



# Natural organic matter undergoes different molecular sieving by adsorption on activated carbon and carbon nanotubes



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## HIGHLIGHTS

- AC adsorbed small MW fractions of NOM before the higher MW fractions.
- CNT adsorbed high MW fractions of NOM and the smallest fraction (MW > 0.4 kDa) was not removed.
- FI indicated the preferential adsorption of microbial derived NOM on AC, and terrestrial derived NOM on CNT.
- BIX indicated the preferential adsorption of freshly produced NOM on AC, while decomposed NOM on CNT.

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## ABSTRACT

We have comprehensively compared the molecular sieving of natural organic matter (NOM) by adsorption on activated carbon (AC) and multi-walled carbon nanotubes (CNT) using different types of NOM. All water samples were characterized using UV–visible and fluorescence spectroscopies as well as high-performance size-exclusion chromatography (HPSEC) before and after adsorption. Adsorption isotherm results fitted well with Freundlich model ( $R^2 = 0.95–0.99$ ) and the model parameters indicated higher adsorption of NOM on CNT than AC. Fluorescence index (FI) and freshness index (BIX) showed preferential adsorption of microbial derived and fresh NOM on AC, whereas, terrestrial derived and decomposed NOM were preferentially adsorbed on CNT. Further, HPSEC revealed that AC adsorbed NOM fractions with small molecular weight (MW) (<0.4 kDa) faster than the fractions with higher MW. In contrast, CNT adsorbed NOM fractions characterized by high MW (>1 kDa) while the smallest fraction (<0.4 kDa) was not adsorbed, possibly due to its hydrophilic character. Our results also demonstrated a good correlation between FI and average MW of NOM ( $R^2 > 0.93$ ). These findings illustrate the influence of the adsorbent's type and characteristics (i.e., porosity and pore size distribution) on the preferential adsorption of different NOM fractions.

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## 1. Introduction

Natural organic matter (NOM) is ubiquitous in natural waters and can cause several problems in water supply systems. For instance, NOM react with chlorine or other disinfectants/oxidants during water treatment processes and form toxic disinfection byproducts (e.g. trihalomethanes, haloacetic acids and haloacetonitriles) (Christman et al., 1983; Kitis et al., 2001, 2002).

Other problems include bad odor and taste of drinking water, and membrane fouling at water treatment plants (Cai et al., 2015; Cheng et al., 2005; Peng et al., 2017). Therefore, several processes for NOM removal have been proposed; such as coagulation (Edzwald, 1993), membrane filtration (Zularisam et al., 2006), oxidation and adsorption (Dastgheib et al., 2004; Cheng et al., 2005). Among them, adsorption is considered as one of the effective methods, and adsorption-based treatment is simple to operate and to design (Bhatnagar and Sillanpää, 2017).

NOM is a mixture of various compounds that include humic substances, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Bjelopavlic et al., 1999; Zhang et al., 2011). These compounds vary in their molecular weight (MW) and adsorption affinity on different adsorbents

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(Fettig, 1999; Mostafa et al., 2014). For instance, Kilduff et al. (1996a) demonstrated that activated carbon (AC) preferentially adsorbs low molecular weight (MW) components from aqueous humic acid solutions. In our recent study on the adsorption of NOM by carbon nanotubes (CNTs), we observed the selective adsorption of certain fractions (i.e., 0.5–2 kDa for humic acids but in the MW range of 1–3 kDa for all fulvic acids and reverse-osmosis isolates). We have also found that the small fraction (MW < 0.4 kDa) was not adsorbed by CNTs, probably due to the hydrophilic nature of such fraction (Ateia et al., 2017a). Further, the presence of NOM fractions showing different MW, hydrophobicity or specific ultraviolet absorbance (SUVA<sub>254</sub>) result in the formation of different disinfection byproducts (DBPs) in the chlorination and chloramination in water treatment process (Hua et al., 2015). Recently, Jiang et al. (2017) reported that removal of intermediate aromatic fraction of NOM by AC reduced the formation of commonly known DBPs (i.e. trihalomethanes). The hydrophobicity and the transphilicity of NOM affect the formation of reactive oxygen species (ROS) through photochemical path (e.g., the hydrophobic and transphilic fractions are the major sources of superoxide, H<sub>2</sub>O<sub>2</sub> and •OH, and the hydrophilic fraction produces singlet oxygen (<sup>1</sup>O<sub>2</sub>)) (Zhang et al., 2014; Zhou et al., 2017). Therefore, this heterogeneous nature of NOM influences their molecular sieving behavior (i.e., fractionation), which affects the performance of water treatment processes.

