

## The control of disinfection by-products precursors by advanced methods of water treatment

Mariola Rajca, Agnieszka Włodyka-Bergier and Michał Bodzek

### ABSTRACT

In the article, the results of the research on reactivity of natural organic matter in regard to disinfection by-products, specifically trihalomethanes (THM) formation, with the use of model waters, are discussed. Additionally, the evaluation of different processes used in water treatment, i.e. photocatalysis, MIEX<sup>®</sup>DOC and membrane processes, is made. It was found that the affinity of particular natural organic matter compounds to form chlorination by-products could be arranged in a series: hydrophobic fraction (HA) > hydrophilic fraction (FA). The applied treatment processes efficiently decreased the concentration of disinfection by-products (DBPs) precursors and characterized with different removal mechanisms. Water treated by means of photocatalysis (specific potential of  $\Sigma$ THM was 30  $\mu\text{g}/\text{mg}$  dissolved organic carbon (DOC) for HA and 12  $\mu\text{g}/\text{mg}$  DOC for FA) revealed lower affinity to form chlorination by-products in comparison with water undergone to MIEX<sup>®</sup>DOC process (specific potential of  $\Sigma$ THM was 38  $\mu\text{g}/\text{mg}$  DOC for HA and 29  $\mu\text{g}/\text{mg}$  DOC for FA). Moreover, combination of those methods with membrane processes efficiently reduced DBPs formation potential. In nanofiltration effluents DBPs potential were very low and equalled to 50  $\mu\text{g}/\text{L}$  for HA and 15  $\mu\text{g}/\text{L}$  for FA.

**Key words** | disinfection by-products, membrane processes, MIEX<sup>®</sup>DOC, photocatalysis, THM precursors

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### ABBREVIATION LIST

AOPs	Advanced oxidation processes	HP-SEC	High performance size exclusion chromatography
BDCM	Bromodichloromethane	MF	Microfiltration
CH	Chloral hydrate	MIEX <sup>®</sup> DOC	Ion exchange process
Da	Dalton	NDMA	N-nitrosodimethylamine
DBCM	Dibromochloromethane	NF	Nanofiltration
DBPs	Disinfection by-products	RO	Reverse osmosis
DOC	Dissolved organic carbon	SUVA	Specific ultraviolet absorbance
FA	Fulvic acid	TBM	Tribromomethane
HA	Humic acid	TCM	Trichloromethane
HAAs	Haloacetic acids	THMs	Trihalomethanes
HNMs	Halonitromethanes	UF	Ultrafiltration
HPI	Hydrophilic fraction	UV <sub>254</sub>	Absorbance
HPO	Hydrophobic fraction		

## INTRODUCTION

The identification of disinfection by-products (DBPs), specifically trihalomethanes (THMs), in water in the 1970s resulted in the start of intensive studies on those, as well as other secondary water contaminants (Sozański & Huck 2007), as they were found to be toxic, genotoxic, mutagenic and carcinogenic. Other hazardous identified water DBPs are: haloacetic acids (HAA), halonitromethanes (HNM) and chloral hydrate (CH) (Włodyka-Bergier *et al.* 2014). In case of potable water dedicated to humans' consumption, all of those contaminants are defined as hazardous ones. Some THM (trichloromethane, bromodichloromethane) and HAA (dichloro-, trichloro-, bromochloro- and dibromoacetic acid) were classified according to the International Agency for Research of Cancer as possibly carcinogenic to humans (group 2B) and CH as probably carcinogenic to humans (group 2A) (IARC 2017). HNM are compounds that can cause high risk to human health. There is no unambiguous evidence of carcinogenicity of these compounds due to the high mortality of experimental animals (Richardson *et al.* 2007).

