (PK-MF) and photocatalysis-ultrafiltration (PK-UF) processes was conducted in photocatalytic membrane reactor (PMR) of volume 20 L with the monochromatic lamp emitting UV 254 nm installed in it. PMR worked in two configurations of membrane filtration. In the first one, the external capillary microfiltration (MF) module (Microza) was used. That module worked with overpressure, used membranes of the nominal pore size 0.1 μm, and made of polyvinylidene fluoride (PVDF). The dose of catalyst TiO_2 was 0.1 g/L. The sequence of 30-min irradiation/30-min without irradiation and continuous membrane filtration was realized. The configuration was used to all considered water samples (HAs, FAs, GR). To describe the samples treated in the configuration with external MF filtration, the following abbreviations are used as follows: HA-MF, FA-MF, and GR-MF.

In the second configuration, the immersed capillary ultrafiltration (UF) module by ZeeWeed installed inside PMR was used. It worked with underpressure and used membranes made of PVDF; their nominal pore size was 25 kDa. The dose of catalyst TiO_2 was 0.2 g/L. The 30-min irradiation of raw water was conducted, after which the 60-min membrane filtration was realized. The second configuration was used only for GR sample. GR-UF is the abbreviation used to describe the sample treated in this configuration.

2.3. Chlorination

Twenty-four-hour chlorination test was carried out to examine the DBPs FP. Water samples were chlorinated using chlorine water (NaClO), with a free chlorine dosage that would result in a residual free chlorine 3–5 mg/L after 24 h. All samples were adjusted to pH = 7 by adding sulfuric acid or sodium hydroxide and phosphate buffer. The chlorinated water samples were incubated at 25 ± 2℃ in amber bottles with PTFE liners. After 24 h, those samples were dechlorinated and DBPs were analyzed.

2.4. Analytical methods

The DBPs concentrations were analyzed using a gas chromatograph with a Trace Ultra DSQII GC-MS mass spectrometer (Thermo Scientific). Helium was used as carrier gas. The Rxi^{TM}-5 ms capillary column (Restek) was used (film thickness 0.5 μm, column length 30 m, column diameter 0.25 mm). The THMs, HANs, HKs, CH, and CP were extracted using the liquid–liquid extraction method with MTBE (methyl tert-butyl ether). The column was heated from 35℃ (9.5 min) to 200℃ (0 min) with the temperature increase rate 40℃/min. The method detection limit was 0.01 μg/L. The HAAs concentrations were analyzed using acidic methanol esterification method [30]. The HAAs were extracted using the liquid–liquid

Table 1
Water quality parameters of raw water and water after photocatalysis-microfiltration treatment

		Concentration levels						
		Raw water			PC treated water			
Parameter	Unit	HAs	FAs	GR	HA-MF	FA-MF	GR-MF	GR-UF
Br^-	mg/L	0.45	0.49	0.29	0.45	0.48	Nd	0.30
NH_4–N	mg/L	0.43	0.14	nd	0.44	0.09	0.24	nd
NO_3–N	mg/L	1.695	1.621	0.701	1.538	1.221	0.194	0.773
NO_2–N	mg/L	nd	nd	nd	nd	nd	0.040	nd
DOC	mg/L	10.05	11.66	6.18	7.79	8.33	4.20	1.96
DON	mg/L	0.36	0.65	2.34	0.39	0.89	2.19	1.77
UV_{254}	cm^{-1}	0.178	0.178	0.088	0.019	0.059	0.021	0.006
$SUVA_{254}$	$L\,mg^{-1}\,m^{-1}$	17.692	15.249	14.239	7.094	7.131	5.000	2.857

Note: nd—not detected.

extraction method with MTBE (methyl tert-butyl ether). In this case 0.9 mL of the extract was transferred into a 15-cm^3 amber vial, then 2 mL of a solution of sulfuric acid in methanol (10%) was added and the vial was placed in water bath at 50˚C for 1 h. After that time, the vial was cooled in 4˚C for 10 min and 5 mL copper (II) sulfate pentahydrate and anhydrous sodium sulfate solution (50 g/L and 100 g/L, respectively) were added. The vial was shaken for 2 min and kept motionless for about 5 min. The upper layer was used for an injection into GC. The column was heated from 40˚C (0 min) to 100˚C (5 min) with the temperature increase rate 40˚C/min, then to 200˚C (0 min) with the temperature increase rate 8˚C/min. The method detection limit was 0.5 μg/L for MCAA and MBAA, 0.01 μg/L for other HAAs.