Today, AC is the commonly used adsorbent in water treatment facilities due to its low cost and facile operation (Shimabuku et al., 2014), and CNTs have been explored as the next-generation adsorbents due to their high surface area, hydrophobicity, porosity, rapid sorption kinetics and simple regeneration techniques (Ateia et al., 2017b, 2017c). However, more insights regarding the fractionation behavior of NOM on AC (i.e. conventional material) in comparison to CNTs (i.e. emerging technologies) are still required for the following reasons. First, there is no report in the literature investigating the link between the preferential adsorption of NOM fractions and their source and/or their freshness level. Second, previous studies tended to use polystyrene sulfonate (PSS) with different MW to represent different NOM fractions when investigating adsorption behaviors on AC (Kilduff et al., 1996b) and CNT (Li et al., 2014). Third, it is difficult to get general conclusions from previous studies due to differences in the origin of the NOM and differences (sometimes limited number) in the techniques and the experimental conditions used for NOM characterization before and after adsorption process. However, it is more accurate to use the real water samples. Herein, we considered the limitations in the literature and comprehensively compared, for the first time, the molecular sieving of NOM on each of AC and CNT. To this end, we run both kinetics and isotherm experiments and used a set of characterization techniques (i.e., UV–vis and fluorescence spectroscopies and high-performance size-exclusion chromatography (HPSEC)). Wastewater-impacted river water samples were collected and two different reverse osmosis (RO) isolates were used to control the levels of NOM concentrations.

## 2. Materials and methods

### 2.1. Materials

Tama river water (RW) was collected at lat. 35°35' N. and long. 139°40' E., about 13 km from the river mouth, on November 15, 2016. Fig. 1 shows the sampling point and the wastewater treatment plants locations. The pH and ionic strength of the collected water were 7.4 and 3.4 mM, respectively. After collection, the water was filtered with 0.2 μm pre-washed filter and stored in a refrigerator (4 °C). Because the concentration of background NOM in the raw water is constant, two standard RO isolates (Nordic Reservoir

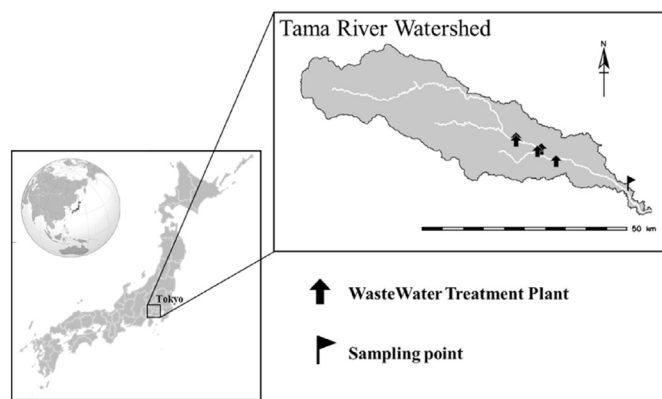


Fig. 1. Map for the river watershed that shows the sampling point and the locations of all wastewater treatment plants.

NOM [NOM1] and Upper Mississippi River NOM [NOM2]) were purchased from the International Humic Substances Society (IHSS) to highlight molecular sieving by the adsorbents. The chemical properties of RW and RO isolates samples are listed in Table 1.

Powdered AC was purchased from Kanto Chemical Co., Inc., Japan and multi-walled CNT was purchased from Chengdu Alpha Nano Technology Co., Chinese Academy of Science, China. Table 2 shows characteristics of both adsorbent. The pore size distribution reported in this study can represent other AC (i.e., micro-pores are dominant) and other CNTs (i.e., meso-pores are dominant).

### 2.2. Preparation of NOM stock solutions

RO isolates samples were dissolved in a 0.01 M NaOH solution to prepare a stock solution of 10 g-NOM/L. The pH of each NOM solution was then adjusted to  $7.0 \pm 0.2$  with 0.01 M HCl or 0.01 M NaOH. The volume of acid or alkali for pH adjustment was considered for the calculation of the final NOM concentration. The ionic strength was adjusted to 3.4 mM using NaCl. All stock solutions were stored in the dark and refrigerated (4 °C) when not in use.

### 2.3. Adsorption isotherms

Based on preliminary kinetic experiments (Section S1 in supplementary files), the equilibrium time was set at 24 h. Adsorption isotherm experiments were conducted with different NOM concentrations [5.0–25 (mg-NOM/L)] and constant adsorbent dose of 250 mg/L. Both stock NOM solutions were diluted in RW or ultrapure water (PW). NOM1 solutions diluted by RW and PW were named as RW1 and PW1, respectively, and NOM2 solutions diluted by RW and PW were named as RW2 and PW2, respectively. After the equilibrium time, samples were collected, filtered (prewashed 0.45 μm polyethersulfone (PES) filter, Membrane Solutions, Tokyo, Japan), and kept refrigerated until measurements. The adsorbed NOM amounts were determined by subtracting the concentration of NOM remaining in the solution from the initial concentration [measured as UV absorbance at 254 nm (UV<sub>254</sub>)]. Changes in NOM concentration in the blank experiments (with no adsorbents) were found to be negligible. All the experiments were conducted at the room temperature.

