



# The use of carbon nanomaterials for removing natural organic matter in drinking water sources by a combined coagulation process

Kadir Özdemir<sup>1</sup>

## Abstract

Carbon nanomaterials are effective adsorbents for water treatment. This study examines natural organic matter (NOM) removal from drinking water with combined coagulation processes using single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). Conventional coagulation using aluminum sulfate (alum) and ferric chloride ( $\text{FeCl}_3$ ) was also conducted using Ulutan Lake water (ULW) samples collected in four seasons. The removal was characterized by ultraviolet absorbance at 254 nm ( $\text{UV}_{254}$ ) and dissolved organic carbon (DOC). The proposed process was more effective than using alum and  $\text{FeCl}_3$ . The highest removal occurred for  $\text{FeCl}_3$  with SWCNTs in winter (94.13% DOC and 96.14%  $\text{UV}_{254}$ ). In spring and fall, DOC (90% and 84.63%) and  $\text{UV}_{254}$  (95.87% and 88.8%) removal was highest when using  $\text{FeCl}_3$  with MWCNTs. The DOC removal was lowest in summer (67–71% for alum and 72–79% for  $\text{FeCl}_3$ ). Summer  $\text{UV}_{254}$  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 reveal that the proposed process is more effective than the conventional coagulants alone in different seasons.

## Keywords

Natural organic matter, carbon nanotubes, coagulation, drinking water, water treatment

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## 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 it can cause undesirable color, taste, and odor.<sup>1</sup> Moreover, NOM is a major organic precursor for disinfection by-products (DBPs) that can form during chlorination, such as trihalomethanes and haloacetic acids.<sup>2–6</sup> The characteristics of NOM may change significantly with the water source and biochemical cycles of the surrounding environments.<sup>7,8</sup> For example, the range of organic structures of NOM can vary seasonally due to intensive rain events, snowmelts, floods, and droughts.<sup>7,9–12</sup>

The NOM in raw water has to be characterized to understand its complexity and heterogeneity.<sup>13–16</sup> NOM is generally divided into hydrophobic, transphilic, and hydrophilic groups based on resin adsorption affinity.<sup>3,17</sup> Total organic matter (TOC), dissolved organic matter (DOC), and UV absorbance

<sup>1</sup> Department of Environmental Engineering, Bülent Ecevit University, İncivez, Zonguldak, Turkey

### Corresponding author:

Kadir Özdemir, Department of Environmental Engineering, Bülent Ecevit University, İncivez, 67100 Zonguldak, Turkey.

Email: kadirozdemir73@yahoo.com



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at 254 nm ( $UV_{254}$ ) are common surrogate parameters for quantifying NOM reactivity in different surface waters.<sup>18</sup> Hydrophobic NOM consists of humic and fulvic acids and is rich in activated functional groups, such as phenolic structures and conjugated double bonds. Hydrophilic NOM is composed of mostly aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates, and sugars.<sup>3,8,19</sup> 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.<sup>7,20,21</sup>

Coagulation is one of the most common methods for removing NOM in water.<sup>22–24</sup> Multivalent salts such as aluminum sulfate (alum) and ferric chloride ( $FeCl_3$ ) have been widely used in water treatment for years.<sup>25,26</sup> The coagulation process is highly effective for the removal of hydrophobic fractions of NOM like humic acid,<sup>27</sup> but the hydrophilic fraction cannot be removed effectively.<sup>27–29</sup> Many researchers have presented other water treatment technologies for NOM removal, including membrane filtration and adsorption technology (e.g. powdered activated carbon and granular activated carbon).<sup>30,31</sup> Several studies achieved 45–80% removal of NOM with combined coagulation and adsorption.<sup>32</sup> Although activated carbon is the most commonly used adsorbent in water treatment,<sup>33,34</sup> carbon nanotubes (CNTs) have been used as an effective adsorbent for the removal of heavy metals, chemicals, and biological components from water in recent years.<sup>35–38</sup> Several studies have shown that CNTs can be effective in the removal of various types of NOM.<sup>39–42</sup>