THM DBPs are the best recognized, and their precursors are organic substances such as humic and fulvic acids and microorganisms' metabolic and decomposition products (Kowal & Świdorska-Bróz 2009). Type and concentration of DBP depend on many factors, among which amount, structure and chemical properties of precursors, type and dose of an oxidant, contact time of precursors and oxidants, as well, and water temperature and pH can be listed (Kowal & Świdorska-Bróz 2009). Mechanisms of DBPs formation as well as identification of organic fractions which appear in water and reveal the highest DBPs formation potential have not been clearly verified yet. In literature, contrary data can be found, as one states that it is the hydrophobic fraction, which is the most reactive during DBPs formation (Chang 2001), while another states it is the hydrophilic one (Pikkarainen 2004).

Nevertheless, the most important effect of researches on water disinfection byproduct are changes in water treatment technology. First of all, more advanced disinfectants, the use of which reduces the amount of formed DBPs are applied, and, secondly, water treatment processes, which are able to efficiently reduce DBPs precursors

concentration, are introduced to treatment systems. Within the latter, one can distinguish such methods like advanced oxidation processes (AOPs), e.g. photocatalysis, during which the decomposition of high molecular weight compounds to low molecular weight ones, up to their complete mineralization to carbon dioxide and water take place. Another interesting process is ion exchange MIEX<sup>®</sup>-DOC, which is found to be efficient in removal of anionic dissolved organic carbon (DOC) compounds as well as inorganic anions such as bromides, sulphates and nitrates. Effective removal of DBPs precursors is also obtained with the use of low pressure driven membrane processes, i.e. microfiltration (MF) and ultrafiltration (UF) (Wang *et al.* 2016; Wray *et al.* 2016), whereas high pressure driven membrane techniques, i.e. nanofiltration (NF) and reverse osmosis (RO) can be used in elimination of already formed DBPs (Wang *et al.* 2007; Uyak *et al.* 2008; Bodzek 2015; Ergan *et al.* 2016).

The aim of the presented research was to evaluate the reactivity of natural organic substances present in raw and treated model waters together with the comparison of different treatment processes: photocatalysis, MIEX<sup>®</sup>-DOC and a combination of photocatalysis and membrane filtration in regard to DBPs formation potential reduction.

## METHODS

In the study, model waters prepared on deionized water matrix were used, in which humic acids (HA) by Sigma-Aldrich, Germany and fulvic acids (FA) by Beijing Multigras Formulation Co. Ltd, China were dissolved.

Waters were treated in the cylindrical reactor of volume 20 L (operational volume 17 L), in which photocatalysis or ion exchange MIEX<sup>®</sup>-DOC processes or hybrid photocatalysis-membrane filtration (MF and NF) processes were run.

Photocatalysis process was performed with the use of commercial powdered titanium dioxide P-25 as a photocatalyst, which was dosed to the system in the amount of 0.1 g/L. Two immersed, low-pressure, 15 W UV lamps emitting radiation of wavelength 254 nm were used. The radiation time was equal 30 min and it was carried out

stepwise, i.e. it was turned on every 30 min, while the water was continuously flowing through the reactor (48 h tests).

In MIEX<sup>®</sup> DOC process, anion exchange, macroporous resin MIEX<sup>®</sup> by Orica Watercare was used. The resin was dosed to water in the form of suspension and in the amount of 10 mL/L, while it was regenerated with 10% of NaCl. The contact time of the resin with the treated water was equal to 30 min, and the resin was dosed to the system every 30 min of the process run (48 h tests). The detail procedure of photocatalysis and MIEX<sup>®</sup> DOC processes performance is discussed in (Rajca 2016a; Rajca 2016b).

In order to determine the potential of DBP formation 24 h test of chlorination and incubation was run. Samples of water were chlorinated with the use of sodium hypochlorite with the dose that enabled to obtain 3–5 mg/L of free chlorine after 24 h. pH of all samples was adjusted to 7 with the use of 1 M sulphuric acid or 1 M sodium hydroxide and 0.5 M phosphate buffer (5 mL buffer per each 250 mL of water). Chlorinated samples were incubated at temperature  $25 \pm 2$  °C in dark glass bottles equipped with the PTFE gasket. After 24 h of incubation samples were dechlorinated and the analysis of selected THMs, i.e. trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane was run. The analysis was made with the use of gas chromatograph Trace Ultra DSQII GC-MS by ThermoScientific.