### 2.4. Analysis

UV<sub>254</sub> was obtained with a UV–visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan). The average MW of all samples

**Table 1**  
Chemical properties of the river water and standard RO isolates used in this study.

Type	Elemental ratio <sup>a</sup>		Carbon species from <sup>13</sup> C NMR (%) <sup>a</sup>			Aroma-ticity <sup>b</sup>	Acidic Functional Groups <sup>a</sup>			M <sub>w</sub> (kDa) <sup>c</sup>	M <sub>n</sub> (kDa) <sup>c</sup>	ρ <sup>d</sup>	SUVA <sub>254</sub> <sup>e</sup>
	H/C	O/C	Aliphatic	Hetero-aliphatic	Aromatic		Carboxyl group (meq/g)	Q <sub>t</sub>	Log K <sub>1</sub>				
NOM1	nd	nd	31	16	19	0.33	nd	nd	nd	1.2	0.5	2.4	3.61
NOM2	0.09	0.83	37	20	19	0.32	12.43	12.51	3.47	1.3	0.75	2.1	2.63
RW	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.76	0.24	3.2	3.63

NOM1: Nordic Reservoir NOM, NOM2: Upper Mississippi River NOM, RW: Tama river water.

<sup>a</sup> International Humic Substances Society.

<sup>b</sup> Aromaticity was computed from aromatic carbon [%]/(aromatic carbon [%] + carbohydrate [%] + aliphatic [%]).

<sup>c</sup> Weight average MW (M<sub>w</sub>) and number average MW (M<sub>n</sub>) were measured using HPSEC.

<sup>d</sup> Polydispersity (ρ) was calculated as M<sub>w</sub>/M<sub>n</sub>.

<sup>e</sup> The specific UV adsorption (SUVA) values were calculated by divided the UV absorbance at 254 nm (m<sup>-1</sup>) by the DOC concentration (mg/L).

**Table 2**  
Characteristics of adsorbents in this study.

Adsorbent	SA (m <sup>2</sup> /g)	PV <sub>Total</sub> (cm <sup>3</sup> /g) [%]	PV <sub>Micro</sub> (cm <sup>3</sup> /g) [%]	PV <sub>Meso</sub> (cm <sup>3</sup> /g) [%]	PV <sub>Macro</sub> (cm <sup>3</sup> /g) [%]	Supplier
AC	1131	0.80 [100]	0.47 [58.6]	0.27 [33.6]	0.07 [8.3]	Wako Chemicals, Japan
CNT	210	0.88 [100]	0.03 [3.4]	0.66 [74.7]	0.20 [22.7]	Alpha Nano, Chinese Academy of Science, China

SA: Surface area (m<sup>2</sup>/g), PV: Pore volume (cm<sup>3</sup>/g), Micro: < 2 nm, Meso: Between 2 and 50 nm, Macro: > 50 nm. The BET surface areas, pore volumes and pore size distributions were measured from nitrogen physisorption data at 77 K obtained with ASAP 2020 analyzer.

were determined by HPSEC unit (Shimadzu Prominence, Kyoto, Japan), a SEC column [Shodex column (SB-803 HQ)], and a mobile phase adjusted to pH 7 [75% phosphate buffer and 25% acetonitrile (Wako Pure Chemicals Ltd, Osaka, Japan)]. Detection of NOM was achieved with a UV detector set at 254 nm. PSS standards (1.0, 4.6, 18, and 67 kDa, Polyscience Inc.) were used as standard MW.

Excitation-emission matrix (EEM) was measured using a fluorescence spectrometer (Shimadzu RF-5300, Kyoto, Japan) and a quartz cuvette (1 cm path length). The range of tested excitation (Ex) wavelength was from 240 to 450 nm at 5 nm intervals, and that of emission (Em) wavelength was from 300 to 600 nm at 2 nm intervals. Raw EEM data were analyzed using the FDOMcorr toolbox (Murphy et al., 2010). Fluorescence intensities are reported in Raman units (RU). The fluorescence index (FI) was determined as the ratio of the emission intensity at 450 nm to that at 500 nm at Ex 370 nm (McKnight et al., 2001). The freshness index (BIX) was also calculated as the ratio of the emission intensity at 380 nm to that at 430 nm at Ex 310 nm (Huguet et al., 2009) (Fig. S2).