Free chlorine was analyzed using the DPD (N,N-diethylphenylendiamine) method (according to Polish Standard PN-ISO 7,393-2). The free chlorine concentration was measured using the Aurius 2021 UV–vis spectrophotometer (Cecil Instruments). The detection limit of the method was 0.03 mg/L. UV_{254} absorbance was analyzed in photometric cuvettes (5-cm length) with the Aurius 2021 UV–vis spectrophotometer (Cecil Instruments). DOC was analyzed using HiPerTOC analyzer (Thermo Scientific). The method detection limit was 0.01 mg/L. The total nitrogen (TN) and NH_4–N were analyzed using Nanocolor tests and the Aurius 2021 UV–vis spectrophotometer. The detection limits was 0.1 mg/L for TN and 0.01 mg/L for NH_4–N. The other nitrogen compounds and bromide ions were analyzed using ion chromatograph 883 Basic IC plus (Metrohm). The detection limits for the NO_2–N and NO_3–N were 0.001 mg/L and for bromide ions—0.01 mg/L. The dissolved organic nitrogen (DON) concentration was calculated as a difference of TN and inorganic nitrogen (NH_4–N, NO_2–N, NO_3–N).

3. Results and discussion

The results for raw water and water after PK-MF/PK-UF treatment have been shown in Table 1. The results of the concentration of DBPs after 24-h chlorination test have been shown in Table 2. The discussion on the results has been presented below.

3.1 FP of C-DBPs

Four THMs and six HAAs were analyzed. The results of experiments on the THMs (sum of TCM, BDCM, DBCM, and TBM) formation potential (THMFP) by a mass unit of DOC and on the HAAs (sum of MCAA, MBAA, DCAA, TCAA, BCAA, and DBAA) formation potential (HAAFP) have been presented in Fig. 1. The results of research on the haloketones (sum of 1,1,1-TCP and 1,1-DCP) formation potential (HKFP) and on chloral hydrate formation potential (CHFP) have been presented in Fig. 2.

THMFP was between 7.16 and 74.76 μg/mg DOC. The highest value of THMFP was observed in the result of chlorination of HAs sample before treatment (74.76 μg/mg DOC) and for GR sample also before treatment (20.50 μg/mg DOC). After the PC process, THMFP decreased for the samples HA-MF, GR-MF, and GR-UF. The only exception was FA-MF sample, for which THMFP increased by 5.01 μg/mg DOC. The significant differences in THMFP values for HAs sample before and after PC-MF treatment can be caused by big changes in TCM concentration after the chlorination of samples treated with PC. TCM concentration after the PC process decreased by 84%, such big changes were not observed for other samples. A higher value of THMFP after PC-UF treatment can be caused by a higher dose of TiO_2. Higher TiO_2 concentration, despite greater DOC removal, can increase THMFP [31].

Other authors [15,16,21] also observed some decrease in specific THMFP in natural waters and model solutions of HAs in a result of PC treatment. The lower ability to form THMs is explained by the fact that organic moieties which form THMs are susceptible to photocatalytic treatment [21]. Large aromatic and long aliphatic chain organic structures were transformed into small and hydrophilic organics during the PC process [16]. THMs precursors are mostly hydrophobic fractions of NOM, a PC process attributed to the increase in hydrophilic ones [15,16].

DBPs formation by FAs after PC oxidation has not been examined by other authors yet. The increase in the specific THMFP for FAs after PC treatment is difficult to interpret. One of possible explanations is that FAs are less susceptible than HAs to form hydrophilic fraction in the effect of PC decomposition. As it can be observed from the results of $SUVA_{254}$ in Table 1, PC treatment of FAs resulted in compounds of more hydrophobic character, aromatic and high-molecular-weight fractions of NOM than in a case of HAs. Such by-products are more susceptible to THMs formation. To explain this phenomena entirely, it would be necessary to conduct complex research on changes of FAs fraction after PC oxidation, and especially on NOM degradation patterns and dynamics.

HAAFP increased as a result of PC treatment: for FA-MF sample by 4.57 μg/mg DOC, for GR-MF—7,83 μg/mg DOC, and for GR-UF—10,87 μg/mg DOC. For HA-MF sample, the relatively high HAAFP

