Removal of natural organic matter in drinking water sources by carbon nanomaterials

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Abstract

Carbon nanomaterials are effective adsorbents for water treatment. The objective of this study is to investigate the natural organic matter (NOM) removal from drinking water with combined coagulation processes using single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Conventional coagulation using aluminum sulfate (alum) and ferric chloride ($FeCl_3$) was also conducted using Ulutan Lake water (ULW) samples collected in four seasons. The removal was characterized by ultraviolet absorbance at 254 nm (UV_{254}) and dissolved organic carbon (DOC). The proposed process was more effective than using alum and $FeCl_3$. The highest removal occurred for $FeCl_3$ with SWCNTs in winter (94.13% DOC and 96.14% UV_{254}). In spring and fall, DOC (90% and 84.63%) and UV_{254} (95.87% and 88.8%) removal was highest when using $FeCl_3$ with MWCNTs. The DOC removal was lowest in summer (67–71% for alum and 72–79% for $FeCl_3$). Summer UV254 removal was similar to DOC removal for combined coagulation. Hydrophobic NOM in winter ULW samples is more easily removed by SWCNTs than by MWCNTs, while MWCNTs were more effective in other seasons. The results explain that the combined coagulation process is more effective than the conventional coagulants alone in different seasons.

Keywords: Natural Organic Matter; Carbon Nanotubes; Coagulation; Drinking Water

1. Introduction

Natural organic matter (NOM) plays an important role in water treatment. Research interest in the structure and properties of NOM in an aquatic environment is growing since they can cause undesirable color, taste, and odor [1]. The NOM in raw water has to be characterized to understand its complexity and heterogenicity [2,3]. NOM is generally divided into hydrophobic, transphilic, and hydrophilic groups based on resin adsorption affinity (e.g., XAD-8 and XAD-4) [4,5]. Total organic matter (TOC), dissolved organic matter (DOC), and UV absorbance at 254 nm (UV_{254}) are common surrogate parameters for quantifying NOM reactivity in different surface waters [6]. Specific ultraviolet absorbance (SUVA) is a significant indicator for defining hydrophobicity. High SUVA means that the organic matters are largely hydrophobic, whereas low SUVA indicates mainly hydrophilic organic compounds [7,8,9]. Coagulation is one of the most common methods for removing NOM in water [10,11]. Multivalent salts such as aluminum sulfate (alum) and $FeCl_3$ have been widely used in water treatment for years [12]. Several studies achieved 45–80% removal of NOM with combined coagulation and adsorption [13].

The objective of this study is to investigate the removal of NOM in drinking water sources through a combination of coagulation with CNTs. Single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) were investigated for their removal efficiencies in the presence of alum and $FeCl_3$ as metal coagulants. Ulutan Lake water (ULW), an important potential source of drinking water, was used in experiments to determine NOM concentrations for each season.

2. Materials and methods

2.1 Source water and sampling

Representative water samples were collected from raw water entering Ulutan Lake at four different times in Zonguldak, Turkey. Ulutan Lake is a reservoir that provides nearly 35000 m^3 of raw water to the drinking-water treatment plant of Zonguldak city. The sampling was done in all four seasons from 2014 to 2015 (with the seasons starting in September 2014, January 2015, April 2015, and July 2015). The physicochemical characteristics of ULW are given in Table 1.

Table 1. Physicochemical characteristics of Ulutan raw water samples (September 2014 – July 2015).

Parameters	Units	Seasons			
		Winter*	Spring*	Fall*	Summer*
pH	-	8.11	7.75	7.70	7.43
Turbidity	NTU	16.5	8.61	5.3	3.42
Conductivity	μS/cm	511	611	593	684
Total hardness	mgCaCO$_3$/L	127	142	130	150
Temperature	^{0}C	5.2	12.1	16.2	25.3
Br$^-$	μg/L	70	90	110	135
TOC	mg/L	6.1	5.85	4.89	5.13
UV$_{254}$	cm^{-1}	0.19	0.14	0.11	0.095
SUVA	L/mg.m	3.12	2.41	2.24	1.85
THMFP	μg/L	363.88	255.64	214.22	180.25

*Average concentration of three months in one season.

2.2. Coagulants

SWCNTs (1–2-nm diameter, 5–30-μm length, purity >90%) were obtained from Cheap Tubes, Inc. (Brattleboro, Vermont, USA). MWCNTs (50–80-nm diameter, 5–9-μm length, purity >90%) were purchased from Sigma Aldrich (St. Louis, Missouri, USA). Aluminum sulfate (Al$_2$SO$_4$*18H$_2$O) and ferric chloride (FeCl$_3$) were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Stock solutions of 10 g/L for both coagulants were prepared by adding 10 g of each chemical to 1 L of ultrapure deionized water and stirring overnight. The coagulants were stored in a refrigerator at 4°C for the duration of the study.