### 3. Results and discussions

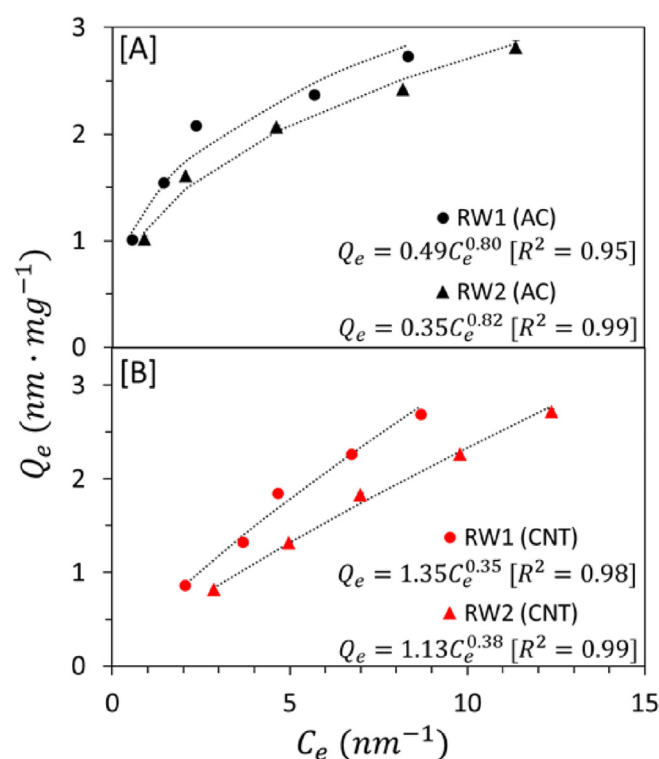
#### 3.1. Adsorption isotherm of NOM on AC and CNT

Fig. 2 shows the adsorption isotherm results on CNT and AC. Freundlich model (Eq. (1)) well fitted the experimental results with R<sup>2</sup> values > 0.95. All model parameters for all experiments were summarized in Table 3.

$$Q_e = K_F C_e^{1/n} \quad (1)$$

where Q<sub>e</sub> (nm<sup>-1</sup>/mg) is the adsorption affinity, C<sub>e</sub> (nm<sup>-1</sup>/L) is the equilibrium concentration, K<sub>F</sub> [(nm<sup>-1</sup>/mg)/(nm<sup>-1</sup>/L)<sup>1/n</sup>] is the Freundlich constant, and 1/n is the Freundlich exponent.

Although the measured surface area of AC was higher than CNT, the adsorption affinity of NOM was higher on CNT than AC as indicated by K<sub>F</sub> values (Table 3). This can be attributed to the difference in the porosity and the pore size distribution between CNT and AC (Table 2). NOM form clusters with an average size around 0.4–4 nm and they can mainly access meso- and macropores of the adsorbents (Karanfil et al., 1999). In this study, micropores, with



**Fig. 2.** Adsorption isotherm for RW1 (i.e. NOM1 + RW) and RW2 (i.e. NOM2 + RW) on [A] AC, and [B] CNT. The experimental data was fitted to Freundlich model (dashed line). The initial NOM concentrations were increased with fixing the CNT concentration at 250 mg/L and equilibrium time at 24 h. The vertical lines show the variations from mean values of duplicate experiments.

pore size less than 2 nm, were dominant in AC, however, CNT showed higher porosity with more than 97% of these pores in the range of meso- and macropores. These observations are in line with previous studies for NOM adsorption on AC and CNT. Kilduff et al. (1996a) reported the preferential adsorption of the lower molecular size natural organic polyelectrolytes by AC from macromolecular solutions obtained from a wide variety of sources. In

**Table 3**  
Parameters of Freundlich model.

Adsorbent	DOM	$K_F$	$1/n$	$R^2$
CNT	RW1	1.35	0.35	0.98
	RW2	1.13	0.38	0.99
AC	RW1	0.49	0.80	0.95
	RW2	0.35	0.82	0.99

The ionic strength was adjusted to 3.4 mM using NaCl. pH was adjusted to  $7.0 \pm 0.2$ .

that study, AC had micropores dominantly (>85%) and it was concluded that the preferential adsorption of small molecules was attributed to pore size distribution of AC (i.e., molecules with smaller size were capable of reaching the adsorbent surface more quickly than larger ones even if the adsorbent pore size was small). In contrast, Hyung and Kim (2008) observed that CNT showed high adsorption affinity of NOM due to its pore size which was accessible by NOM.