Table 2
Concentration of DBPs in raw and treated water

		Concentration levels						
		Raw water			PC treated water			
Parameter	Unit	HAs	FAs	GR	HA-MF	FA-MF	GR-MF	GR-UF
TCM	µg/L	584.85	55.11	115.39	91.96	43.82	38.15	18.15
BDCM	µg/L	147.60	21.54	10.64	90.00	36.74	4.45	5.94
DBCM	µg/L	18.02	6.55	0.60	48.56	18.80	0.68	1.68
TBM	µg/L	0.84	0.34	0.03	3.65	2.05	0.03	0.10
ΣTHM	µg/L	*751.30*	*83.54*	*126.66*	*234.17*	*101.40*	*43.30*	*25.88*
MCAA	µg/L	16.99	16.27	6.58	38.05	8.81	6.93	14.17
MBAA	µg/L	5.93	5.51	14.18	6.27	10.07	26.04	23.75
DCAA	µg/L	281.14	35.10	39.53	2.79	35.13	45.18	9.00
TCAA	µg/L	341.00	26.80	36.41	36.77	29.66	16.69	4.09
BCAA	µg/L	23.99	11.89	2.46	11.61	16.83	4.74	1.14
DBAA	µg/L	1.70	2.40	0.23	3.87	7.55	0.84	0.69
ΣHAA	µg/L	*670.74*	*97.96*	*99.40*	*99.36*	*108.05*	*100.43*	*52.83*
TCAN	µg/L	0.36	0.04	0.03	0.25	0.03	0.04	0.03
DCAN	µg/L	45.47	6.74	6.70	6.54	5.16	4.00	1.94
BCAN	µg/L	4.25	3.05	1.86	5.53	7.11	1.44	1.55
DBAN	µg/L	0.65	0.25	0.24	1.23	1.44	0.28	0.30
ΣHAN	µg/L	*50.73*	*10.07*	*8.83*	*13.55*	*13.73*	*5.77*	*3.82*
1,1-DCP	µg/L	0.71	1.24	0.88	1.05	1.21	0.84	0.89
1,1,1-TCP	µg/L	24.92	6.05	3.85	10.28	6.19	6.23	1.18
ΣHK	µg/L	*25.63*	*7.29*	*4.73*	*11.33*	*7.41*	*7.07*	*2.07*
CH	µg/L	25.74	10.97	19.60	17.51	24.13	8.91	4.16
CP	µg/L	1.38	1.11	1.85	1.07	1.10	1.00	0.78

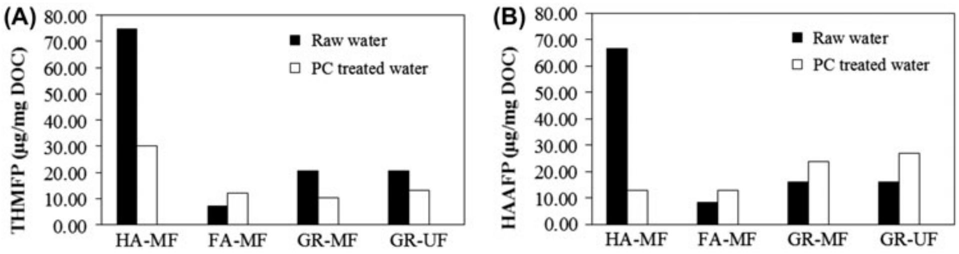

Fig. 1. THMs and HAAs formation potential: (A) THMFP per DOC and (B) HAAFP per DOC.

increase was observed after PC-MF treatment—from 66.74 to 12.75 µg/mg DOC. In this sample, significant (close to 90%) decrease in TCAA concentration was observed after the PC process (Table 2)—from 341.00 to 36.77 µg/L, and 99% decrease in DCAA (from 281.14 to 2.79 µg/L). These two factors could cause the HAAFP decrease in this sample. Despite the decrease in DOC concentration in all samples after PC treatment (Table 1), the increase in HAAs concentration in some samples was observed (Table 2): MCAA in HA-MF and GR-UF samples, MBAA in all samples, DCAA in GR-MF sample, TCAA in FA-MF sample, BCAA in FA-MF and GR-MF samples, and DBAA in all samples. In a literature, there are reports on a possible increase in TCAA concentration after PC process [26].

The increase in the specific HAAFP can be explained by the increase in hydrophilic substituents in an effect of PC oxidation process [16,21]. After UV irradiation, more carboxyl and carbonyl carbon atoms appeared, which create low-molecular-weight carboxylic acids—the major precursors of HAAs [32]. The decrease in HAAFP observed for PC treatment of HAs can be caused by different reactivities of organic compounds from Sigma-Aldrich HAs and other studied waters on the co-exposure of PC oxidation and chlorination. Analogous lower reactivities of HAs in model solutions in comparison with natural waters were also reported by Liu et al. [32]. The main HAAs precursors are hydrophilic fractions; however, HAAs precursors can also be hydrophobic fractions [15], especially in the case of TCAA [16]. Observing the results in Table 2 for model water with HAs—TCAA was one of the main formed HAAs, analogously as for THMs, the increase in hydrophilic fractions concentration after PC treatment occurred together with the decrease in formation of TCAA and HAAs.

