

# Activated carbon and organic matter characteristics impact the adsorption of DBP precursors when chlorine is added prior to GAC contactors

Cagri Utku Erdem <sup>a</sup>, Mohamed Ateia <sup>a, b</sup>, Chao Liu <sup>a, c</sup>, Tanju Karanfil <sup>a, \*</sup>

<sup>a</sup> Department of Environmental Engineering and Earth Science, Clemson University, SC, 29634, United States

<sup>b</sup> Department of Chemistry, Northwestern University, Evanston, IL, 60208, United States

<sup>c</sup> Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

## ARTICLE INFO

### Article history:

Received 24 March 2020  
Received in revised form  
1 June 2020  
Accepted 2 July 2020  
Available online 5 July 2020

### Keywords:

Activated carbon  
Porosity  
Pre-chlorination  
Disinfection byproducts  
Br-DBPs  
Natural organic matter  
Effluent organic matter

## ABSTRACT

Pre-chlorination (i.e. dosing chlorine prior to granular activated carbon (GAC) contactors) was recently introduced as a promising method to reduce the formation of disinfection byproducts (DBPs). However, our understanding on the effect of natural organic matter (NOM) and GAC characteristics on pre-chlorination efficiency is still elusive. Thus, we have designed this systematic study to investigate the effects of GAC characteristics (i.e. surface area, pore size, and surface charge) on the subsequent reduction of DBP formation using five well-characterized adsorbents with three different NOM under three initial Br<sup>-</sup> concentrations. The results revealed that the adsorption of halogenated DBPs precursors mostly occurs in the mesoporous region (i.e. 2 nm < pore size < 50 nm) of the adsorbents. Subsequently, pre-chlorination before treatment with HD3000 (i.e. GAC with the highest mesoporous surface area) decreased the formation of DBPs by 58%. Furthermore, oxidation of GAC increased the surface acidity and negatively impacted the adsorption of halogenated DBP precursors, which suggests basic GACs as promising adsorbents when applying pre-chlorination. In addition, experiments with different NOM showed that pre-chlorination was effective with higher aromatic NOM (i.e. high specific ultraviolet absorbance (SUVA<sub>254</sub>)). However, pre-chlorination of NOM with low SUVA<sub>254</sub> has decreased the adsorption of some DBP precursors which resulted in increased formations of haloacetic acid (HAA) and total organic halogen (TOX). Also, experiments with effluent organic matter (EfOM) showed that pre-chlorination did not increase the adsorption of DBP precursors in low SUVA<sub>254</sub> wastewater effluents. Besides, increasing initial Br<sup>-</sup> concentration increased the formation of brominated DBPs (Br-DBPs) and the adsorbed Br-DBP precursors. This study gives in-depth understanding of the mechanisms, advantages, and limitations of pre-chlorination as a potential method to control DBPs formation.

© 2020 Elsevier Ltd. All rights reserved.

## 1. Introduction

Chlorine disinfection is commonly applied during water treatment to inactivate pathogenic microorganisms; however, it can also lead to the formation of unintended disinfection by-products (DBPs) due to the reaction between chlorine and natural organic matter (NOM). Besides, the presence of bromide (Br<sup>-</sup>) - which is not toxic itself - results in the formation of brominated DBPs (Br-DBPs) that are more toxic than their chlorinated analogues (Plewa et al.,

2017; Richardson et al., 2007). Therefore, the elimination of DBPs precursors (e.g. coagulation, ion exchange, and adsorption) is critical to minimize DBP formation.

Environmental Protection Agency considers granular activated carbon (GAC) adsorption among the best available technologies to remove synthetic organic compounds, taste and odor causing compounds, and NOM in water and wastewater treatment plants (Chen et al., 1997; Karanfil et al., 1999; Matsui et al., 2015). However, two major drawbacks were reported for GAC application. First, fouling of GAC pores by NOM fractions with high molecular weight (i.e. > 10 kDa) (Ding et al., 2008; Newcombe et al., 1997; Velten et al., 2011). Second, GAC is not effective to remove Br<sup>-</sup> and other inorganic DBPs' precursors, which elevates the formation of Br-

\* Corresponding author.

E-mail address: [tkaranf@clemson.edu](mailto:tkaranf@clemson.edu) (T. Karanfil).

Abbreviations			
ACF	Activated Carbon Fiber	DN	Dissolved Nitrogen
BAA	Bromoacetic Acid	DOC	Dissolved Organic Carbon
BAN	Bromoacetonitrile	EfOM	Effluent Organic Matter
BCAA	Bromochloroacetic Acid	GAC	Granular Activated Carbon
BCAN	Bromochloroacetonitrile	HAA	Haloacetic Acid
Br <sup>-</sup>	Bromide	HAN	Haloacetonitrile
Br-DBP	Brominated Disinfection By-product	MRL	Minimum Reporting Level
BSF	Bromide Substitution Factor	NOM	Natural Organic Matter
CAA	Chloroacetic Acid	RSSCT	Rapid Small-Scale Column Test
CAN	Chloroacetonitrile	RW	Raw Water
Cl <sup>-</sup>	Chloride	SR	Suwannee River
DBAA	Dibromoacetic Acid	SUVA <sub>254</sub>	Specific Ultraviolet Absorbance at 254 nm
DBAN	Dibromoacetonitrile	TBAA	Tribromoacetic Acid
DBCAA	Dibromochloroacetic Acid	TBM	Tribromomethane
DBCM	Dibromochloromethane	TCAA	Trichloroacetic Acid
DBP	Disinfection By-product	TCAN	Trichloroacetonitrile
DCAA	Dichloroacetic Acid	TCM	Trichloromethane
DCAN	Dichloroacetonitrile	THM	Trihalomethane
DCBAA	Dichlorobromoacetic Acid	TOX	Total Organic Halogen
DCBM	Dichlorobromomethane	TW	Treated Water
		UFC	Uniform Formation Conditions
		U-TOX	Unknown-Total Organic Halogen

DBPs due to the increased ratio of Br<sup>-</sup> to dissolved organic carbon (DOC) (Chen et al., 2017; Krasner et al., 2016; Watson et al., 2016).