The application of CNTs has several advantages in many functional areas, including water treatment. However, they also have significant impacts on safety and the environment.<sup>43</sup> The release of CNTs into the environment can have harmful impacts on natural ecosystems.<sup>43</sup> In addition, CNTs might damage DNA and could have harmful effects on organs if introduced into the body.<sup>44,45</sup> The biological effects of CNTs occur if they can enter the body or a biological system at a sufficient level.<sup>46</sup> CNTs also have the potential to influence biochemical processes or cell biology processes and directly or indirectly affect biological systems.<sup>46</sup> Research has shown that CNTs can enter the body through the skin, respiratory tract, or gastrointestinal tract. They can deposit in several organs within the body and may thus cause many adverse biological effects.<sup>47–50</sup>

Interactions between CNTs and NOM are likely to alter trends in DBP formation. In addition to direct reaction with chlorine-based disinfectants, CNTs are likely to influence DBP production through their ability to concentrate NOM on their surfaces through sorption.<sup>51–53</sup> Thus, it is reasonable to expect that these same surface functionalities may also react with chemical disinfectants to yield undesirable by-products with adverse effects on human health. Many of them have been classified as possible human carcinogens and have been regulated by several international regulatory agencies worldwide.<sup>54</sup> Also, CNTs can leak from water purification operations into

the surrounding water, soil, and air. The fate and transport processes that can act on nanomaterials after their release include photochemical transformation, oxidation and reduction, dissolution, precipitation, adsorption, and biotransformation, among other biogeochemically driven processes.<sup>55,56</sup> They could be hydrolytically disintegrated and could be oxidized photochemically and biologically in water matrices. CNTs could react with various biomolecules such as DNA, RNA, proteins, and enzymes, which might lead to toxic effects, especially on aquatic flora and fauna. For example, nanomaterials can react with humic acids and result in a nanoscale coating,<sup>57</sup> which is comparable to protein coronas in mammalian systems.<sup>58</sup>

These factors strongly change the aggregation, deposition, and toxic properties of CNTs.<sup>59,60</sup> Novel synthesis methods have produced new properties of CNTs that have attracted attention from governments because of their uncertain effects on the environment and human health.<sup>61</sup> The presence of CNTs could potentially stimulate the oxidation of other metals in aquatic and terrestrial environments and release toxic ions.<sup>62</sup> However, several methods could be applied to remove environmental CNTs. First, enzymatic treatments are effective in degrading CNTs upon release into the environment. Zhao et al.<sup>63</sup> presented an eco-friendly enzymatic way to degrade and eliminate transformed CNTs from the environment. Membrane filtration has also been used to eliminate CNTs from solutions,<sup>64</sup> and a simple coagulation technique was effective for collecting CNTs after use.<sup>65</sup> According to the Health and Safety Executive,<sup>66</sup> waste containing CNTs must be classified and labeled as hazardous waste. Therefore, after purification of CNTs used in experimental studies, the CNT waste must be sealed carefully using double layers of polyethylene bags. Combustion of waste containing CNTs is preferred as pyrolysis above 500°C completely oxidizes the CNTs.

In recent years, many studies have focused on CNTs and their adsorption properties. CNT adsorbent materials can remove a wide range of heavy metals, organic compounds, and biological contaminants, including bacteria and viruses. For example, Long and Yang<sup>67</sup> reported a significantly higher dioxin removal efficiency with CNTs than with activated carbon. Li et al.<sup>68</sup> showed that CNTs are good fluoride adsorbents with superior capability to activated carbon. Lu et al.<sup>69</sup> demonstrated that both  $NaClO$ -oxidized single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs) are effective  $Zn^{2+}$  sorbents. Amin et al.<sup>70</sup> found that CNTs (especially SWCNTs) are efficient and rapid adsorbents for removing ethylbenzene. This method could therefore be used to maintain high water quality. Chen et al.<sup>71</sup> investigated the adsorption of chlorophenols on pristine and functionalized SWCNTs (hydroxylated SWCNTs and carboxylated SWCNTs). Duijneveldt et al.<sup>72</sup> focused on the small-angle scattering studies of SWCNTs dispersed with sodium dodecyl sulfate in order to characterize the adsorption.