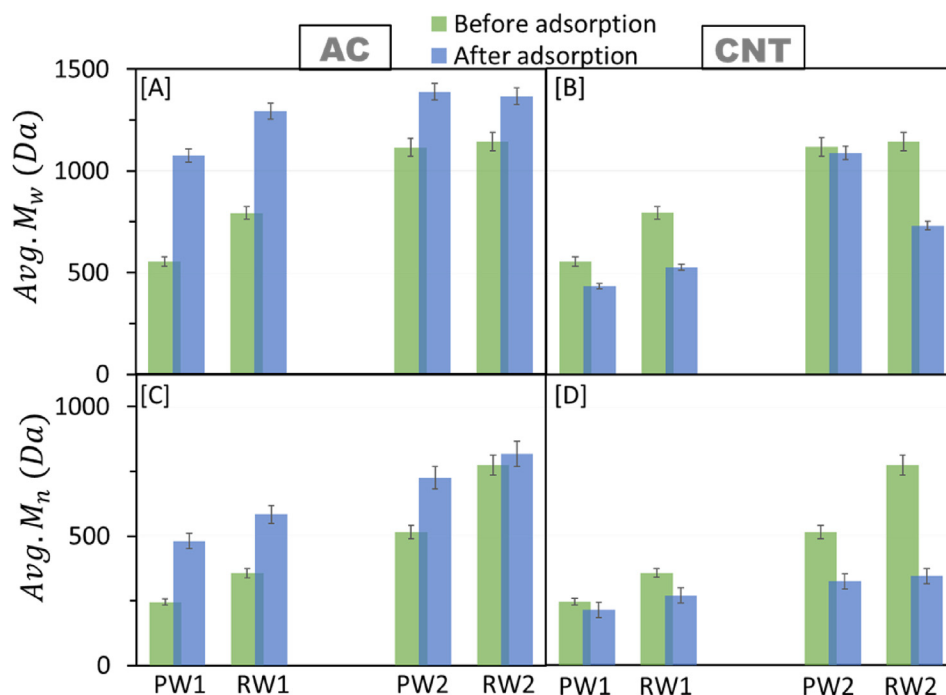
Further,  $SUVA_{254}$  of NOM1, as an indicator of aromaticity, was higher than that of NOM2 (Table 1). Thus, adsorption affinity of NOM1 was higher than NOM2 for both adsorbents. This positive correlation between adsorption affinity and  $SUVA_{254}$  values was previously observed for adsorption of NOM on carbonaceous materials. Karanfil et al. (1999) tested the adsorption of six types of NOM on AC, and found a good correlation between the order of NOM uptake and  $SUVA_{254}$ . Ateia et al. (2017a) reported a strong linear relationship between adsorption affinity of NOM on CNT and  $SUVA_{254}$  values of NOM regardless of the source of NOM (i.e., humic acids with high  $SUVA_{254}$  values showed higher adsorption affinity than fulvic acids with low  $SUVA_{254}$  values). Also, Hyung and Kim (2008) tested adsorption affinity of 9 types of NOM on CNT, and found the adsorption capacity was closely related to the aromatic group content in NOM. For graphene oxide, Cai et al. (2015) observed decreasing of solution  $SUVA_{254}$  values through the organic matter sorption to graphene for 4 types of HA (Suwannee River humic acid standard II, Elliott Soil humic acid standard, Pahokee Peat humic acid standard and Leonardite humic acid

standard), 2 types of FA (Suwannee River fulvic acid standard II and Nordic lake fulvic acid reference), and 2 types of RO isolated NOM (Suwannee River natural organic matter and Nordic lake natural organic matter), that were derived from river, lake, soil or peat, and it indicated that aromatic contents were preferentially adsorbed by graphene.

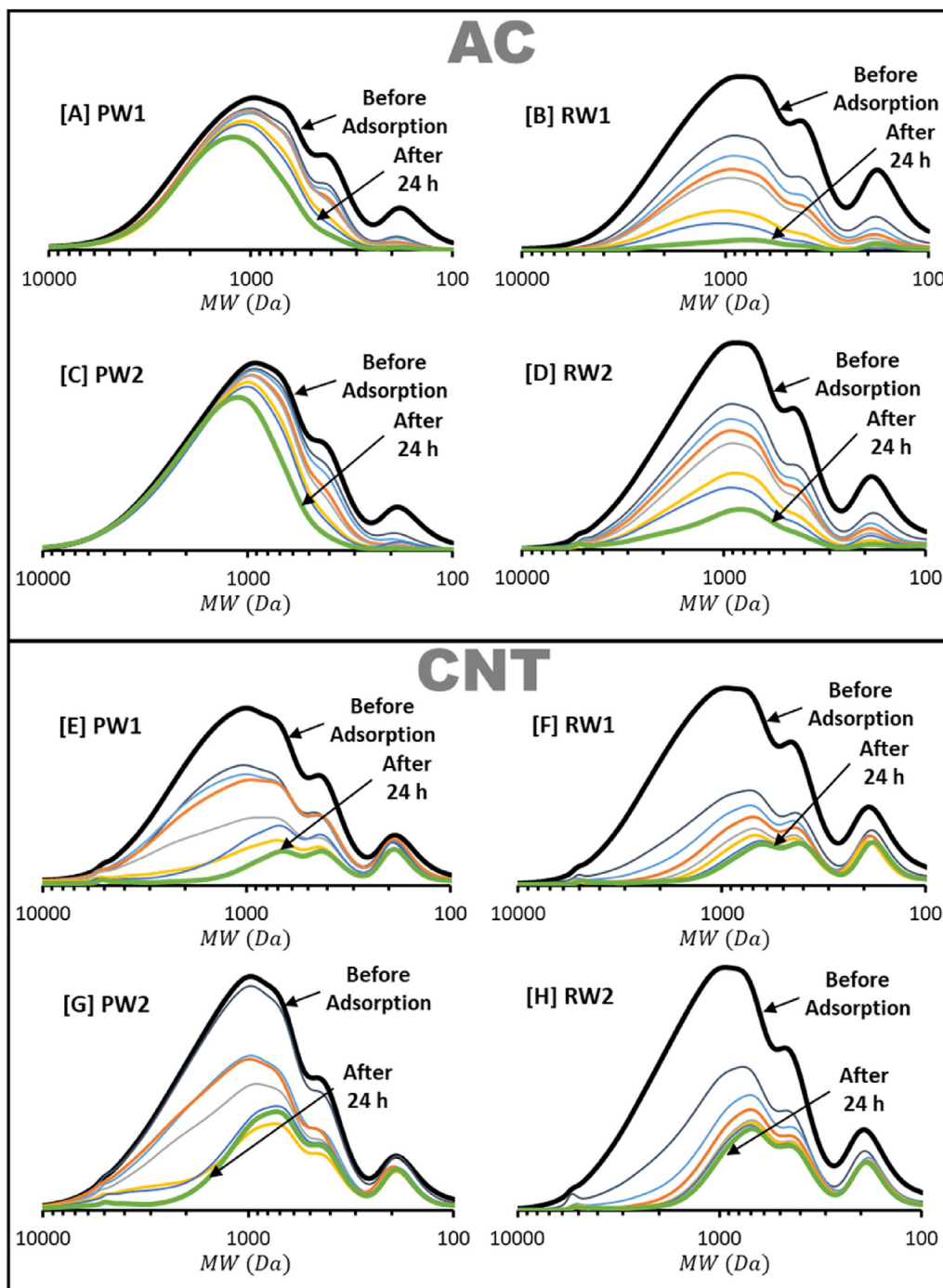
### 3.2. Change in MW distribution after NOM fractionation by AC and CNT