Recent studies have suggested that adding chlorine prior to GAC contactors may reduce subsequent DBP formation. Jiang et al. (2017) have reported on the effect of pre-chlorination of a solution containing Suwannee River (SR) NOM and 2 mg/L Br<sup>-</sup> on the formation of trihalomethane (THM), haloacetic acids (HAA) and total organic halides (TOX) with rapid small-scale column tests (RSSCTs). Their results showed an increased bed volume of water treated before the breakthrough of THM and HAA and decreased formation of Br-DBPs and TOX. Then, they examined the effects of initial Br<sup>-</sup> concentration and chlorine contact time on the effectiveness of pre-chlorination and reported that pre-chlorination could double the TOX removal under tested experimental conditions (Jiang et al., 2018). However, a recent study by Fischer et al. (2019) has showed a decreased formation of THMs, while HAA-formation was not affected by the applying pre-chlorination. The different observations in the current literature might be attributed to the limited number of studies as well as the variations in the tested GACs, NOM sources, and experimental conditions.

Herein, we designed this systematic study to answer three key questions: 1) What are the main characteristics of GAC that affect the removal of DBPs' precursors after pre-chlorination? 2) Is pre-chlorination effective for different types of organic matters? and 3) What is the effect of Br<sup>-</sup> concentration on the pre-chlorination efficiency? We addressed such limitations in the literature and targeted elucidating the adsorption mechanisms of halogenated organic matter by GACs by comparing the adsorption results to those of activated carbon fibers (ACFs), which have well-defined pore-sizes and surface areas.

## 2. Material and methods

### 2.1. Chemicals and reagents

Reagent grade chemicals and standards were used in all experiments. Summary of used chemicals, standards and adsorbents can be found in **Text S1** of the supplementary material.

### 2.2. Tested NOM and experimental conditions

Three different NOM isolates and two different EfOM were used in this study in order to see the effect of organic matter aromaticity on its adsorption with and without pre-chlorination. Suwannee River NOM (SR) was purchased from International Humic Substances Society, while two other NOM isolates were previously extracted from raw and treated water (RW and TW, respectively) of a water treatment plant in South Carolina, USA. The detailed procedures for the extraction of these isolates have been reported elsewhere (Song et al., 2009). Two EfOM samples collected from different wastewater treatment plants in South Carolina (WW1 and WW2). SR and RW had a high SUVA<sub>254</sub> values of 4.3 and 4.0 L/mg-m, respectively (i.e. an indication of NOM in higher aromatic character), while TW, WW1 and WW2 had a lower SUVA<sub>254</sub> value of 2.6, 1.3 and 2.1 L/mg-m, respectively, which suggests more hydrophilic nature of this NOM (Karanfil et al., 2002). Previous studies have reported positive correlations between SUVA<sub>254</sub> and NOM molecular size (Ateia et al., 2017; Hua et al., 2015) suggesting that both SR and RW are likely to have higher molecular size relative to TW. Summary of characteristics of NOMs and EfOM solutions was presented at **Table 1**.

The DOC concentrations of NOM and EfOM solutions were adjusted to 2 mg/L to compare the behavior of organic matter with different SUVA<sub>254</sub> values at the same organic carbon levels during the experiments. To prepare working solutions, each NOM isolate was dissolved in Milli-Q water (18 MΩ cm, Millipore) and EfOM solutions were filtered with pre-washed 0.45 μm hydrophilic polyethersulfone membrane filters. The pH of NOM & EfOM solutions was adjusted to 7.5 with 10 mM phosphate buffer. Experiments were conducted at three different Br<sup>-</sup> concentrations (in the absence of Br<sup>-</sup>, 200 and 800 μg/L) by spiking Br<sup>-</sup> in NOM solutions. Br<sup>-</sup> concentration is between 10 and 3000 μg/L in surface waters due to industrial activities, sea intrusions and wastewater discharges (Magazinovic et al., 2004). In this study, 200 and 800 μg/L Br<sup>-</sup> concentrations were selected to simulate pre-chlorination and adsorption behavior under moderate and high levels of Br<sup>-</sup> to increase the formation of Br-DBPs.

**Table 1**  
Characteristics of NOMs and EfOM used in this study.

Water	DOC (mg/L)	DN (mg/L)	NH <sub>3</sub> (mg/L)	SUVA (L/mg·m)	Cl <sup>-</sup> (mg/L)	Br <sup>-</sup> (μg/L)
SR NOM	2.0	0.1	<MRL	4.3	0.04	<MRL
RW NOM	2.0	0.1	<MRL	4.0	0.02	<MRL
TW NOM	2.0	<MRL	<MRL	2.6	<MRL	<MRL
WW1	2.0	0.2	0.02	1.3	21	12
WW2	2.0	1.9	0.04	2.1	65	<MRL

MRL: Minimum Reporting Level.

### 2.3. Activated carbons and their characterization

F400 (bituminous coal based GAC, Calgon) and HD3000 (lignite based GAC, Norit) were selected for this study due to their wide applications at water treatment plants. Each carbon sample obtained from manufacturer was crushed and sieved to obtain samples of 200–325 mesh size (average particle diameter: 45–75 μm) for further experiments. ACF10 and ACF20L were based on phenol formaldehyde and were supplied by American Kynol Company. The ACF pore structures is more homogenous than GAC which helps differentiate the effective pore sizes on the adsorption of NOM. In order to change the surface charge of the GAC, 1 g of HD3000 was oxidized in 100 mL of nitric acid (70% GR, ACS grade) for 6 h on a magnetic stirrer. Then the oxidized carbon (HD3000A) was rinsed several times with distilled deionized water and pH of eluent was checked until all nitric acid is washed out from carbon pores. All five adsorbents were characterized for their BET surface area, pore size distribution, and pH of point of zero charge (pH<sub>PZC</sub>) and details of these methods have been reported elsewhere (Dastgheib et al., 2004).

Table 2 shows the selected characteristics of activated carbons used in the experiments. Among all adsorbents, HD3000 and HD3000A had the lowest BET surface areas (i.e. 613 and 580 m<sup>2</sup>/g respectively), followed by ACF10 and F400 with comparable BET surface areas (i.e. 844 and 832 m<sup>2</sup>/g respectively), while ACF20L had the largest BET surface area of 1426 m<sup>2</sup>/g. Although ACF10 and ACF20L both consists of micropores, ACF10 had mostly primary micro pores (<1 nm) and ACF20L had mostly secondary micro pores (1–2 nm). F400 is more microporous than HD3000 and HD3000A, whose pore structure mostly consist of mesopores. ACF10, ACF20L, F400 had neutral to basic surface characteristics as indicated the pH<sub>PZC</sub> values, while HD3000 had slightly acidic characteristics. After nitric acid activation, HD3000 appeared to maintain relatively its pore distribution and total surface area, but a significant decrease was observed on its surface acidity (low pH<sub>PZC</sub>).

### 2.4. Pre-chlorination, adsorption and chlorination experiments

All experiments were conducted in 125 mL bottles in dark and under headspace-free conditions at room temperature (21 ± 1 °C). Three steps followed to conduct pre-chlorination experiments, which are pre-chlorination, adsorption and final chlorination.