The aim of this study is to examine the removal of NOM in drinking water sources through a combination of coagulation with CNTs. SWCNTs and MWCNTs were investigated

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

Parameters	Units	Seasons			
		Winter <sup>a</sup>	Spring <sup>a</sup>	Fall <sup>a</sup>	Summer <sup>a</sup>
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	mg=CaCO <sub>3</sub> /L	127	142	130	150
Temperature	°C	5.2	12.1	16.2	25.3
Br <sup>-</sup>	μg/L	70	90	110	135
TOC	mg/L	6.1	5.85	4.89	5.13
UV <sub>254</sub>	cm <sup>-1</sup>	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

TOC: total organic matter; UV<sub>254</sub>: ultraviolet absorbance at 254 nm; SUVA: specific ultraviolet absorbance; THMFP: trihalomethane formation potential.  
<sup>a</sup>Average concentration of 3 months in one season.

for their removal efficiencies in the presence of alum and FeCl<sub>3</sub> as metal coagulants. Ulutan Lake water (ULW), an important source of drinking water, was used in experiments to determine NOM concentrations for each season. SWCNTs and MWCNTs are used as coagulant materials to remove NOM in ULW by a new water treatment technique involving a novel combined coagulation process.

## Materials and methods

### 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 35,000 m<sup>3</sup> of raw water to the drinking water treatment plant of Zonguldak. The sampling was done in all four seasons from 2014 to 2015 (with seasons starting in September 2014, January 2015, April 2015, and July 2015). The physicochemical characteristics of ULW are given in Table 1. The ranges throughout the year were as follows: pH: 7.43–8.11; turbidity: 3.42–16.5 Nephelometric Turbidity Unit (NTU); conductivity: 511–684 μS/cm; total hardness: 127–150 mg CaCO<sub>3</sub>/L; bromide: 70–135 μg/L; and temperature: 5.2–25.3°C. The NOM surrogate parameters TOC, UV<sub>254</sub>, SUVA, and trihalomethane formation potential (THMFP) had ranges of 4.89–6.1 mg/L, 0.095–0.19 per centimeter, 1.85–3.12 L/mg·m, and 180.25–363.88 μg/L, respectively. Raw water samples were stored in 5-L glass containers and rapidly shipped to the laboratory. The samples were passed through 0.45-μm membrane filter papers within 24 h and stored in a refrigerator at 4°C to retard microbial activity prior to use.

### 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<sub>2</sub>SO<sub>4</sub>·18H<sub>2</sub>O) and FeCl<sub>3</sub> 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.

### 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<sub>3</sub> +10 mL of H<sub>2</sub>SO<sub>4</sub>) 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 (Model Branson 3510 Ultrasonic Cleaner, Connecticut, NISH, 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 by other researchers in previous CNT studies.<sup>73,74</sup> After purifying the CNTs, the CNT waste was sealed carefully using double layers of polyethylene bags and transported to solid waste incineration plants with other hazardous wastes from the laboratory.<sup>66</sup>

### 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 r/min. 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 r/min for 2 min, flocculation at 30 r/min for 15 min and at 20 r/min for 20 min.

At similar coagulant dosages, the FeCl<sub>3</sub> consistently outperformed alum for DOC removal. These results are consistent with other studies.<sup>75,76</sup> A dosage of 100 mg/L of alum and FeCl<sub>3</sub> 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. The optimum combined coagulant dosage for ULW was determined as 40 mg/L. After the jar tests were completed, the coagulated water samples were passed through 0.45- $\mu$ m membrane filters for DOC analysis.

### Chlorination procedure

THMFP measurements were conducted in accordance with standard method 5710 B of the American Public Health Association.<sup>77</sup>

### Analytical methods

DOC analyses were performed with a Shimadzu TOC-5000 analyzer equipped with an auto sampler<sup>77</sup> according to the combustion–infrared method described in standard method 3510 B.<sup>77</sup> The sample is injected into a heated reaction chamber packed with a platinum-oxide catalyst oxidizer to oxidize organic carbon into carbon dioxide gas. UV<sub>254</sub> absorbance measurements were performed in accordance with standard method 5910 B<sup>77</sup> 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- $\mu$ m membrane filter to remove turbidity, which can interfere with the measurement. Distilled ultrafiltered 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.<sup>77</sup>

## Results

### Seasonal variations of NOM in ULW

Table 2 illustrates the impact of seasonal variations of NOM in ULW. The concentrations of NOM were characterized with the surrogate parameters DOC, UV<sub>254</sub>, SUVA, and THMFP, which give information about the NOM structure and reactivity in raw water. The highest average DOC concentrations were observed in winter (5.44 mg/L), whereas the lowest were determined in summer (4.89 mg/L). Similarly, the highest UV<sub>254</sub> measurements were recorded in winter (0.176 per centimeter) and the lowest value of 0.113 per centimeter was measured in summer.