NOM contains mixtures of natural polymers that vary in the aromatic content and adsorption capacities. From the HPSEC measurements,  $M_n$  represents the change in  $M_w$  and  $M_w$  reflects the change in MW distribution (Kothawala et al., 2012). As shown in Table 1, avg.  $M_w$  values were lower for RW (0.76 kDa) than RO isolates samples (1.2–1.3 kDa). This can be attributed to the impact of wastewater effluent that has abundance of low molecular weight compounds as compared to RO isolates (Dong et al., 2010). Interestingly, the fractionation behavior of NOM was different for AC and CNT. Before adsorption, NOM1 had avg.  $M_w$  of 1.2 kDa and avg.  $M_n$  of 0.5 kDa. Meanwhile, NOM2 had avg.  $M_w$  of 1.3 kDa and avg.  $M_n$  of 0.75 kDa. As shown in Fig. 3, the values of avg.  $M_w$  and avg.  $M_n$  for the residual fractions of NOM increased after adsorption on AC and decreased after adsorption on CNT. This indicates that AC removed small NOM fractions before the larger fractions. On the other hand, CNT tended to preferentially remove NOM fractions having higher MW. All experiments were repeated by dissolving NOM1 and NOM2 in ultrapure water (indicated by PW1 and PW2) and they showed a similar trends.

We have further tracked the changes in MW distribution over time for both adsorption (Fig. 4). It should be noticed that AC removed all fractions of NOM, however, CNT did not adsorb NOM fraction with MW < 0.4 kDa. Apparently, this fraction with small MW had hydrophilic character and can not be removed by CNT. Ateia et al. (2017a) reported the similar results of the lack of uptake of the small fraction for adsorption of NOM on CNT, and NOM



**Fig. 3.** Changes in [A], [B] the ave.  $M_w$  and [C], [D] avg.  $M_n$  for PW1, PW2, RW1 and RW2 on AC and CNT.  $C_e$  was  $\sim 3.5 \text{ nm}^{-1}$ , pH was fixed at  $7 \pm 0.2$  and equilibrium time was 24 h.



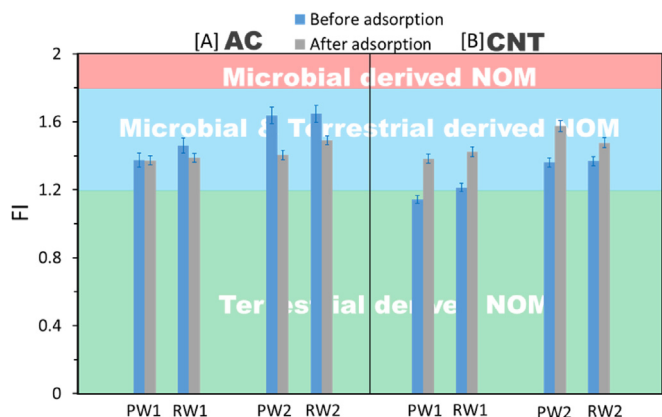
**Fig. 4.** Changes in the molecular compositions weight of PW1, PW2, RW1 and RW2 after adsorption on AC and CNT using HPSEC. Samples were collected at 5 min, 15 min, 30 min, 1 h, 3 h, 6 h and 24 h. Adsorbent concentration was fixed at 250 mg/L and pH was  $7 \pm 0.2$ .