The analysis of molecular weight of organic compounds (FA) was made with the use of high performance size exclusion chromatography (HP-SEC) carried out at DIONEX ICS-2,500 chromatograph equipped with UV-VIS AD 25 detector by Dionex (USA). The results of chromatographic analysis are discussed in detail in (Włodyka-Bergier *et al.* 2014; Rajca 2016a; Rajca 2016c; Rajca *et al.* 2017).

The statistical analysis was used to assess if the use of analyzed water treatment processes has a statistically significant impact on the THM formation potential. It was performed with R Studio (version 1.0.143), for a statistically significant level  $p < 0.05$ . F-test of equality of variances was done prior the main statistical analysis, which was a T-test to compare equality of means (between raw water and one treated with MIEX<sup>®</sup> DOC, and between raw water and one treated with photocatalysis). If a mean was unequal, Welch's T-test correction was used.

## RESULTS AND DISCUSSION

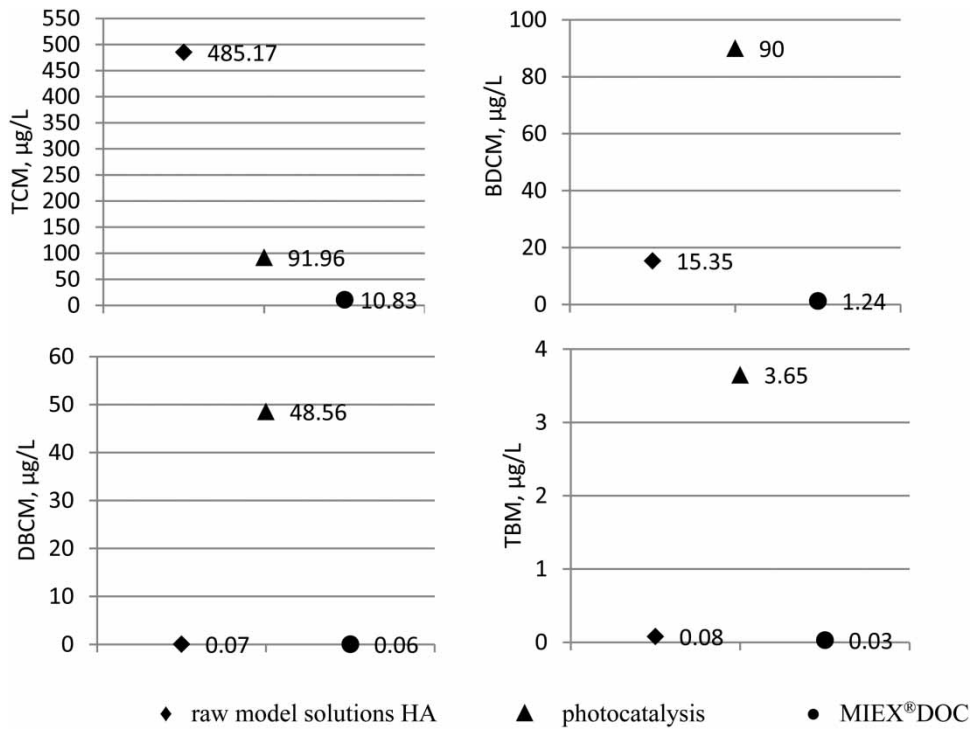
THMs are the main and the most numerous group of halogenated organic DBPs. They appear in water at low concentrations ( $\mu\text{g/L}$ ) and are classified as water micropollutants (Nawrocki 2010). Their concentration in potable water has to be obligatory monitored (Regulation 2015).

In Figures 1 and 2 the impact of natural organic matter type and water treatment process on the potential of selected THMs formation (trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) in chlorinated raw and treated model water solutions is presented.