2.3. Purified CNTs

One gram of raw CNTs was dispersed into a 100-ml flask containing 40 ml of mixed acid solutions (30 ml of HNO$_3$ +10ml of H$_2$SO$_4$) for 24 h to remove metal catalysts (Ni nanoparticles). After cleaning, the CNTs were again dispersed in a 100-ml flask containing 40 ml of mixed acid solutions, which were then shaken in an ultrasonic cleaning bath (Branson 3510 Ultrasonic Cleaner, Connecticut, USA) and heated at 80◦C in a water bath for 2 h to remove amorphous carbon. After cooling to room temperature, the mixture was filtered with a 0.45-μm glass-fiber filter, and the solid was washed with deionized water until the pH of the filtrate was 7. The filtered solid was then dried at 80◦C for 2 h to obtain the purified CNTs. This test procedure of purified CNTs has been used in other researchers in previous CNT studies [14,15].

2.4. Jar test procedure for coagulation experiments

Prior to the jar test, stock solutions containing 5000 mg/L of the SWCNTs and MWCNTs were prepared by adding 1 g of the CNTs to 200 mL of DI water and stirring with a magnetic stirrer at 600 rpm. The applied coagulant doses ranged from 0 to 100 mg/L. The jar test setup procedures were performed using a Phipps and Bird six-paddle jar test apparatus. The jars were round beakers with 1-L capacity. The jar test mixing conditions for the first setup were as follows: rapid mixing at 150 rpm for 2 min, flocculation at 30 rpm for 15 min and at 20 rpm for 20 min.

At similar coagulant dosages, the ferric chloride consistently outperformed alum for DOC removal. A dosage of 100 mg/L of alum and $FeCl_3$ resulted in the maximum DOC removal in ULW sample coagulation. However, based on economic and engineering considerations, 80 mg/L was selected as the optimum coagulant dosage. When the combined coagulation was analyzed, preliminary testing was applied to determine the optimal coagulant dose for raw water samples. For ULW, the optimum combined coagulant dosage was determined as 40 mg/L. After the jar tests were completed, the coagulated water samples were passed through 0.45-μm membrane filters for DOC analysis.

2.5. Analytical methods

DOC analyses were performed with a Shimadzu TOC-5000 analyzer equipped with an auto sampler [16] according to the combustion-infrared method described in Standard Method 3510 B [16]. The sample is injected into a heated reaction chamber packed with a platinum-oxide catalyst oxidizer to oxidize organic carbon into CO_2 gas. UV_{254} absorbance measurements were performed in accordance with Standard Method 5910 B [16] using a Shimadzu 1608 UV–vis spectrophotometer at a wavelength of 254 nm with a 1-cm quartz cell. The samples were first passed through a 0.45-μm membrane filter to remove turbidity, which can interfere with the measurement. Distilled ultra-filtered (DIUF) water was used as the background correction in the spectrophotometer. THM concentrations were determined with liquid–liquid extraction method according to standard method 6232 B [16].

3. Results and Discussion

3.1. DOC removal with coagulation using SWCNTs

Figure 1 shows the change in DOC when increasing the doses of SWCNTs with the addition of alum and $FeCl_3$ in the jar-testing procedure. The largest DOC removal using only SWCNTs was recorded in winter (81.13%), followed by fall (63.5%), spring (69.08%), and summer (56.23%). As mentioned, winter showed the highest DOC removal efficiency, while summer had the lowest when using only SWCNTs. For all seasons, a significant increase of about 10% in the removal of DOC occurred with the addition of alum. Removal of 80% or higher was achieved in winter. These findings are explained by the different properties of SWCNTs and MWCNTs. Since the surface area of SWCNTs is larger than that of MWCNTs, and their diameter is also smaller, the removal of DOC in winter is higher than the removal of hydrophilic NOM in other seasons. This outcome has been determined in other studies that investigated the removal of NOM [17].
With the addition of alum, the removal percentages of DOC remained constant at SWCNT doses of 50 mg/L or greater, with 88.7% for winter, 72% for fall, 79.2% for spring, and 67.11% for summer (Figure 1). Many studies have shown that $FeCl_3$ is more effective than alum because of the higher charge density of ferric coagulants [18]. With the addition of $FeCl_3$, the removal