HKFP (Fig. 2(A)) was between 0.62 μg/mg DOC for FAs sample before treatment and 2.55 μg/mg DOC for HAs sample before PC treatment. For compounds from HKs group, for all water samples except HAs, HKFP increase was observed after PC treatment—by 0.26 μg/mg DOC for FAs sample, 0.92 μg/mg DOC for GR-MF, and 0.29 μg/mg DOC for GR-UF. For HAs sample, the decrease in HKs formed by DOC unit was observed (by 1.10 μg/mg DOC). After UV irradiation more hydrophilic fractions appeared, including low-molecular-weight acetones, ketones, and keto acids [21,32]—it is a reason why the increase in specific HKFP can be also observed. The intermediate products of FAs chlorination can cause the HKs formation [33], which explains the increase in HKPT after PC treatment of FAs. However, NOM from surface water can also be decomposed to the potential HKs precursors. Similar as in the case of THMs and HAAs, the decrease in HKFP after PC treatment of Sigma-Aldrich humic acids can be explained by the lower susceptibility of model HAs on decomposition to compounds of lower molecular weight [16,21,32].

In the case of CH (Fig. 2(B)), the increase in CHFP after PC treatment was observed only for FAs sample (by 1.96 μg/mg DOC). For this sample, the CH concentration increase after PC-MF treatment was observed—from 10.97 to 24.13 μg/L. For other samples such a phenomenon was not observed. The highest value of CHFP was observed for raw GR water (3.17 μg/mg DOC) and the lowest value—for FAs sample before PC treatment (0.94 μg/mg DOC). One of the effects of UV treatment can be the decomposition of the high-molecular-weight organic matter to smaller organic compounds, such as aldehydes—the main CH precursors [32]. The potential of NOM to form CH has been increased only in the case of PC oxidation of FAs, which probably indicates that aldehydes or acetaldehydes are mainly formed in this process.

3.2. FP of N-DBPs

Due to the presence of carbon and nitrogen atoms in the molecules of HANs and halonitromethanes, haloacetonitriles (sum of TCA, DCA, BCA, and DBA) formation potential (HANFP) was analyzed in regard to the organic carbon content in a sample and to the organic nitrogen and chloropicrin FP in regard to organic carbon content and nitrogen one (Figs. 3 and 4).

HANFP was between 0.86 and 5.05 μg/mg DOC, and between 2.63 and 140.92 μg/mg DON. The highest HANFP was observed for HAs sample both in raw water and in PC-MF treated water. The increase in HANFP (in a relation to DOC) after the PC process was observed only for FAs sample (by 0.79 μg/mg DOC) and for GR-UF one (0.52 μg/mg DOC). The similar relations were observed for CPFP per DOC. For FAs sample, CPFP increased by 0.03 μg/mg DOC after PC-MF treatment, while for GR-UF sample—by 0.10 μg/mg DOC. Both for HANs and CP, the FP per 1 mg of DON was higher after the PC process for each analyzed sample. For CP, the highest FP was observed for GR-UF sample after treatment (0.40 μg/mg DOC) and for HAs sample in raw water (3.83 μg/mg DON).

For some water samples, the increase in HANs concentration was observed after the 24-h chlorination test for water treated with PC (Table 2): in HAs sample for DBAN, in FAs sample—BCAN and DBAN, in GR sample—DBAN (minor increase). Whereas, in the reports of other authors [26], the PC process increased the concentration of DCAN, DBAN, and BCAN.

The organic compounds containing nitrogen are perceived as the main precursors of HANs and CP

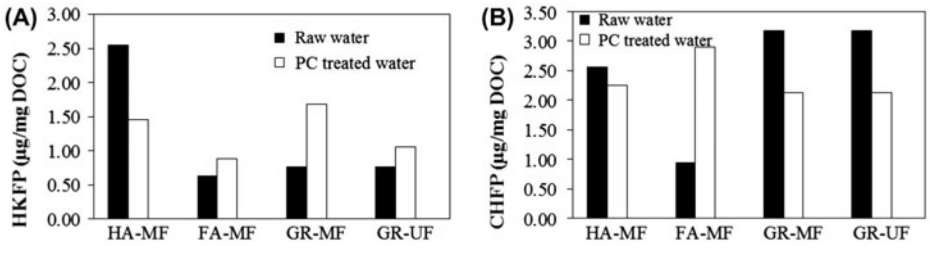

Fig. 2. Haloketones and chloral hydrate formation potential: (A) HKFP per DOC and (B) CHFP per DOC.