Hydrophobicity is determined using the SUVA parameter (the UV<sub>254</sub> absorbance divided by the DOC concentration). The high SUVA in winter (3.25 L/mg·m) indicates that the organic matter is composed of hydrophobic organic materials with high molecular weight. The low SUVA (1.88 L/mg·m) in summer shows that ULW contains organic materials that are mostly of aliphatic carbon and nitrogenous compounds.<sup>9,13,78</sup> These observations illustrate that the range of organic components of NOM in ULW changes mainly in winter owing to storm water runoff after rainfall events, snowmelts in mountain regions, or flooding.<sup>11–13</sup> Furthermore, the ULW in summer also experiences the diffusion of sediments, plankton, and bacteria

**Table 2.** Seasonal characterization of surrogate parameters of NOM in ULW.

Season	DOC <sup>a</sup> mg/L	UV <sub>254</sub> <sup>a</sup> Per cm	SUVA <sup>a</sup> L/mg·m	THMFP <sup>a</sup> $\mu$ g/L
Winter	5.44	0.176	3.25	340.55
Spring	4.89	0.122	2.51	246.73
Fall	5.19	0.113	2.37	227.46
Summer	5.13	0.122	2.2	214.76

DOC: dissolved organic carbon; UV<sub>254</sub>: ultraviolet absorbance at 254 nm; SUVA: specific ultraviolet absorbance; THMFP: trihalomethane formation potential.

<sup>a</sup>Average concentration of 3 months in one season.

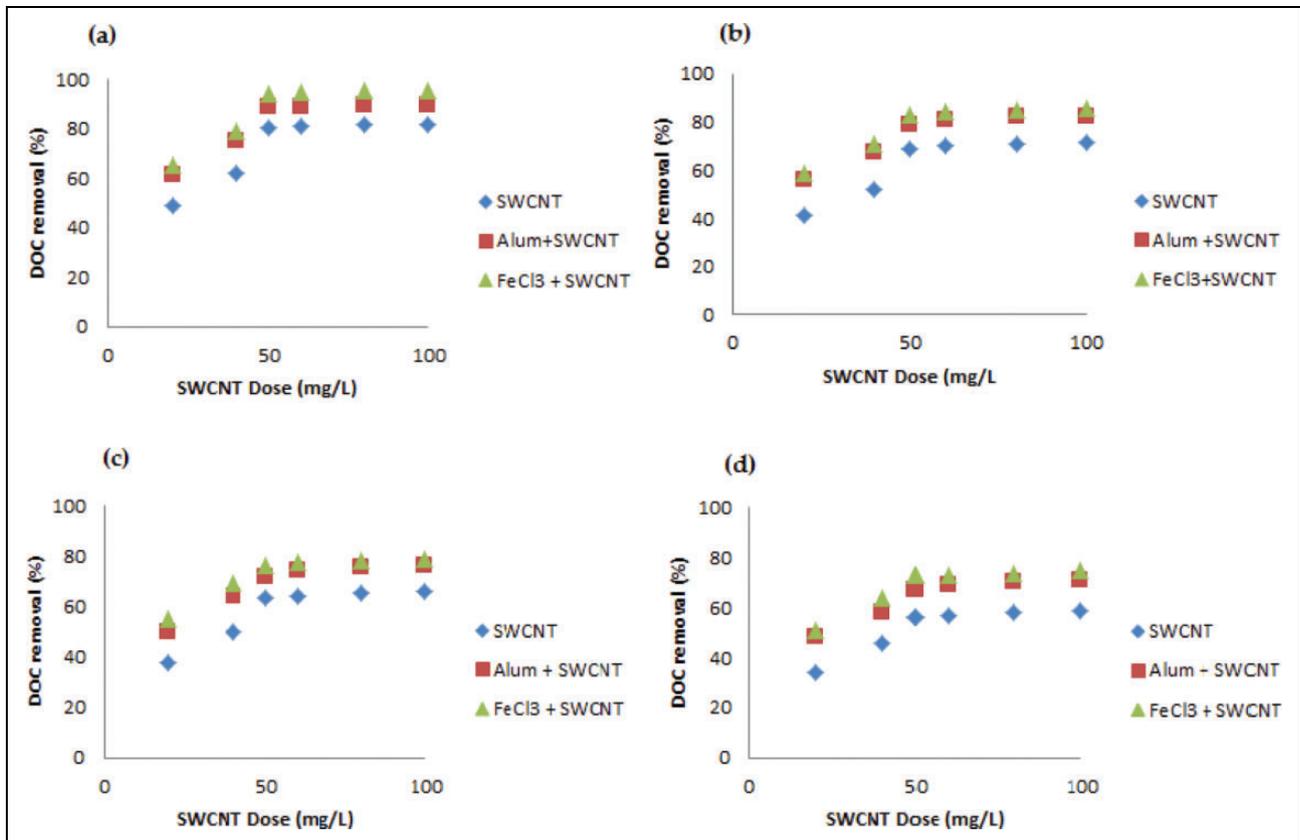
remains, in addition to the production of effluents from wastewater treatment plants. ULW contains mainly high concentrations of hydrophilic NOM with low molecular weights.<sup>79,80</sup>