**Table 2**  
Selected characteristics of adsorbents used in this study.

Adsorbent	S <sub>A</sub> BET (m <sup>2</sup> /g)	V <sub>T</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> [%] (<1 nm)	V <sub>micro</sub> [%] (<2 nm)	V <sub>meso</sub> [%] (2–50 nm)	V <sub>macro</sub> [%] (>50 nm)	pH <sub>PZC</sub>
ACF10	844	0.397	97	99	0	1	6.2
ACF20L	1426	0.699	51	93	6	1	8.5
F400	832	0.415	45	78	21	1	7.7
HD3000	613	0.271	8	26	73	1	5.5
HD3000A	580	0.362	6	21	78	1	2.1

SA: Surface area. V: Pore volume. pH<sub>PZC</sub>: pH of point of zero charge.

#### 2.4.1. Pre-chlorination

In order to both minimize HOCl dose and have a residual chlorine after 30 min, 2 mg/L HOCl was selected as a pre-chlorine dose (DOC and HOCl was at 1:1 mass ratio). After 30 min pre-chlorination, residual chlorine was measured with N,N-diethyl-p-phenylenediamine (DPD) method using a Varian UV–Vis spectrophotometer at 515 nm wavelength. Then pre-chlorinated samples were quenched with ascorbic acid (1:1 M ratio).

#### 2.4.2. Adsorption

After pre-chlorination step, 50 mg/L GACs and ACFs were separately added into pre-chlorinated and non-pre-chlorinated bottles. All bottles were put on a rotary tumbler for 24 h. Afterwards, each bottle was filtered with Pall Supor 0.45 μm pore size membrane filters, and samples were transferred into clean 125 mL bottles for final chlorination.

#### 2.4.3. Final chlorination

The formation of DBPs from GAC treated waters was performed under Uniform formation conditions (UFC) that all tested waters will have the same residual HOCl after 24h (Summers et al., 1996). Based on chlorine demand test of each water, samples were chlorinated for 24 h. Residual 1 mg/L free chlorine was quenched with ascorbic acid (1:1 M ratio).

To gain mechanistic understanding, the formation of THM, HAA, HAN and TOX was measured and compared after each step. Detailed information for the analysis of DBP and TOX, and Bromide Substitution Factor (BSF) calculation can be found in Text S2. Duplicated bottles were used for adsorption and DBP extraction experiments.

## 3. Results & discussion

### 3.1. Effect of GAC characteristics on adsorption of DBPs precursors

In this study, the effectiveness of each adsorbent was evaluated using two indicators. First, we quantified selected DBPs (i.e. THM, HAA and haloacetonitrile (HAN)) at different steps of the experiments to examine the effects of different treatment scenarios on the removal of the selected DBP precursors. Second, we measured the changes in chlorinated and brominated TOX to better understand the effects of each treatment step on both known and unknown TOX. The formation of THM, HAA, HAN and TOX using SR

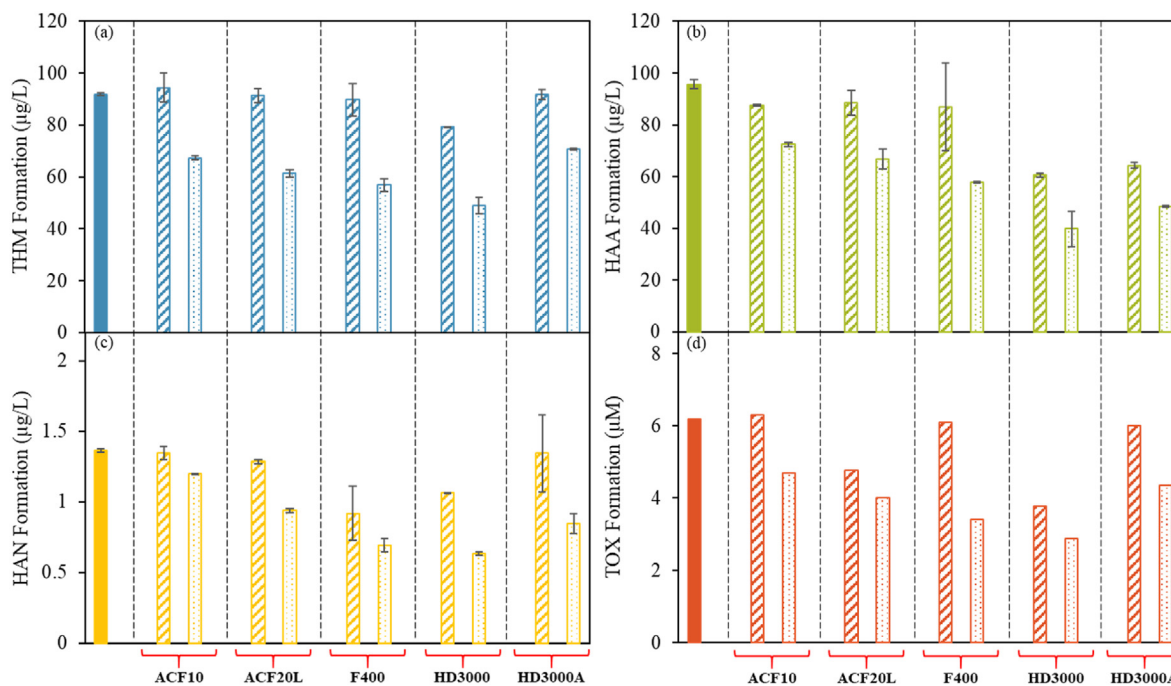
NOM is presented in Fig. 1. THM formation at UFC condition was 92 µg/L, and the THM speciation followed an order of DCBM > DBCM > TCM > TBM (Fig. S1a). Without pre-chlorination, no difference was observed between the formed THM of the untreated water and the treated waters with ACF10 or ACF20L. Apparently, the pore sizes of both ACF (i.e. < 2 nm) were smaller than NOM clusters that can range between 0.4 and 4 nm (Li et al., 2003; Shimizu et al., 2018). On the other hand, when pre-chlorination was applied prior to adsorption, UFC THM formation after adsorption decreased by 27% and 32% respectively for ACF10 and ACF20L (Fig. 1a). This suggests that pre-chlorination resulted in enhanced adsorption of THM precursors in primary and secondary micropores of both ACFs. HAA formation at UFC condition was 96 µg/L, and the speciation order was TCAA > BDCAA > BCAA > DCAA > DBCAA > DBAA > CAA > TBAA > BAA (Fig. S1b) and similar trends were also observed for HAA formation; pre-chlorination prior to ACF adsorption decreased subsequent HAA UFC formation by 24% and 30% respectively (Fig. 1b). Furthermore, HAN formation decreased by 10% and 30% for ACF10 and ACF20L, respectively (Fig. 1c), which suggests that HAN precursors adsorbed better in secondary micropores than only primary micropores. Moreover, without pre-chlorination ACF20L decreased the TOX formation by removing unknown portion of chlorinated TOX and brominated TOX; however, with pre-chlorination known portion of chlorinated TOX and brominated TOX further decreased. In general, ACF20L absorbed 6–20% more DBP precursors than the ACF10 with pre-chlorination (Fig. 1d), which was attributed to the secondary micropores (1–2 nm) of ACF20L, which can adsorb bigger size molecules as compared ACF10 which mainly consists of primary micropores (<1 nm).