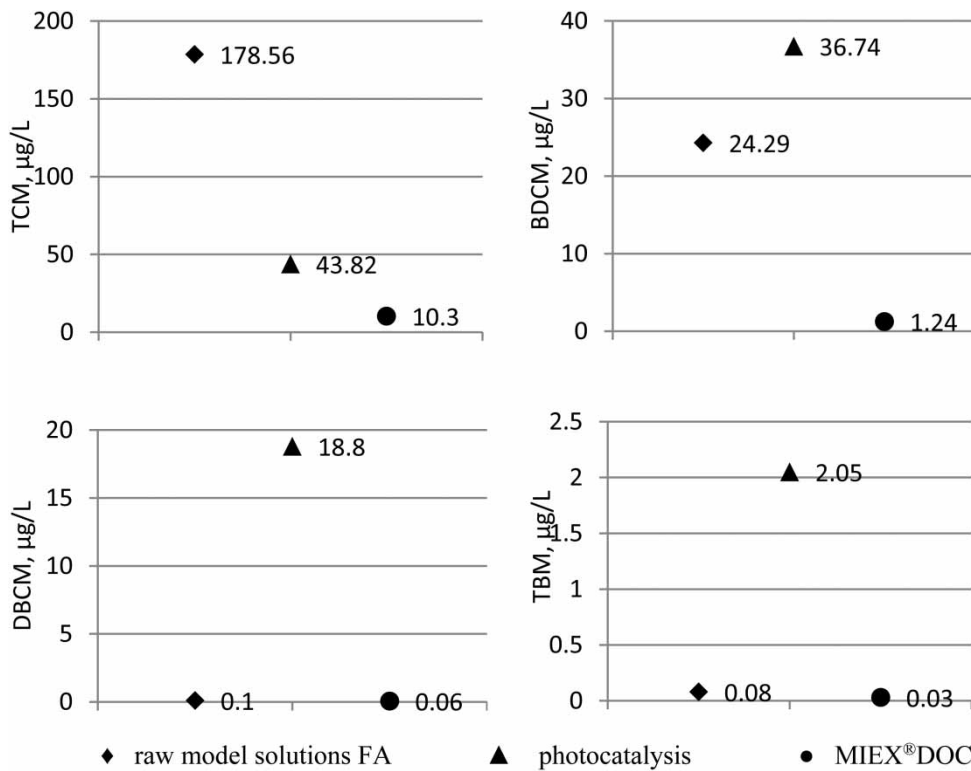
Statistically significant differences between the formation potential of THM and  $\Sigma\text{THM}$  in model solutions and in treated water were noticed for all cases (except DBCM and TBM after MIEX<sup>®</sup> DOC process), both for HA and FA model solutions.

It has already been mentioned that the contrary data on mechanism of DBPs formation as well as indication on type of organic fraction, i.e. hydrophobic (HPO) or hydrophilic (HPI), with higher affinity to their formation can be found in the literature. From a practical point of view, both absorbance  $\text{UV}_{254}$  and DOC parameters can be used as indicators identifying HPO and HPI, while their ratio ( $\text{UV}_{254}/\text{DOC}$ ) enables to determine specific ultraviolet absorbance (SUVA). The latter parameter corresponds to the change of hydrophobic–hydrophilic character of natural organic substances. The higher the SUVA value is, the more hydrophobic character of a compound can be stated. In Table 1, parameters determined for investigated waters are presented. Golea *et al.* (2017) in their research presented a direct correlation between  $\text{UV}_{254}$  and DOC parameters in refer to DBPs, especially in case of THM (correlation coefficients equal to 0.82 and 0.91). They also found a strong correlation with HAA in raw water, which turned to be weaker than treated water. Authors explained such a phenomenon by lower content of strongly reactive HPO fraction accompanied with the presence of less reactive compounds, which also participated in DBPs formation.