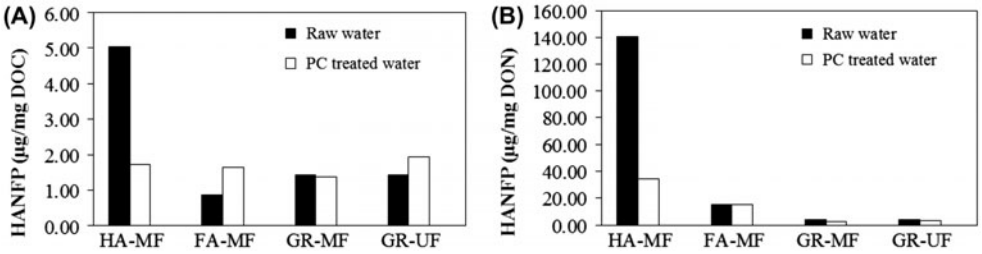

Fig. 3. Haloacetonitriles formation potential: (A) HANFP per DOC and (B) HANFP per DON.

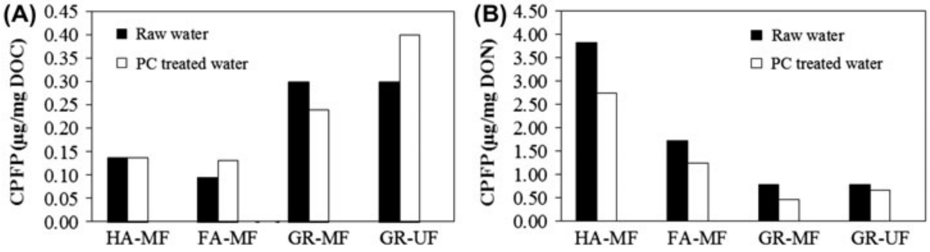

Fig. 4. Chloropicrin formation potential: (A) CPFP per DOC and (B) CPFP per DON.

[34,35]. Several research reports confirmed that hydrophilic fractions of NOM cause the high concentration of N-DBPs, while hydrophobic ones—the low one [36,37]. In the authors' opinion, the increase in potential formation of N-DBPs after PC treatment can be influenced by the increase in NOM hydrophilicity and/or NOM nitration [27,30]. As it can be observed in Table 1, PC oxidation resulted in increase in organic nitrogen in the samples of model water with HAs and FAs, respectively, by 0.03 mg/L and 0.24 mg/L. In the sample of water with FAs after PC process for both HANs and CP, the increase in FP for N-DBPs (per DOC) has been observed. In a case of HAs after PC oxidation process, virtually in all cases (for HANFP per DOC and DON, for CPFP per DON) the decrease in FP for N-DBPs has been observed. In this case, similarly as for C-DBPs, this phenomena can be explained by the low reactivity of the model HAs solution. For samples GR-MF and GR-UF, it can be observed that the increase in TiO_2 dose can cause the changes in a distribution of the precursors of HANs and CP. Although DON decreased in these samples after PC treatment (Table 1), HANs and CP formation increased for GR-UF, which is probably caused by the increase in NOM hydrophilicity, corresponding to the values of $SUVA_{254}$ for these samples (Table 1).

3.3. Formation of brominated DBPs

The bromine incorporation factor (BIF) describes the molar contribution of the brominated DBPs and is a measure of the DBPs portion that is partially or totally brominated [38]. The equations to calculate BIF for THMs, HAAs, dihaloacetic acids (DHAAs), HANs, and dihalocetonitriles (DHANs) are following [39,40]:

$$\mathrm{BIF-THM} = \frac{[\mathrm{BDCM}] + 2\ [\mathrm{DBCM}] + 3\ [\mathrm{TBM}]}{3\ ([\mathrm{TCM}] + [\mathrm{BDCM}] + [\mathrm{DBCM}] + [\mathrm{TBM}])} \tag{1}$$

$$\mathrm{BIF-HAA} = \frac{[\mathrm{MBAA}] + [\mathrm{BCAA}] + 2\ [\mathrm{DBAA}]}{2\ ([\mathrm{MCAA}] + [\mathrm{MBAA}] + [\mathrm{DCAA}] + [\mathrm{BCAA}] + [\mathrm{DBAA}] + [\mathrm{TCAA}])} \tag{2}$$

$$\mathrm{BIF-DHAA} = \frac{[\mathrm{BCAA}] + 2\ [\mathrm{DBAA}]}{2\ ([\mathrm{DCAA}] + [\mathrm{BCAA}] + [\mathrm{DBAA}])} \tag{3}$$

$$\mathrm{BIF-HAN} = \frac{[\mathrm{BCAN}] + 2\,[\mathrm{DBAN}]}{2\,([\mathrm{TCAN}] + [\mathrm{DCAN}] + [\mathrm{BCAN}] + [\mathrm{DBAN}])} \quad (4)$$

$$\mathrm{BIF-DHAN} = \frac{[\mathrm{BCAN}] + 2\,[\mathrm{DBAN}]}{2\,([\mathrm{DCAN}] + [\mathrm{BCAN}] + [\mathrm{DBAN}])} \quad (5)$$