In terms of the behavior of GAC, F400 was able to remove some DBP precursors and THM, HAA and TOX formation decreases were less than without pre-chlorination. However, with pre-chlorination the formation of THM, HAA and TOX decreased by 40–45% (Fig. 1).

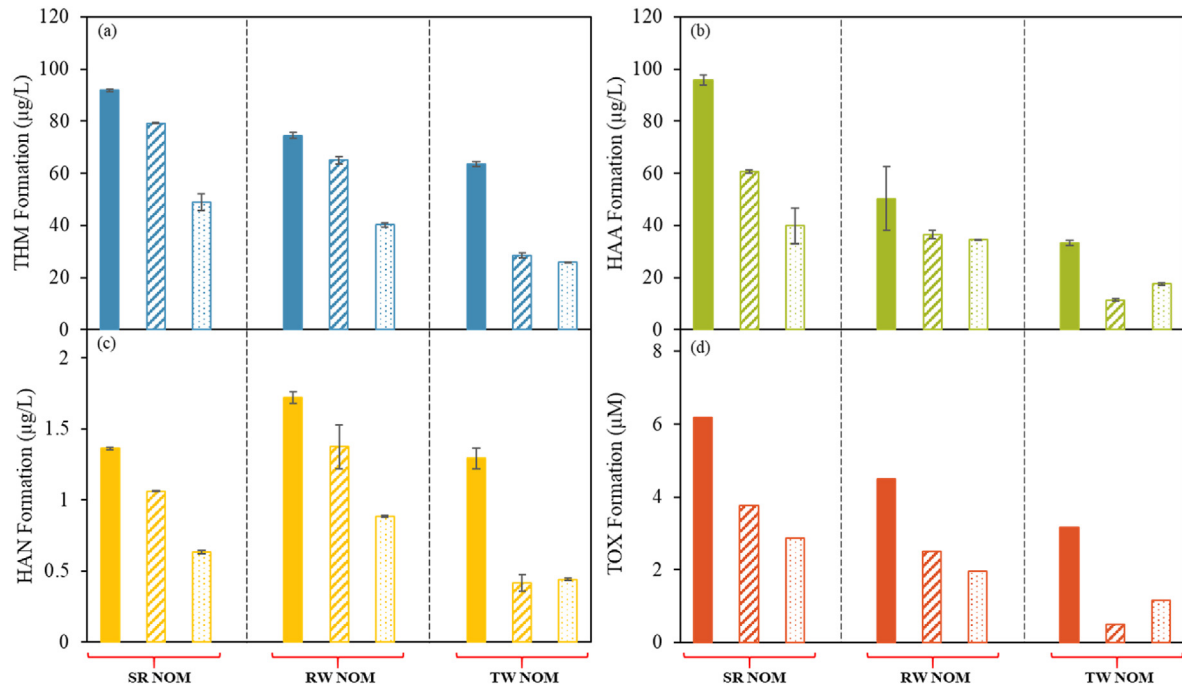
HD3000 has relatively smaller surface area than the other adsorbents. Yet, it exhibited a considerable removal of DBP precursors (up to 39%) even without pre-chlorination. With pre-chlorination, it showed up to 58% decrease in THM, HAA, HAN and TOX formation (Fig. 1). Moreover, in terms of the speciation highest decrease was observed for brominated THM, HAA, and HAN than their chlorinated precursors with pre-chlorination (Fig. S1). Nitric acid modified HD3000A, showed lower reductions - up to 36% - in THM, HAN and TOX formation than HD3000 without pre-chlorination. This is mainly due to same charge on the carbon surface and NOM molecules at the pH of the experiments (Karanfil et al., 1999; Sánchez-Polo et al., 2007). On the other hand, HAA precursor removal was not affected by the surface charge change and remain relatively similar for both HD3000 and HD3000A (Fig. 1b). With pre-chlorination, similar to other adsorbents, HD3000A performance is also improved, but DBP formation decreased by up to 20% compared to HD3000.

### 3.2. Effect of NOM characteristics on pre-chlorination effectiveness

Since HD3000 showed a better performance than the other adsorbents in the previous experiments with SR NOM, it was selected for the following experiments to evaluate the effect of NOM characteristics (i.e., high  $SUVA_{254}$  vs low  $SUVA_{254}$ ) in the presence of 200 µg-Br<sup>-</sup>/L. Fig. 2 shows the concentrations of THM, HAA, HAN, and TOX after chlorination of the solutions containing SR, RW and TW NOM, and Fig. S2 shows the speciation of all DBP classes. At the same DOC level, SR NOM showed higher THM, HAA and TOX formation than RW and TW NOM solutions, which was attributed to its highest  $SUVA_{254}$  value, while HAN formation was comparable for all three NOM. THM speciation was similar for SR and RW solutions, as their  $SUVA_{254}$  values were similar (4.3 and 4.0 L/mg·m respectively) (Ateia et al., 2019). TW NOM solution, however, formed more brominated species (e.g. TBM) which was



**Fig. 1.** Five different adsorbents effect on the adsorption of (a) THM, (b) HAA, (c) HAN and (d) TOX precursors and intermediates under with/without pre-chlorination of SR NOM. UFC: solid color, without pre-chlorination: diagonal stripes, and with pre-chlorination: dotted. Experimental conditions: [DOC] = 2 mg/L, [Br<sup>-</sup>] = 200 µg/L, pH = 7.5, pre-chlorination = 30 min, adsorption = 24 h, chlorination time = 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 2.** Three different NOMs' (a) THM, (b) HAA, (c) HAN and (d) TOX formations under with/without pre-chlorination. UFC: solid color, without pre-chlorination: diagonal stripes and with pre-chlorination: dotted. Experimental conditions: [DOC] = 2 mg/L,  $[Br^-]$  = 200 µg/L, pH = 7.5, pre-chlorination = 30 min, adsorption = 24 h, chlorination time = 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

attributed to more efficient bromination of low  $SUVA_{254}$  waters (Hua et al., 2015; Soyluoglu et al., 2020; Wang et al., 2014). With pre-chlorination, THM formation decreased by additional 33% for both SR and RW solutions as compared to without pre-chlorination, while the pre-chlorination on the TW did not result in additional reduction in THM. Similarly, pre-chlorination did not improve the adsorption of two EfOM (Fig. S3a). With the lower  $SUVA_{254}$  values, TW NOM, WW1 and WW2 were likely consisting of lower molecular weight and more hydrophilic fractions, and pre-chlorination did not seem to make additional difference in their adsorption.