The results of the presented study, showed in Figures 1 and 2, confirmed that hydrophobic fraction (HA) revealed higher potential of DBPs formation, whereas hydrophilic



**Figure 1** | The change of potential of THM formation in raw and treated HA model solutions. ♦ raw model solutions HA ▲ photocatalysis ● MIEX®DOC.



**Figure 2** | The change of potential of THM formation in raw and treated FA model solutions. ♦ raw model solutions FA ▲ photocatalysis ● MIEX®DOC.

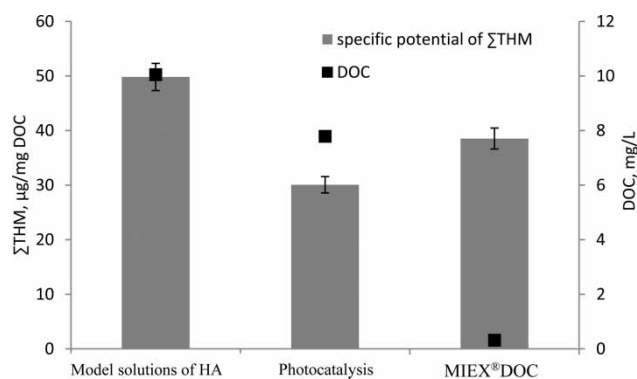
**Table 1** | Indicator identifying HA and FA in investigated water solutions

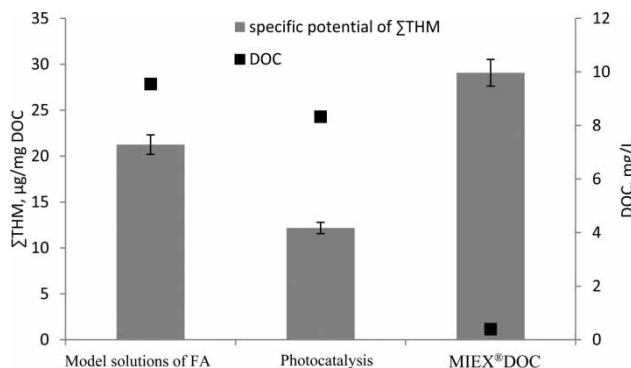
Samples	UV <sub>254</sub> 1/m	DOC gC/m <sup>3</sup>	SUVA m <sup>2</sup> /gC·m
Raw model water solutions			
model solutions, HA	54.4	10.1	5.39
model solutions, FA	20.6	12.6	1.63
Treated water solutions			
after photocatalysis, HA	12.2	7.79	1.56
after photocatalysis, FA	2.86	8.22	0.35
after MIEX <sup>®</sup> DOC, HA	15.7	4.80	3.27
after MIEX <sup>®</sup> DOC, FA	2.30	2.78	0.83

fraction (FA) characterized with lower affinity to water recontamination. The total amount of THMs established for HA was equal to ca. 560 µg/L, while for FA it was ca. 200 µg/L. The significant differences observed within research results indicate the complexity in humic substances composition, despite that these are compounds of one group. Those substances reveal different features such as: color intensity, polymerization rate, molecular weight, carbon and oxygen content, ionic exchange capacity and solubility rate. The content of carbon and color intensity increases with the increase of both the polymerization rate and molecular weight (HA > FA). On the other hand, oxygen content and solubility rate are affected by the rate of polymerization (FA > HA). Both humic and fulvic acids contain a number of functional groups, such as: carboxylic, phenolic, alcoholic, methoxy, carbonyl, ether, ester and chionidic ones, within their structure. FA contain more functional groups of acidic character (especially carboxylic ones), thus their acidity is much higher in comparison with HA and equals 900–1,400 mval/100 g, while for HA it is 400–870 mval/100 g HA. The significant difference in observed in FA and HA structure is the location of oxygen within a compound particle. In case of FA, oxygen is mostly bonded in functional groups, while in FA it is bonded with aromatic ring. Those differences result in different affinity of discussed compounds to THMs formation. The discussed results indicate that the higher rate of THMs formation is revealed by HA. The highest concentration among investigated THMs, which formed raw water was measured for TCM, next for BDCM, while the lowest was for DBCM and TBM. However, different potential of THMs