The THMFP values in winter, spring, fall, and summer were measured as 340.55, 246.73, 227.46, and 214.76  $\mu$ g/L, respectively. These results suggest that higher DOC and UV<sub>254</sub> values produce more THMs. As the hydrophobic organic matter is chlorinated with different chlorine dosages, higher THM concentrations form in ULW samples than the hydrophilic fraction of NOM with respect to SUVA levels. Similar results were obtained in other studies.<sup>4,78</sup>

### Combined coagulation using CNTs

**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<sub>3</sub> in the jar test 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 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.<sup>30,31</sup>

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<sub>3</sub> is more effective than alum because of the higher charge density of ferric coagulants.<sup>81,82</sup> With the addition of FeCl<sub>3</sub>, the removal percentages of DOC were 94.13% in winter, 76% in fall, 83% in spring, and



**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. DOC: dissolved organic carbon; SWCNT: single-walled carbon nanotube.

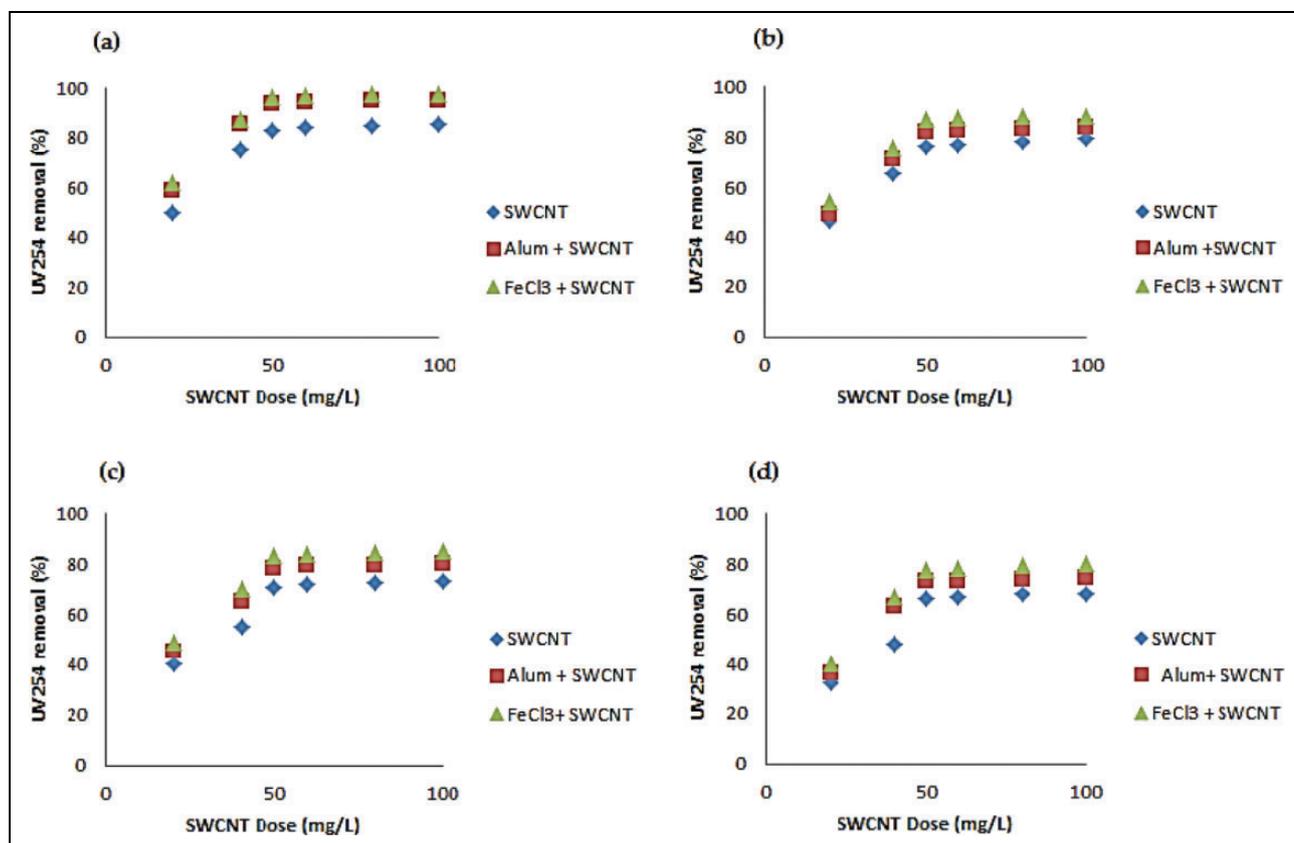
72.64% in summer. With the application of FeCl<sub>3</sub>, the maximum removal percentage of DOC is achieved in winter (>90%). However, the lowest was observed in summer as about of 65%, followed by spring and fall (75% and 70%, respectively). Previous studies have explained that coagulation is not effective for the removal of the hydrophilic fraction of NOM,<sup>83,84</sup> which is why the removal ratio of DOC was lower in summer.