On the other hand, HAA formation showed different trend than THM formation. SR NOM showed up to 2.5 times higher HAA formation than RW and TW solutions. Without pre-chlorination, HAA formation decreased by 27, 37 and 66% for SR, RW and TW NOM, respectively (Fig. 2b). However, pre-chlorination further decreased HAA formation only for SR NOM, but not for RW and TW NOM solutions. Although, there was a small difference in the total HAA formation between with and without pre-chlorination at RW NOM, the main difference was in the speciation of HAAs. While, without pre-chlorination, HD3000 reduced more the formation of chlorinated HAA species by removing its precursors, with pre-chlorination this trend changed to more brominated species and less brominated HAAs formed (e.g. TBAA) (Fig. S2b). Interestingly, compared to without pre-chlorination there was a 19% increase in the HAA formation of TW NOM with pre-chlorination (Fig. 2b) and no additional improvement for WW1 and WW2 (Fig. S3b). It was reported that low molecular weight molecules have low adsorption affinity (Karanfil et al., 1999) and this can be the reason on HAA formation increase, as pre-chlorination breaks NOM into smaller size than HAA precursors become less absorbable. While one study suggested that pre-chlorination can help decrease HAA formation (Jiang et al., 2017), another reported no effect (Fischer et al., 2019).

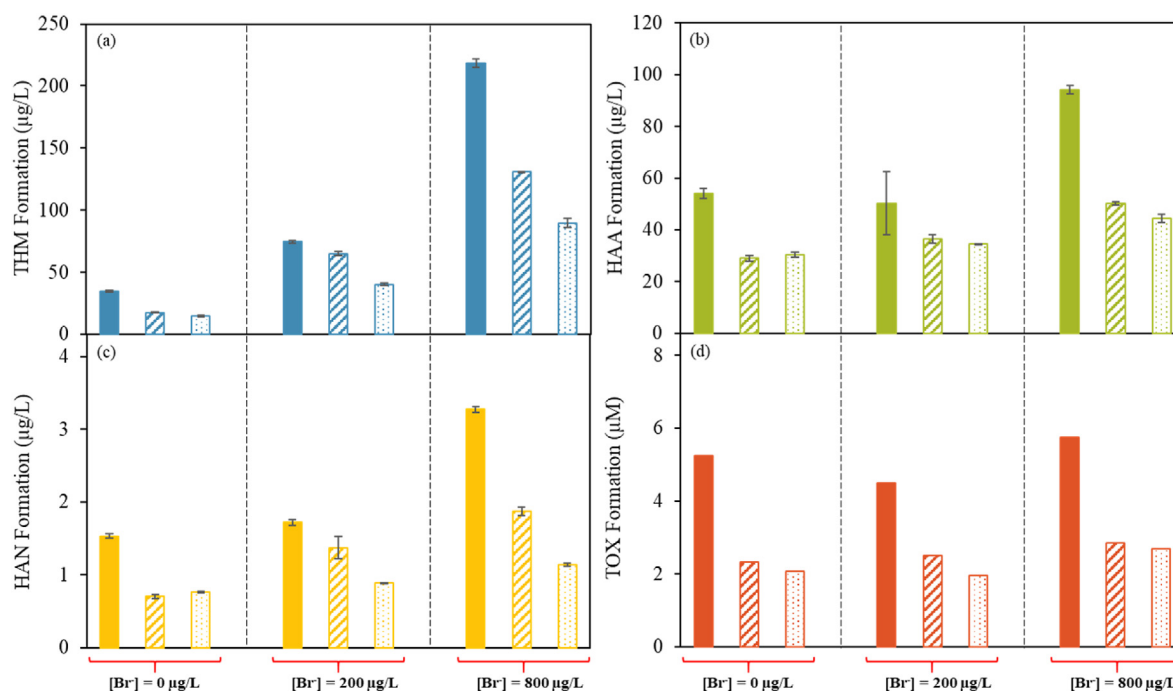
The trends for the decrease in HAN formation were similar to those of THM formation. Without pre-chlorination HAN formation decreased 17% for both SR and RW NOM and 68% for TW NOM

(Fig. 2c). The formation of HANs was higher for WW1 and WW2 than the NOMs because of the higher nitrogen content and without pre-chlorination formation of HANs decreased by 30% for WW1 and WW2 (Fig. S3c). On the other hand, with pre-chlorination HAN formation on SR and RW NOM decreased by 30%, but did not have an effect at TW NOM. Similar to SR and RW NOMs pre-chlorination improved the adsorption of HAN precursors and additional 15% decrease observed for both WW1 and WW2 (Fig. S3c).

Even though pre-chlorination showed either no effect or little increase on DBPs formation for low  $SUVA_{254}$  NOM (i.e. TW NOM), it is also critical to consider the effects on TOX formation, as it helps to see overall halogenated DBP precursor removals. Without pre-chlorination, the TOX formation decrease was 39% and increased to 54% with pre-chlorination for SR NOM (Fig. 2d). Similarly, with pre-chlorination TOX formation decrease was 44% and increased to 57% at RW NOM. These additional 13–15% TOX formation decrease mostly happened on unknown portion of chlorinated TOX and brominated TOX at SR and RW NOM solutions (Fig. S2d). On the other hand, with pre-chlorination TOX formation removal decreased from 84% to 63% at TW NOM. Moreover, while pre-chlorination improves 15% TOX removal on WW1, it did not show any effect on WW2 (Fig. S3d). These trends suggest that pre-chlorination affects the adsorption of known and unknown halogenated DBP precursors differently on low and high  $SUVA_{254}$  organic matter as their characteristics are different.