formation was observed in case of treated waters. Moreover, type and amount of formed DBPs were found to depend on treatment method applied. In case of MIEX<sup>®</sup>DOC treatment, total sum of THMs determined in chlorinated sample was 90% lower than in case of raw waters, regardless of organic matter type present in the solution. Photocatalytic treatment characterized with lower efficiency and enabled 50% decrease of THMs sum for both types of organic matter. However, if particular THMs were considered, it was found that 70% reduction in TCM was obtained, but it was accompanied with the increase of concentration of other compounds, i.e. BDCM, DBCM, and TBM. It was explained by modifications and degradation of natural substances, which took place during photo-oxidation and led to formation of organic by-products (Rajca 2016c), which possessed higher affinity to form BDCM, DBCM and TBM than substances present in raw solutions.

Despite the decrease of total amount of THMs, the increase of concentration of three products of this undesired group of compounds was an unfavorable phenomenon. Nevertheless, considering the absolute reactivity of DBPs precursors, which remained in treated solutions, photocatalysis was found to be more advantageous than MIEX<sup>®</sup>DOC process. The evaluation covered the determination of specific potential to  $\Sigma$ THM formation in reference to unit organic carbon mass. It showed the reactivity of 1 mg of organic carbon in reference to THM formation considering organic substances, which remained in solutions after particular treatments. The summary of the obtained results is shown in Figures 3 and 4.