The molar concentration of individual DBPs should be used in the above Eqs. (1–5). The values of BIF factor are in a range from 0 (no brominated species) to 1 (totally brominated, for example, pure TBM for THMs, pure DBAA for HAAs, and pure DBAN for HANs). BIF values for THMs and HANs are presented in Fig. 5, for HAAs and DHAAs in Fig. 6. For all considered groups, the ratio of brominated species was higher after PK treatment. In a case of THMs, the highest increase in BIF was observed for HAs sample (from 0.06 to 0.22) and FAs one (from 0.10 to 0.21). For GR, the highest BIF increase was observed in the sample after UF treatment (by 0.07), while it was only 0.01 for GR sample treated with PC-MF.

The similar relations were observed for HANs. In the case of compounds from this group, BIF increased by 0.19 in the case of chlorination of HAs sample treated with PC-MF (in comparison with chlorinated raw water) and by 0.17 in an case of FAs and only by 0.03 for GR-MF sample. For GR-UF sample, the relatively high increase in BIF was observed (0.12). Due to a low share of TCAN in the sum of all HANs, BIF for DHANs was very similar to BIF for HANs for all analyzed samples.

A different situation was noticed for BIF values in the case of HAAs and DHAAs. The increase in BIF-HAA after PC-MF treatment was observed (0.07 for all samples) and for GR-UF as well (0.13). In the case of DHAAs, a very high increase (0.45) in BIF was observed for HA-MF sample, while it was only 0.08 for FA-MF sample, 0.02 for GR-MF sample, and 0.06 for GR-UF one.

Although the concentration of brominated DBPs usually depends on the bromide concentration in water, the higher values of BIF after PC-MF treatment do not correspond to the higher concentration of bromide ions in samples (Table 1). Thus, the higher share of brominated DBPs was probably caused by changes in quality of organic matter after the PC process. Bromide ions are more reactive with hydrophilic and low-molecular-weight organic precursors than with their hydrophobic and high-molecular-weight counterparts [27,28], which can result in forming higher amount of bromine-containing DBPs after PC treatment. Moreover, higher concentration of TiO_2 used in PC configuration with UF can cause an increase in BIF in GR-UF sample in comparison with GR-MF one.

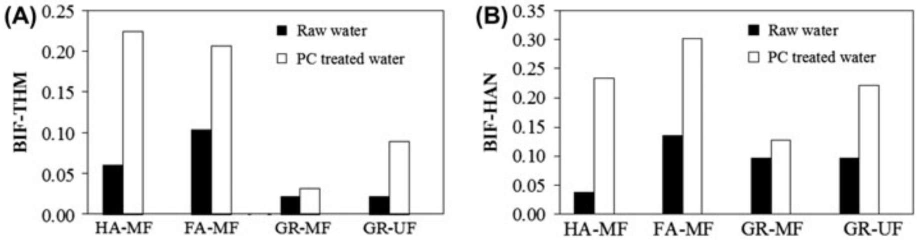

Fig. 5. Bromine incorporation factor (BIF): (A) for THMs and (B) for HANs.

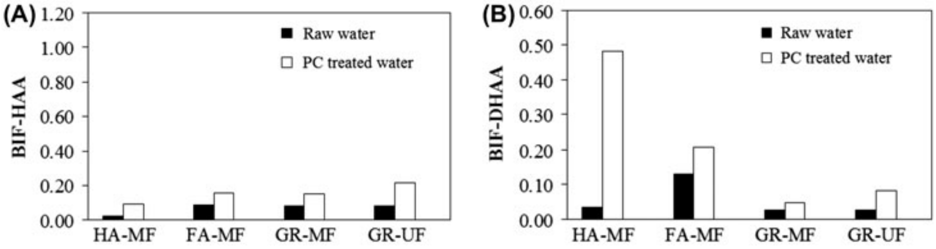

Fig. 6. Bromine incorporation factor (BIF): (A) for HAAs and (B) for DHAAs.