### 3.3. Effect of $Br^-$ concentration on adsorption

$Br^-$  concentration is an important factor when considering the formation and the speciation of DBPs. Thus, solutions of SR, RW and TW NOM were treated with four adsorbents under three different  $Br^-$  concentrations (in the absence of  $Br^-$ , 200 and 800 µg/L). Fig. 3 shows THM, HAA, HAN and TOX formation for RW NOM solution with HD3000 treatment. Speciation of DBPs for all NOM solutions can be found in Fig. S4, Fig. S5 and Fig. S6. When  $Br^-$  concentration



**Fig. 3.** Formation of (a) THM, (b) HAA, (c) HAN and (d) TOX under three different  $\text{Br}^-$  concentration with/without pre-chlorination of RW NOM. UFC: solid color, without pre-chlorination: diagonal stripes and with pre-chlorination: dotted. Experimental conditions:  $[\text{DOC}] = 2 \text{ mg/L}$ ,  $[\text{Br}^-] = 0\text{--}200\text{--}800 \text{ }\mu\text{g/L}$ ,  $\text{pH} = 7.5$ , pre-chlorination = 30 min, adsorption = 24 h, chlorination time = 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

was increased to 200 and 800  $\mu\text{g/L}$ , THM speciation shifted from TCM to TBM on RW (Fig. S4a), SR and TW NOMs (Fig. S5a, Fig. S6a). As the formation of THMs increased, the pre-chlorination effect on the removal of THM precursors became more obvious at RW (Fig. 3a and Fig. S4a) and SR NOMs (Fig. S5a), but not at TW NOM (Fig. S6a). The THM formation difference between without pre-chlorination and with pre-chlorination under 800  $\mu\text{g/L}$   $\text{Br}^-$  concentration increased to 19%, 21% and 1% for RW, SR and TW NOM solutions (Fig. 3a, Fig. S5a and Fig. S6a).

Similar to THM speciation, HAA formation was shifted towards more brominated species (i.e. TBAA) as the  $\text{Br}^-$  concentration increases. In the absence of  $\text{Br}^-$  pre-chlorination did not showed effect, and as the  $\text{Br}^-$  concentration increases, HD3000 adsorption decreased the formation of HAAs by 53% (Fig. 3b and Fig. S4b). As the  $\text{Br}^-$  concentration increases more HAA precursors removed at SR NOM and the formation difference between without and with pre-chlorination increased to 14% (Fig. S5b); however,  $\text{Br}^-$  concentration increases did not make a big difference at RW NOM. On the other hand, under all three  $\text{Br}^-$  concentrations formation of HAAs increased 10–20% at TW NOM (Fig. S6b).

While DCAN was the only species in the absence of  $\text{Br}^-$ , the formation almost became only DBAN at 800  $\mu\text{g/L}$   $\text{Br}^-$  concentration for all NOM solutions (Fig. S4c, Fig. S5c and Fig. S6c). With pre-chlorination HAN formation of RW NOM and SR NOM decreased additionally 22% and 27%, respectively (Fig. 3c and Fig. S5c) and no additional decrease was observed for TW NOM solution (Fig. S6c).

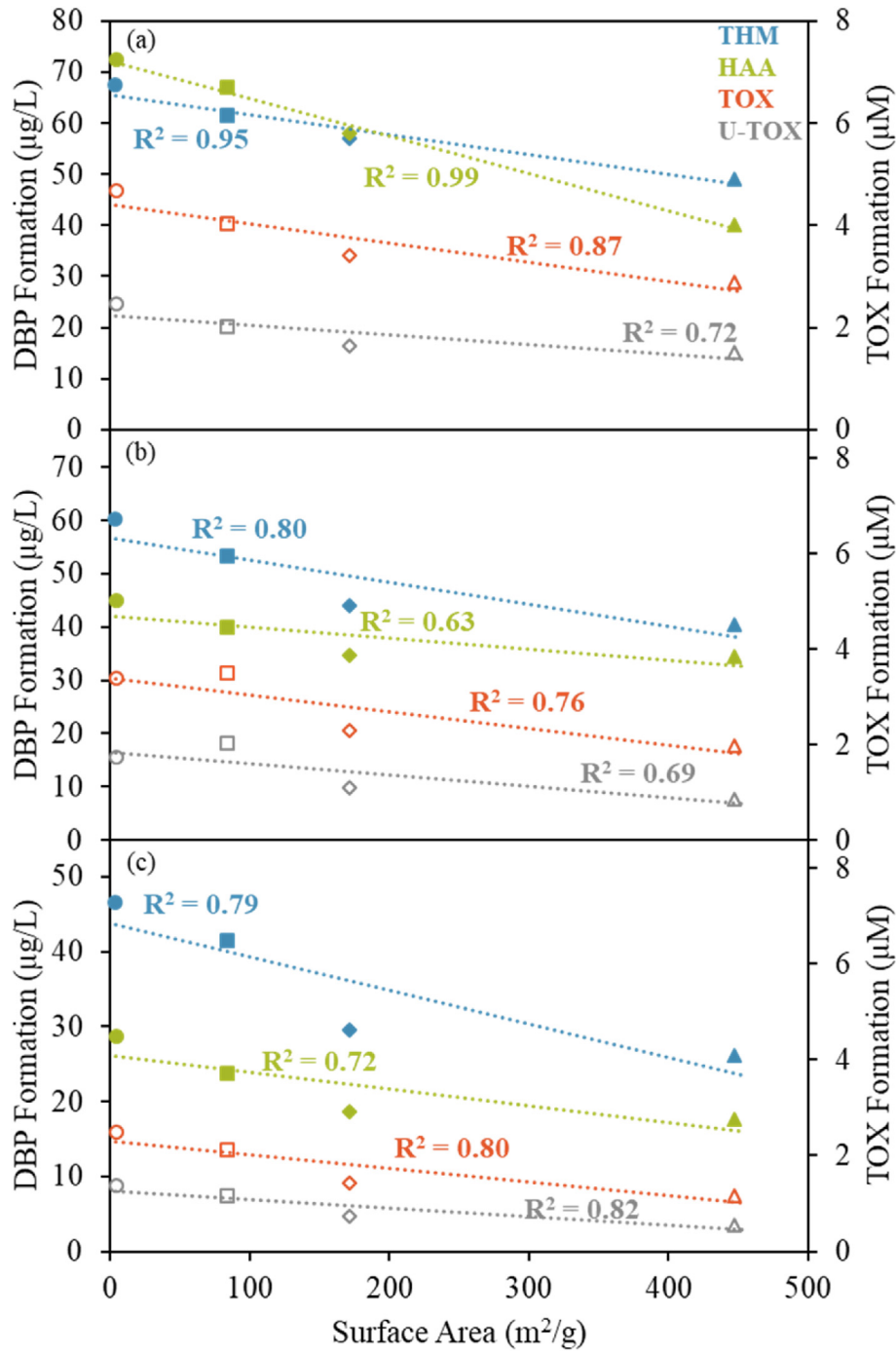
TOX formation removals increased by 5–10% with pre-chlorination on RW NOM (Figs. 3d) and 18–25% on SR NOM solution (Fig. S5d). Interestingly, on TW NOM solution in the absence of  $\text{Br}^-$  TOX formation was 20% higher with pre-chlorination than without pre-chlorination; however, as the  $\text{Br}^-$  concentration increases both without and with pre-chlorination TOX formations became similar (Fig. S6d).