**Figure 3** | Changes of specific potential of  $\Sigma$ THM formation in raw and treated model solutions of HA.

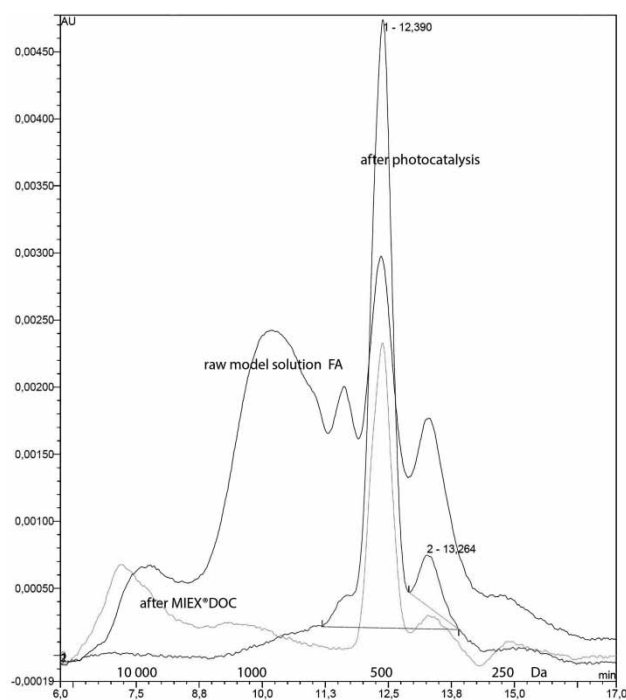


**Figure 4** | Changes of specific potential of  $\Sigma$ THM formation in raw and treated model solutions of FA.

It was observed that specific potential of solutions treated via photocatalysis was lower than the one obtained for water after MIEX<sup>®</sup>DOC treatment. Moreover, a slight increase of specific potential expressed in  $\mu\text{g } \Sigma\text{THM}/\text{mg DOC}$ , established for fulvic acids solution treated via MIEX<sup>®</sup>DOC was observed. It indicated on diversified reactivity of compounds which remained in water after treatment with particular processes. Despite the fact that DOC measured in water after MIEX<sup>®</sup>DOC was much lower (0.4 mg/L) than DOC measured in water after photocatalysis (ca. 8 mg/L), the reactivity of precursors, which remained in MIEX<sup>®</sup>DOC effluent was high, while for photocatalysis effluent it was low. The same dependence was observed in the case of model water with humic acids, in which post-photocatalysis precursors revealed lower affinity than post-MIEX<sup>®</sup>DOC precursors. Nevertheless, the increase of potential after treatment was not observed as in case of FA solution, but oppositely, it was decreased by ca. 30%. It indicated on differences in mechanisms of removal of organic substances in investigated water treatment processes. During MIEX<sup>®</sup>DOC process ion exchange and adsorption of contaminants on resin's particles took place with no impact on their chemical character and structure. Photocatalytic oxidation, on the other hand, resulted in the change of chemical character and structure of organic substances. The phenomenon was also confirmed by other researches (Choi & Choi 2010; Spiliotopoulou *et al.* 2015). Due to the decomposition of high molecular weight compound during photocatalysis, the amount of low molecular weight compounds in the solution increased and even exceeded their share in raw solutions (as it was observed

for FA) (Figure 5). However, the reactivity of low molecular weight THMs precursors was lower than high molecular weight ones, and the latter compounds were the ones that remained in water after the MIEX<sup>®</sup>DOC process (Figure 4). The proper analysis used for confirmation of discussed assumption was distribution of molecular weights of fulvic acids performed with the use of high performance size exclusion chromatography HP-SEC. The results of the analysis are shown in Figure 5.

At chromatograms of FA model solution substances of molecular weight ranging from 250 to 11,000 Da were identified, whereas compounds of molecular weight 540–580 Da mostly appeared, while particles below 300 Da were present in the lowest extent. Moreover, the distribution of molecular weight of compounds, which remained in water after particular treatment, was significantly different. Photocatalysis process enabled 100% removal of compounds of weight above 800 Da, whereas the share of compounds of weight 540–580 Da increased. In case of water treated via MIEX<sup>®</sup>DOC, the presence of compounds of higher molecular weight above 8,000 Da was stated, whereas the share of smaller particles decreased, but the removal rate of particles

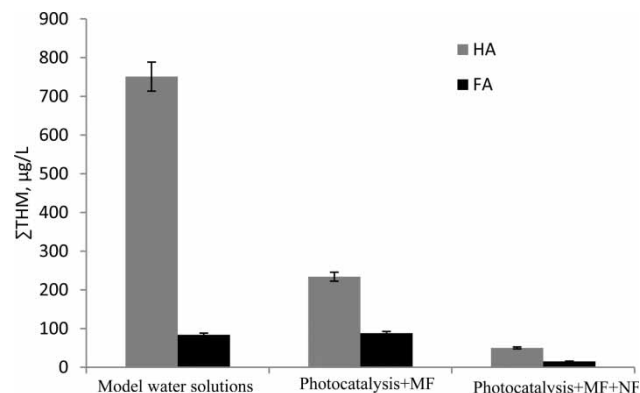


**Figure 5** | Chromatogram (SEC) which are presenting molecular weight distribution of FA.



of weight 540–580 Da was the lowest. It was explained by the highest share of those compounds in raw water and by the competitiveness of other lower molecular weight compounds for active sites of MIEX<sup>®</sup>DOC resin. The comparison of chromatographic peaks showed in Figure 5 enables to conclude, that photocatalysis was efficient for removal of high molecular weight compounds, and decrease of their concentration was accompanied with the increase of the share of lower molecular weight compounds. On the other hand, MIEX<sup>®</sup>DOC process effectively eliminated compounds of lower molecular weight, while the removal of high molecular weight compounds was poor. The dependence confirmed different characters of contaminants removal mechanisms during the investigated processes. The main goal of photocatalysis process, which involves the use of hydroxyl radical OH<sup>•</sup> of high oxidation potential (2.6 V) to oxidation of investigated compounds, is to obtain almost complete mineralization connected with formation of CO<sub>2</sub> and H<sub>2</sub>O. In the process, the significant amount of hydrophobic organic compounds is transformed to lower molecular weight hydrophilic compounds. Additionally, degradation pathway observed for HA is much longer than the one of FA. During MIEX<sup>®</sup>DOC ion exchange process, exchangeable ions present in the resin structure are exchanged to ions of the same charge. In this case, organic macromolecules of ionic character, which are negatively charged, are exchanged by chlorides present in active centers of the resin. The performed studies proved, that the ion exchange process enabled better removal of low molecular weight humic fraction (Figure 5), while high molecular weight compounds remained in water. Properties of those substances caused their removal mechanism to be based on ion exchange/adsorption, resulting of interactions between resin grains and organic macromolecules.