4. Conclusions

As the results of the experiment have provided, the photocatalytic process enhanced with membrane filtration can influence the FP of the DBPs. The FP values for several DBPs have been analyzed for model samples with humic and fulvic acids and for surface water from Goczalkowice Reservoir, which was additionally treated in the PMR. The results of these analyses allowed to form the following conclusions:

- For compounds from THMs group and CH, the decrease in their FP has been observed for all samples, except one with fulvic acids.
- The FP of HAAs and HKs increased after the PC process, the relationship was not observed only for the sample with humic acids.
- The increase in FP of nitrogen containing DBPs per mg DON has not been observed.
- Despite the decrease in DOC concentration, which was observed in water samples after treatment, the increase in FP for HANs and CP (per mg DOC) was observed in the sample of model water with fulvic acids after PC treatment and in the sample of surface water after the treatment in PMR.
- The share of brominated DBPs increased in all samples of water treated in the PC process, the share was higher in the case of the treatment in the PMR, in which the higher doses of TiO_2 was applied.

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References

[1] J. Leenheer, J.-P. Croué, Peer reviewed: Aquatic organic matter, Environ. Sci. Technol. 37(1) (2003) 18A–26A.

[2] H. Song, J. Shao, Y. He, B. Liu, X. Zhong, Natural organic matter removal and flux decline with PEG-TiO_2-doped PVDF membranes by integration of ultrafiltration with photocatalysis, J. Membr. Sci. 405–406 (2012) 48–56.

[3] E. Erdim, E. Soyer, S. Tasiyici, I. Koyuncu, Hybrid photocatalysis/submerged microfiltration membrane system for drinking water treatment, Desalin. Water Treat. 9 (2009) 165–174.

[4] K. Philippe, C. Hans, J. MacAdam, B. Jefferson, J. Hart, S. Parsons, Photocatalytic oxidation of natural organic matter surrogates and the impact on trihalomethane formation potential, Chemosphere 81 (2010) 1509–1516.

[5] K. Choo, R. Tao, M. Kim, Use of a photocatalytic membrane reactor for the removal of natural organic matter in water: Effect of photoinduced desorption and ferrihydrite adsorption, J. Membr. Sci. 322 (2008) 368–374.

[6] C. Jung, H. Son, The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water, Korean J. Chem. Eng. 25 (4) (2008) 714–720.

[7] Q. Wei, D. Wang, Q. Wei, C. Qiao, B. Shi, H. Tang, Size and resin fractionations of dissolved organic matter and trihalomethane precursors from four typical source waters in China, Environ. Monit. Assess. 141 (2008) 347–357.

[8] F. Rosario-Ortiz, S. Snyder, I. Suffet, Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries, Water Res. 41 (2007) 4115–4128.

[9] J. Kim, Y. Chung, D. Shin, M. Kim, Y. Lee, Y. Lim, D. Lee, Chlorination by-products in surface water treatment process, Desalination 151 (2002) 1–9.

[10] R. Sadiq, M. Rodriguez, Disinfection by-products (DBPs) in drinking water and predective models for their occurrence: A review, Sci. Total Environ. 321 (2004) 21–46.

[11] U.S. EPA, Edition of the Drinking Water Standards and Health Advisories. U.S. Environmental Protection Agency, Washington, DC, 2011.

[12] S. Sciacca, G. Conti, Mutagens and carcinogens in drinking water, Mediterr. J. Nutr. Metab. 2 (2009) 157–162.

[13] S. Ahmed, M. Rasul, W. Martens, R. Brown, M. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, Desalination 261 (2010) 3–18.

[14] S. Patsios, V. Sarasidis, A. Karabelas, A hybrid photocatalysis-ultrafiltration continuous for humic acids degradation, Sep. Purif. Technol. 104 (2013) 333–341.

[15] F. Kent, K. Montreuil, R. Brookman, R. Sanderson, J. Dahn, G. Gagnon, Photocatalytic oxidation of DBP precursors using UV with suspended and fixed TiO_2, Water Res. 45 (2011) 6173–6180.

[16] A. Li, X. Zhao, H. Liu, J. Qu, Characteristic transformation of humic acid during photoelectrocatalysis process and its subsequent disinfection byproduct formation potential, Water Res. 45 (2011) 6131–6140.

[17] P. Yao, K. Choo, M. Kim, A hybridized photocatalysis-microfiltration system with iron oxide-coated membranes for the removal of natural organic matter in water treatment: Effects of iron oxide layers and colloids, Water Res. 43 (2009) 4238–4248.

[18] M. Mori, T. Sugita, A. Mase, T. Funatogawa, M. Kikuchi, K. Aizawa, S. Kato, Y. Saito, T. Ito, H. Itabashi, Photodecomposition of humic acid and natural organic matter in swamp water using TiO_2-coated ceramic foam filter: Potential for the formation of disinfection byproducts, Chemosphere 90 (2013) 1359–1365.