percentages of DOC were 94.13% in winter, 76% in fall, 83% in spring, and 72.64% in summer. With the application of FeCl₃, the maximum removal percentage of DOC is achieved in winter (>90%). However, the lowest was observed in summer as about of 65%, followed by spring and fall (75% and 70%, respectively).
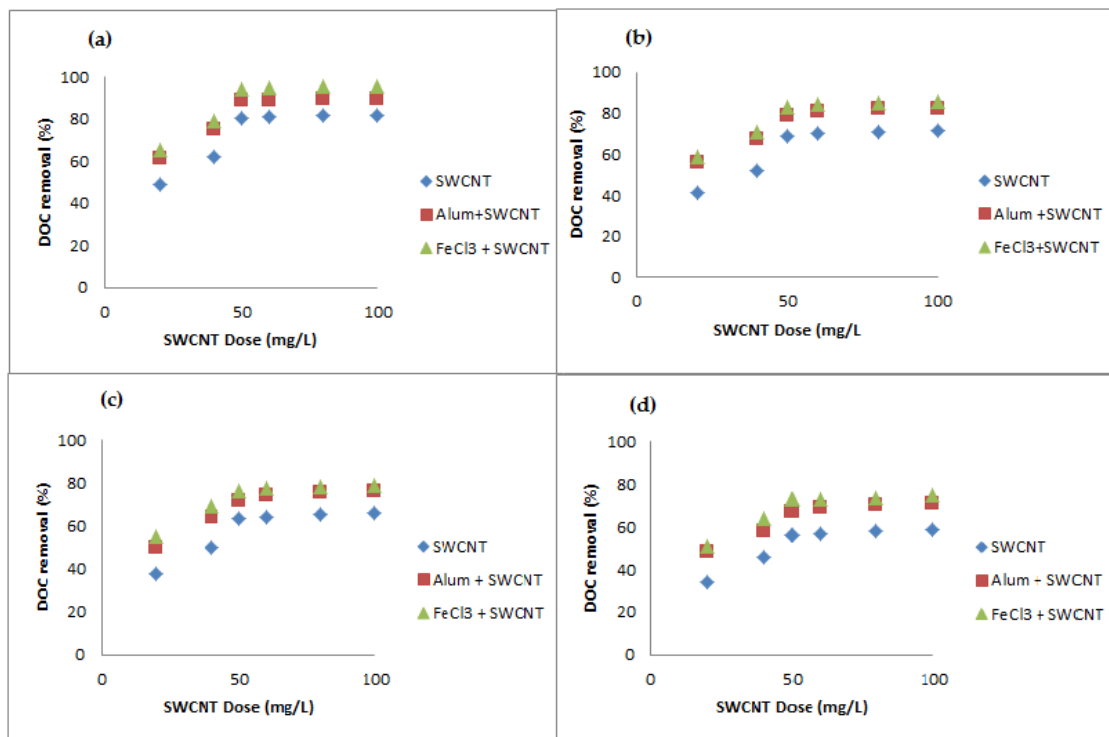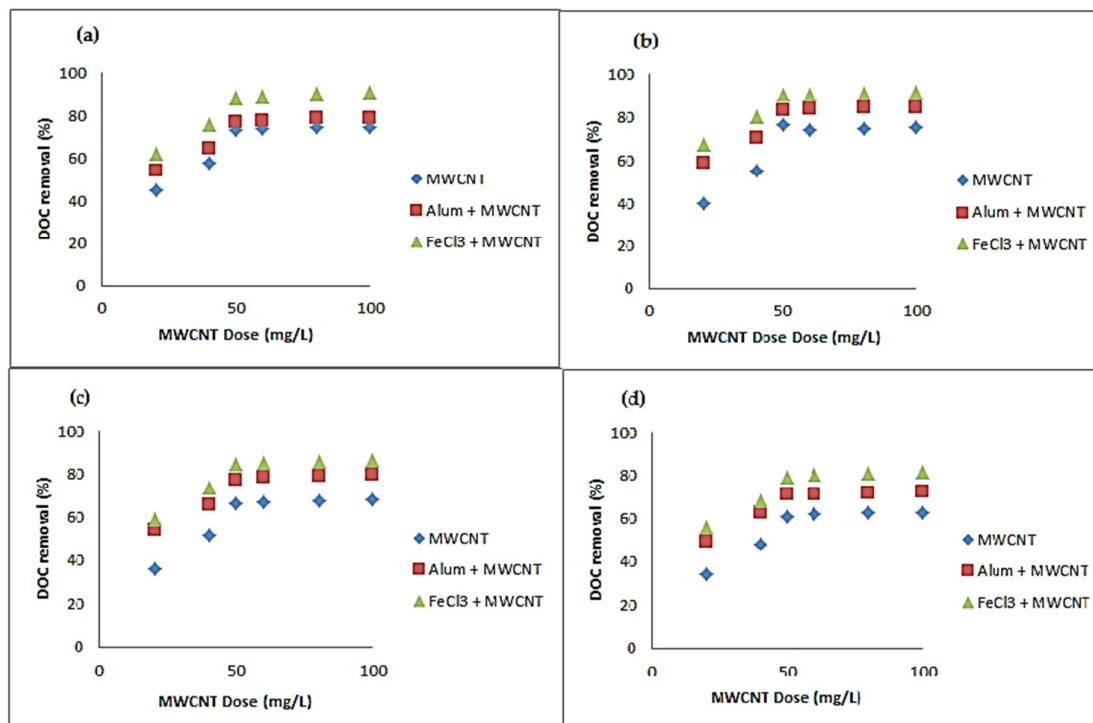

Figure 1. Removal of DOC by SWCNTs and combined coagulation using jar test for **(a)** winter, **(b)** spring, **(c)** fall, and **(d)** summer. Optimum coagulant dose = 50 mg /L.