Nevertheless, it can be sum up that high efficiency of THMs precursors was obtained during applied treatment methods (photocatalysis, MIEX<sup>®</sup>DOC). The enhancement of those processes with low and high pressure driven membrane processes, such as: MF, UF or NF may significantly improve the quality of produced water. In Figure 6, the results of the studies obtained during treatment of model water via photocatalysis enhanced with microfiltration and nanofiltration are shown. The combination of photocatalysis



**Figure 6** | The impact of contaminants type and water treatment system on potential of ΣTHMs formation.

and MIEX<sup>®</sup>DOC processes with microfiltration aims to keep photocatalyst particles or resin grains in the reactor and separate them from purified water. The application of nanofiltration as the third stage of the treatment enables polishing of treated water and decreases concentration of DBPs precursors.

The THMs formation potential values established for raw model solutions were equal to ca. 150 µg/L in the case of FA and ca. 700 µg/L for HA. The treatment of water in photocatalytic microfiltration membrane resulted in a significant decrease of HA solution potential (from ca. 700 µg/L to 234 µg/L) and, to a lesser extent, of FA solution potential (from ca. 150 µg/L to 90 µg/L), but the reactivity of compounds was significantly reduced. The application of nanofiltration as a second stage of membrane treatment resulted in further reduction of THMs formation potential, which finally reached 50 µg/L for HA solution 15 µg/L for FA solution. It indicated high efficiency of nanofiltration in removal of THMs precursors, i.e. HA and FA. Additionally, Ersań et al. (2016) reported that nanofiltration was found to be efficient not only in removal of precursors of THMs, but also of HNMs (halonitromethanes) and NDMA (N-nitrosodimethylamine). In their study, they obtained high retention coefficients (72–97%) of THMs precursors in surface water, regardless of type on nanofiltration membrane applied. Moreover, the rate of removal of THMs precursors was always higher than in the case of HNM and NDMA precursors. To conclude, nanofiltration can be regarded as an efficient method of treatment of waters contaminated with NOM, however, in order to prevent fouling

phenomenon, the process should be used as a part of an integrated system, as it was shown during studies, results of which are presented in Figure 6, i.e. photocatalysis + MF + NF system.

## CONCLUSIONS

- The results of the studies indicated on hydrophobic fraction (HA) to be responsible for DBP production in higher extent than hydrophilic fraction (FA). The type of fraction (HA, FA) was found to have an impact on a kind of THM compound formed. Hydrophobic fraction revealed higher affinity to TCM formation than hydrophilic fraction, while in case of other compounds, i.e. BDCM, DBCM and TBM both fraction characterized with similar potential to their formation.
- It was found that reactivity of THMs precursors present in raw water as well as ones remaining in water after treatment had a significant impact on the selection of treatment process. The results of the studies showed, that waters treated via photocatalysis process characterized with lower chlorination DBPs formation potential than water after MIEX<sup>®</sup>DOC process.
- The undesired phenomenon of microfiltration membrane fouling was observed in photocatalysis-MF system, which was caused by poorer removal of FA and HA during photocatalysis itself. The latter was a result of both, the photocatalyst loses (during recirculation within reactor-membrane module-reactor) and the lack of possibility of capillary membranes aeration. However, the significant improvement in DBPs concentration decrease was obtained during the preceding nanofiltration process. In nanofiltration effluents, DBPs potential were very low and equal to 50 µg/L for HA and 15 µg/L for FA.

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