Figure S7 presents the comparison of BSF among THM, di-HAA and tri-HAA at 200  $\mu\text{g/L}$   $\text{Br}^-$  concentration on SR, RW and TW

NOM. In general, TW BSF values were higher than SR and RW NOM, which was attributed to its lower  $\text{SUVA}_{254}$  value. As the hydrophobicity increases, chlorine competes with bromine to react with aromatic moiety of the organic matter and forms more chlorinated DBPs than brominated ones, which cause to lower BSFs (Hua et al., 2006). Without pre-chlorination only carbon adsorption increased the BSF values after treatment which can be attributed to higher  $\text{Br}^-/\text{DOC}$  ratio since only DOC was removed by carbon adsorption. On the other hand, with pre-chlorination after the treatment the BSF values were less than without pre-chlorination. THM, di-HAA and tri-HAA BSF values decreased additionally up to 13%, 21% and 42% respectively (Fig. S7). Interestingly, TW NOM BSF values decreased as well with pre-chlorination, although the formation of THMs and HAAs were similar between without and with pre-chlorination on TW NOM. This further supports that pre-chlorination increases the adsorption of brominated DBPs' precursors. Furthermore, we checked the bromate formation in all pre-chlorinated samples and it was below the minimum reporting level ( $<10 \text{ }\mu\text{g/L}$ ), which indicated that BSF reduction was not caused by bromate formation.

#### 3.4. Correlation between GAC surface area and DBP formation

To examine the effect of pore size distribution, THM, HAA, TOX and unknown TOX (U-TOX) formation were plotted as a function of surface area for three different NOM types. Fig. 4 shows the mesoporous surface area vs DBP formation correlations for SR, RW and TW NOM with pre-chlorination. THM and HAA correlation  $R^2$  values were higher than 0.79 and 0.63, respectively, and SR NOM correlations were the highest among the other two NOM solutions (Fig. 4a). While all three NOM showed good correlations with TOX formations ( $R^2 > 0.76$ ), the correlations with U-TOX were also high ( $R^2 > 0.69$ ) which suggests not only the known portion of TOX precursors was removed by mesoporous surface area, but also unknown halogenated precursors were removed as well. This



**Fig. 4.** Mesoporous surface area vs DBP formation correlations with (a) SR, (b) RW and (c) TW NOM solutions. DBP data: solid, TOX data: empty. ACF10: circle, ACF20L: square, F400: diamond and HD3000: triangle. Experimental conditions: [DOC] = 2 mg/L, [Br<sup>-</sup>] = 200 µg/L, pH = 7.5, pre-chlorination = 30 min, adsorption = 24 h, chlorination time = 24 h.

indicates that with pre-chlorination, as the mesoporous surface area increases the adsorption of unknown DBP precursors also increases, and pre-chlorination not only improves regulated DBP precursor adsorption, but also it improves unknown DBP precursor adsorption. Although, we did not see an improvement with pre-chlorination on TW NOM, the  $R^2$  was higher than 0.72, which suggests that most of the adsorption of DBP precursors occur on the mesoporous region even for lower  $SUVA_{254}$  NOM solution. Moreover, several correlations were also investigated (e.g., with micropore or macropore surface area etc.), but the analyses did not result in any good correlations (data not shown).

#### 4. Conclusions

This study showed that carbon porosity, NOM characteristics, Br<sup>-</sup> concentration change the effectiveness of NOM and EfOM adsorption by GAC when pre-chlorination was applied. Pre-chlorination improved the adsorption of both chlorinated and brominated DBP precursors with tested ACFs and GACs. Adsorption of halogenated DBP precursors did not increase with increasing surface area of adsorbents, on the contrary HD3000 - which has the lowest surface area-adsorbed more halogenated DBP precursors than the all other adsorbents because of its high mesoporosity.

Although all adsorbents removal performance was increased with pre-chlorination, GAC with basic characteristic (HD3000) adsorbs more halogenated DBP precursors than GAC with an acidic characteristic (HD3000A). Measured DBPs and TOX decreases showed that pre-chlorination is more effective on organic matter with higher aromaticity. Furthermore, pre-chlorination decreased the adsorption of certain DBP precursors (e.g. HAAs) with low SUVA<sub>254</sub> NOM, which suggest that as hydrophobicity increases the effectiveness of pre-chlorination also increases. Formation of Br-DBPs is increased by elevated Br<sup>-</sup> concentration, and with pre-chlorination the adsorbents removed more Br-DBPs precursors than chlorinated ones which decreased BSF values. Although ACF performance is also increased with pre-chlorination, correlation between DBP formation and surface area showed that the adsorption of halogenated DBP precursors occurs primarily on mesoporous region of the adsorbent. Results from this study suggest that water treatment plants with high Br<sup>-</sup> concentration in their raw water can control DBP formation by applying chlorine before the GAC filters. To this end, choosing microporous to mesoporous GAC types can further decrease the formation of DBPs.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.116146>.