3.2. DOC removal with coagulation using MWCNTs

Figure 2 compares the removal of DOC when increasing the doses of MWCNTs with the addition of chemical coagulants during the jar-test procedure. Similar to SWCNTs, the highest percentage of DOC removal using only MWCNTs was obtained as about 73% in winter. Also, although the removal percentage of DOC was slightly lower in winter using only MWCNTs (73.4%) than using SWCNTs (81.13%), the remaining seasons experienced relatively high levels of NOM removal using only MWCNTs, with removal percentages of 76.54%, 66.44%, and 61% for spring, fall, and summer, respectively (Figure 2). The MWCNTs indicated a significantly higher removal capacity for DOC in spring, fall, and summer.
Compared to the other seasons, the significant increase in the removal capacity of the MWCNTs detected in summer could be the result of the ionic strength. The ionic strength of ULW in summer (conductivity = 684 µS/cm) is higher than that of spring (conductivity = 611 µS/cm), fall (conductivity = 593 µS/cm), and winter (conductivity = 511 µS/cm). Therefore, the increasing ionic strength generally resulted in increased DOC removal with MWCNTs. Moreover, the higher ionic strength resulted in reduced electrostatic interactions with the CNTs. Thus, MWCNTs are more effective in the removal of the hydrophilic portion of NOM. The increase in the removal capacity of the MWCNTs detected in summer could be a result of the increase in the pH (pH 8.11) compared with that in winter (pH 7.43), spring (pH 7.75), and fall (pH 7.70) (Table 1). As the pH increases, the NOM may become less compact and more

separated owing to increased electrostatic repulsion, resulting in an overall increase in removal capacity.

Figure 2. Removal of DOC by MWCNTs and combined coagulation using jar test for **(a)** winter, **(b)** spring, **(c)** fall, and **(d)** summer. Optimum coagulant dose = 50 mg /L.

As shown Figure 2, the addition of alum increases DOC levels in all four seasons. The removal of DOC also remained constant at MWCNTs doses of 50 mg/L or greater (74.21% in winter, 83.1% in spring, 77.5% in fall, and 71.1% in summer). With the addition of FeCl$_3$, the maximum removal of DOC in all four seasons occurred at MWCNT doses of 50 mg/L.

The combined coagulation experiments demonstrate that the hydrophobic NOM in ULW was more easily removed by SWCNTs than by MWCNTs, whereas the hydrophilic NOM in the three seasons other than winter was more easily removed by MWCNTs than by SWCNTs.

4. Conclusion

The coagulation experiments showed that SWCNTs were generally more powerful than MWCNTs for removing the hydrophobic portion of NOM in winter because of the larger surface area of the SWCNTs. Although the hydrophilic removal in spring and fall was slightly higher with MWCNTs and conventional coagulant, and the majority of hydrophilic NOM was removed by using MWCNTs and FeCl$_3$ in summer. Combined coagulation treatment generally resulted in higher removal of DOC in ULW samples. DOC removal was 63.05% with the use of only FeCl$_3$ in winter, whereas the removal ratio increased by about 30% with the combined use of FeCl$_3$ and SWCNTs. The removals were lower when using only conventional coagulants in spring and fall, while the highest was recorded with FeCl$_3$ and CNTs. For example, the DOC removal with only FeCl$_3$ was about 50% in spring and nearly 44% in fall, but the addition of SWCNTs increased the removals to 83% in spring and nearly 77% in fall. Furthermore, among the other seasons, using FeCl$_3$ and MWCNTs produced the largest amount of DOC (80.5%) removal in summer.

The combined coagulation treatment using carbon nanomaterials was more efficient than the conventional coagulant in the removal of NOM from ULW. The removal percentage of the hydrophilic portion of NOM is very low for coagulation with only alum or $FeCl_3$, but the removal increases significantly with the combined coagulation. This phenomenon may result from the CNTs having л–л electron donor–acceptor interactions and hydrophobic interactions for the removal mechanism. Depending on their relative surface charge, the CNTs are more effective in NOM removal when using the combined coagulation process. This finding has been confirmed by many studies [19,20]. Therefore, the combined coagulation process can be used in water treatment plants instead of conventional coagulation in order to remove NOM effectively.

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