fractions with MW of  $<0.4$  kDa were likely to be hydrophilic that can not be adsorbed by CNT. Nevertheless, the porous nature of AC allowed this small fraction to be adsorbed to the inner pores by diffusion (Kilduff et al., 1996b). This observation was further examined by checking EEM of the residual fractions in the following section.

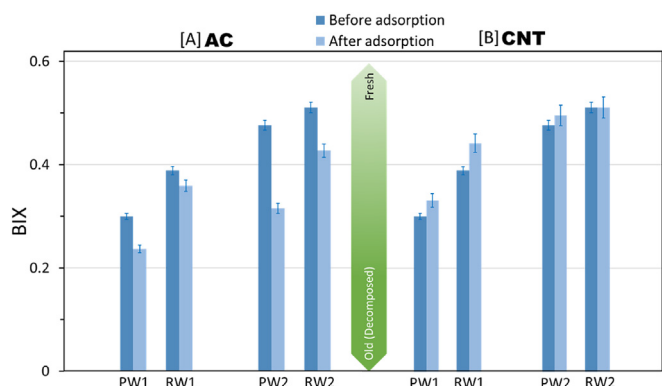
### 3.3. Effect of NOM source and age on the fractionation by AC and CNT

The values of FI reflect the source of NOM (i.e.,  $FI < 1.2$ :

terrestrial derived NOM,  $FI = 1.2$ – $1.8$ : mixture of terrestrial and microbial derived NOM, and  $FI > 1.8$ : microbial derived NOM) (Huguet et al., 2009). Thus, tracking the variations in FI values was previously used to check the changes in NOM during several different treatment processes in water treatment plants (Lavonen et al., 2015) or to monitor the compositional changes in humic substances after ozonation treatments (Rodríguez et al., 2014). In our study, all samples seemed initially to be a mixture of terrestrial and microbial derived NOM with FI values around 1.6. However, the residual NOM after adsorption on AC was different than CNT (Fig. 5). The decrease in FI values in AC experiment suggests that



**Fig. 5.** Changes in value of fluorescence index (FI) of PW1, PW2, RW1 and RW2 after adsorption on [A] AC and [B] CNT.  $C_e$  was  $\sim 3.5 \text{ nm}^{-1}$ , pH was fixed at  $7 \pm 0.2$  and equilibrium time was 24 h.



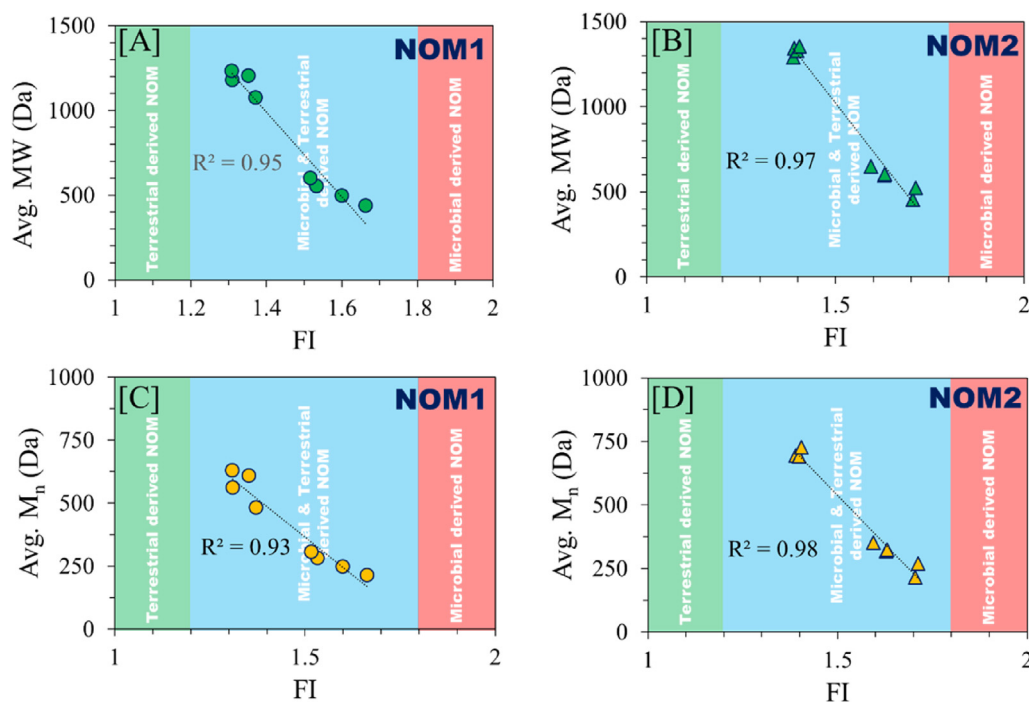
**Fig. 6.** Changes in the values of freshness index (BIX) of PW1, PW2, RW1 and RW2 after adsorption on [A] AC and [B] CNT.  $C_e$  was  $\sim 3.5 \text{ nm}^{-1}$ , pH was fixed at  $7 \pm 0.2$  and equilibrium time was 24 h.