[19] T. Bond, E. Goslan, S. Parsons, B. Jefferson, Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX and nanofiltration, Water Res. 44 (2010) 1645–1653.

[20] L. Tercero Espinoza, F. Frommel, Formation of brominated products in irradiated titanium dioxide suspensions containing bromide and dissolved organic carbon, Water Res. 42 (2008) 1778–1784.

[21] S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas, R. Amal, TiO_2 photocatalysis of natural organic matter in surface water: Impact on trihalomethane and haloacetic acid formation potential, Environ. Sci. Technol. 42 (16) (2008) 6218–6223.

[22] S. Liu, M. Lim, R. Fabris, C. Chow, K. Chiang, M. Drikas, R. Amal, Removal of humic acid using TiO_2 photocatalytic process – Fractionation and molecular weight characterization studies, Chemosphere 72 (2008) 263–271.

[23] S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas, G. Korshin, R. Amal, Multi-wavelength spectroscopic and chromatography study on the photocatalytic oxidation of natural organic matter, Water Res. 44 (2010) 2525–2532.

[24] D. Gerrity, B. Mayer, H. Ryu, J. Crittenden, M. Abbaszadegan, A comparison of pilot-scale photocatalysis and enhanced coagulation for disinfection byproduct mitigation, Water Res. 43 (2009) 1597–1610.

[25] T. Tan, M. Ng, M. Lim, S. Liu, C. Chow, M. Drikas, D. Wang, R. Amal, Removal of natural organic matter using UVC/TiO_2 photocatalysis process coupled with coagulation treatment, Chemeca Conference, 18–21 September 2011, Sydney, Australia.

[26] M. Bekbolet, C. Uyguner, H. Selcuk, L. Rizzo, A. Nikolaou, S. Meriç, V. Belgiorno, Application of oxidative removal of NOM to drinking water and formation of disinfection by-products, Desalination 176 (2005) 155–166.

[27] B. Lyon, A. Dotson, K. Linden, H. Weinberg, The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment, Water Res. 46 (2012) 4653–4664.

[28] D. Cassan, B. Mercier, F. Castex, A. Rambud, Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool, Chemosphere 62 (2006) 1507–1513.

[29] T. Bond, M. Templeton, N. Graham, Precursors of nitrogenous disinfection by-products in drinking water – A critical review and analysis, J. Hazard. Mater. 235–236 (2012) 1–16.

[30] Water Research Foundation and EPA, Impact of UV location and sequence on by-product formation, Water Research Foundation, Denver, CO, 2012.

[31] A. Matilainen, A.M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, Rev. Chemosphere 80 (2010) 351–365.

[32] W. Liu, Z. Zhang, X. Yang, Y. Xu, Y. Liang, Effects of UV irradiation and UV/chlorine co-exposure on natural organic matter in water, Sci. Total Environ. 414 (2012) 576–584.

[33] X. Yang, C. Shang, P. Westerhoff, Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination, Water Res. 41 (2007) 1193–1200.

[34] W. Lee, P. Westerhoff, J.-P. Croué, Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, N-Nitrosodimethylamine, and trichloronitromethane, Environ. Sci. Technol. 41 (2007) 5485–5490.

[35] M. Templeton, M. Nieuwenhuijsen, N. Graham, T. Bond, L. Huang, Z. Chen, Review of the current toxicological and occurrence information available on nitrogen-containing disinfection by-products, Imperial Consultants, London, 2010.

[36] A. Dotson, P. Westerhoff, S. Krasner, Nitrogen enriched dissolved organic matter (DOM) isolates and their affinity to form emerging disinfection by-products, Water Sci. Technol. 60 (2009) 135–143.

[37] A. Włodyka-Bergier, T. Bergier, The influence of organic matter quality on the potential of volatile organic water chlorination products formation, Arch. Environ. Prot. 37 (2011) 25–35.

[38] Y. Hou, W. Chu, M. Ma, Carbonaceous and nitrogenous disinfection by-product formation in the surface and ground water treatment plants using Yellow River as water source, J. Environ. Sci. 24(7) (2012) 1204–1209.

[39] R. Francis, M. Small, J. VanBriesen, Multivariate distributions of disinfection by-products in chlorinated drinking water, Water Res. 43 (2009) 3453–3468.

[40] E. Goslan, S. Krasner, M. Bower, S. Rocks, P. Holmes, L. Levy, S. Parsons, A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland, Water Res. 43 (2009) 4698–4706.