### References

- Ateia, M., Apul, O.G., Shimizu, Y., Muflihah, A., Yoshimura, C., Karanfil, T., 2017. Elucidating adsorptive fractions of natural organic matter on carbon nanotubes. *Environ. Sci. Technol.* 51, 7101–7110. <https://doi.org/10.1021/acs.est.7b01279>.
- Ateia, M., Erdem, C.U., Ersan, M.S., Ceccato, M., Karanfil, T., 2019. Selective removal of bromide and iodide from natural waters using a novel AgCl-SPAC composite at environmentally relevant conditions. *Water Res.* 156, 168–178. <https://doi.org/10.1016/j.watres.2019.03.028>.
- Chen, C., Apul, O.G., Karanfil, T., 2017. Removal of bromide from surface waters using silver impregnated activated carbon. *Water Res.* 113, 223–230. <https://doi.org/10.1016/j.watres.2017.01.019>.
- Chen, G., Dussert, B.W., Suffet, I.H., 1997. Evaluation of granular activated carbons for removal of methylisoborneol to below odor threshold concentration in drinking water. *Water Res.* 31, 1155–1163. [https://doi.org/10.1016/S0043-1354\(96\)00362-4](https://doi.org/10.1016/S0043-1354(96)00362-4).
- Dastgheib, S.A., Karanfil, T., Cheng, W., 2004. Tailoring activated carbons for enhanced removal of natural organic matter from natural waters. *Carbon* 42, 547–557. <https://doi.org/10.1016/j.carbon.2003.12.062>.
- Ding, L., Snoeyink, V.L., Mariñas, B.J., Yue, Z., Economy, J., 2008. Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter. *Environ. Sci. Technol.* 42, 1227–1231. <https://doi.org/10.1021/es0710555>.
- Fischer, N., Ghosh, A., Talabi, B., Seidel, C., Westerhoff, P., 2019. Chlorine addition prior to granular activated carbon contactors improves trihalomethane control. *AWWA Water Sci* 1, e1119. <https://doi.org/10.1002/aws2.1119>.
- Hua, G., Reckhow, D.A., Abusallout, I., 2015. Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere* 130, 82–89. <https://doi.org/10.1016/j.chemosphere.2015.03.039>.
- Hua, G., Reckhow, D.A., Kim, J., 2006. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. *Environ. Sci. Technol.* 40, 3050–3056. <https://doi.org/10.1021/es0519278>.
- Jiang, J., Li, W., Zhang, X., Liu, J., Zhu, X., 2018. A new approach to controlling halogenated DBPs by GAC adsorption of aromatic intermediates from chlorine disinfection: effects of bromide and contact time. *Separ. Purif. Technol.* 203, 260–267. <https://doi.org/10.1016/j.seppur.2018.04.050>.
- Jiang, J., Zhang, X., Zhu, X., Li, Y., 2017. Removal of intermediate aromatic halogenated DBPs by activated carbon adsorption: a new approach to controlling halogenated DBPs in chlorinated drinking water. *Environ. Sci. Technol.* 51, 3435–3444. <https://doi.org/10.1021/acs.est.6b06161>.
- Karanfil, T., Kitis, M., Kilduff, J.E., Wigton, A., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural organic matter. *Environ. Sci. Technol.* 33, 3225–3233. <https://doi.org/10.1021/es9810179>.
- Karanfil, T., Schlautman, M.A., Erdogan, I., 2002. Survey of DOC and UV measurement practices with implications for SUVA determination. *J. Am. Water Works Assoc.* 94, 68–80. <https://doi.org/10.1002/j.1551-8833.2002.tb10250.x>.
- Krasner, S.W., Lee, T.C.F., Westerhoff, P., Fischer, N., Hanigan, D., Karanfil, T., Beita-Sandí, W., Taylor-Edmonds, L., Andrews, R.C., 2016. Granular activated carbon treatment may result in higher predicted genotoxicity in the presence of bromide. *Environ. Sci. Technol.* 50, 9583–9591. <https://doi.org/10.1021/acs.est.6b02508>.
- Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Res.* 37, 4863–4872. <https://doi.org/10.1016/j.watres.2003.08.018>.
- Magazinovic, R.S., Nicholson, B.C., Mulcahy, D.E., Davey, D.E., 2004. Bromide levels in natural waters: its relationship to levels of both chloride and total dissolved solids and the implications for water treatment. *Chemosphere* 57, 329–335. <https://doi.org/10.1016/j.chemosphere.2004.04.056>.
- Matsui, Y., Nakao, S., Sakamoto, A., Taniguchi, T., Pan, L., Matsushita, T., Shirasaki, N., 2015. Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: effects of adsorbent and adsorbate characteristics. *Water Res.* 85, 95–102. <https://doi.org/10.1016/j.watres.2015.08.017>.
- Newcombe, G., Drikas, M., Hayes, R., 1997. Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Res.* 31, 1065–1073. [https://doi.org/10.1016/S0043-1354\(96\)00325-9](https://doi.org/10.1016/S0043-1354(96)00325-9).
- Plewa, M.J., Wagner, E.D., Richardson, S.D., 2017. TIC-Tox: a preliminary discussion on identifying the forcing agents of DBP-mediated toxicity of disinfected water. *J. Environ. Sci.* 58, 208–216. <https://doi.org/10.1016/j.jes.2017.04.014>.
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res. Rev. Mutat. Res.* 636, 178–242. <https://doi.org/10.1016/j.mrrev.2007.09.001>.
- Sánchez-Polo, M., Rivera-Utrilla, J., Salhi, E., von Gunten, U., 2007. Ag-doped carbon aerogels for removing halide ions in water treatment. *Water Res.* 41, 1031–1037. <https://doi.org/10.1016/j.watres.2006.07.009>.
- Shimizu, Y., Ateia, M., Yoshimura, C., 2018. Natural organic matter undergoes different molecular sieving by adsorption on activated carbon and carbon nanotubes. *Chemosphere* 203, 345–352. <https://doi.org/10.1016/j.chemosphere.2018.03.197>.
- Song, H., Orr, O., Hong, Y., Karanfil, T., 2009. Isolation and fractionation of natural organic matter evaluation of reverse osmosis performance and impact of fractionation parameters. *Environ. Monit. Assess.* 153, 307–321.
- Soyluoglu, M., Ersan, M.S., Ateia, M., Karanfil, T., 2020. Removal of bromide from natural waters: bromide-selective vs. conventional ion exchange resins. *Chemosphere* 238, 124583. <https://doi.org/10.1016/j.chemosphere.2019.124583>.
- Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., Owen, D., 1996. Assessing DBP yield: Uniform formation conditions. *J. Am. Water Works Assoc.* 88, 80–93. <https://doi.org/10.1002/j.1551-8833.1996.tb06573.x>.
- Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H.P., von Gunten, U., Boller, M., Meylan, S., 2011. Characterization of natural organic matter adsorption in granular activated carbon adsorbents. *Water Res.* 45, 3951–3959. <https://doi.org/10.1016/j.watres.2011.04.047>.
- Wang, Y., Le Roux, J., Zhang, T., Croué, J.P., 2014. Formation of brominated disinfection byproducts from natural organic matter isolates and model compounds in a sulfate radical-based oxidation process. *Environ. Sci. Technol.* 48, 14534–14542. <https://doi.org/10.1021/es503255j>.
- Watson, K., Farré, M.J., Knight, N., 2016. Comparing a silver-impregnated activated carbon with an unmodified activated carbon for disinfection by-product minimisation and precursor removal. *Sci. Total Environ.* 542, 672–684. <https://doi.org/10.1016/j.scitotenv.2015.10.125>.