microbial derived NOM were preferentially removed. In the same manner, the increase in FI values after NOM adsorption on CNT showed preferential adsorption of terrestrial derived NOM (Ateia et al., 2017a). Ateia et al. (2017d) and McKnight et al. (2001) reported that terrestrial derived NOM are richer with aromatic moieties and have higher MW than microbial derived NOM. Therefore, these results also support the observations discussed in the previous section of the changes in MW distribution.

In addition, BIX was employed as an indicator of the age or the freshness of the NOM (i.e., NOM with lower BIX values are relatively older than those with higher BIX values) (Lavonen et al., 2015). Unlike the change in FI, BIX values for the residual NOM after adsorption reduced clearly only on AC and the change after adsorption on CNT was not significant (Fig. 6). This decrease indicates the preferential adsorption for freshly produced NOM fractions over decomposed NOM on AC. These freshly produced NOM can be microbial derived, which were characterized by lower C/N ratio and lower aromaticity than decomposed NOM (Hunt and Ohno, 2007; Wang et al., 2015). Our results illustrate that changes in the adsorbent's morphology would influence their preferential adsorption of NOM fractions.

#### 3.4. Tracking changes in $M_w$ and $M_n$ using FI

Previous studies showed that using fluorescence parameters might be used to indicate NOM size (Huguet et al., 2010). In our study, we reported the property of FI to track the change in MW of NOM. Fig. 7 shows that FI has strong correlation with both of in avg.  $M_w$  and avg.  $M_n$  as indicated by  $R^2$  values (0.93–0.98). Lee et al. (2015) combined EEM datasets with parallel factor analysis (PARAFAC) to assess the adsorption affinity of NOM fractions with different molecular size on graphene oxide. They reported a positive relationship between avg.  $M_w$  and the ratio between two PARAFAC components. However, this linear relationship was confirmed only for the range up to 2 kDa of avg.  $M_w$ . Further, Shimabuku et al. (2014) and Mostafa et al. (2014) reported that FI correlated with avg.  $M_w$  of surface waters and wastewaters from



**Fig. 7.** The relationship between fluorescence index (FI) and avg.  $M_w$  [A, B] and avg.  $M_n$  [C, D] for NOM1 and NOM2 after adsorption on AC or CNT.

different sources. Recently, Shimabuku et al. (2017) studied the adsorption of fluorescing NOM granular AC and found a strong correlation between FI values and avg.  $M_w$  of NOM. Thus, they concluded that FI appears to be a better surrogate for NOM molecular sieving than aromaticity. From our results and previous studies, FI is explained as a good indicator for both avg.  $M_w$  and MW distribution of NOM because of high correlations between both FI and  $M_w$ , and FI and  $M_n$ .

#### 4. Conclusions

This paper presented a comprehensive study to compare the molecular sieving of NOM on AC and CNT using different types of NOM. By using a suite of NOM characterization techniques, we concluded the finding as follows:

- Experimental results well-fitted to Freundlich model ( $R^2 > 0.95$ ) and the model parameters indicated NOM had a higher adsorption affinity on CNT than AC.
- AC adsorbed small MW fractions of NOM before the higher MW fractions.
- CNT adsorbed high MW fractions of NOM and the smallest fraction (MW < 0.4 kDa) was not removed probably due to its hydrophilic character.
- FI indicated the preferential adsorption of microbial derived NOM on AC, and terrestrial derived NOM were preferentially adsorbed on CNT.
- BIX indicated the preferential adsorption of freshly produced NOM on AC, while decomposed NOM were preferentially adsorbed on CNT.
- FI linearly correlated to avg.  $M_w$  and avg.  $M_n$ , which suggest that FI can be used to track MW of NOM samples.

Due to the wide variety of NOM samples in natural environments, these findings would further clarify the adsorption behavior of NOM on AC and CNT in natural waters and/or the potential application of CNTs for water treatment. Thus, more studies should be conducted to deeply investigate the effect of water quality parameters (e.g., pH, ionic strength, temperature, etc.) on the molecular sieving of NOM on different adsorbents. Further studies should also examine molecular sieving of NOM using sensitive techniques (e.g., mass spectroscopy) to elucidate its relationship to the formation of DBPs or ROS.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.03.197>.

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