**UV<sub>254</sub> removal with coagulation using SWCNTs.** UV<sub>254</sub> is a surrogate organic parameter for defining the aromatic content of NOM in water. Figure 3 compares the removal of UV<sub>254</sub> when increasing the doses of SWCNTs with the addition of alum and FeCl<sub>3</sub> coagulants for four seasons. The percentages removed according to UV<sub>254</sub> using only SWCNTs were about 82%, 76%, 71%, and 65% for winter, spring, fall, and summer, respectively (Figure 2). High UV<sub>254</sub> removals of 93.74% were obtained with the application of alum and SWCNTs in winter, with 81.6% in spring, 78.32% in fall, and 71.87% in summer. Higher UV<sub>254</sub> removal was observed with FeCl<sub>3</sub> + SWCNT than with alum. The greatest UV<sub>254</sub> removal of 96.14% was determined in winter using FeCl<sub>3</sub> + SWCNT. The other UV<sub>254</sub> removals by FeCl<sub>3</sub> + SWCNT were 86.6% in spring, 83.21% in fall, and 77.68% in summer. This result

shows that the large aromatic portion of NOM in winter was preferentially removed by the coagulation process, and the removal percentages of hydrophobic compounds were higher than those of hydrophilic compounds. These results are consistent with other studies.<sup>13,81,85</sup>

Comparing Figures 1 and 2, the UV<sub>254</sub> removal was higher than the DOC removal for all seasons. For instance, although the percentage of DOC removal using alum + SWCNT was 88.7% in winter, the percentage of UV<sub>254</sub> removal was 93.74% under the same conditions. This observation could be explained by UV<sub>254</sub> reflecting the more aromatic compounds in the structure of NOM. Compared to DOC, UV<sub>254</sub> is a better indicator for the reactivity of the compounds that comprise aquatic humic matters than for the DOC present in the ULW samples. Therefore, it is concluded that coagulation generally removes a large amount of UV-absorbing substances in water and to a greater extent than DOC.

**DOC removal with coagulation using MWCNTs.** Figure 3 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



**Figure 2.** Removal of UV254 by SWCNTs and combined coagulation using jar test from (a) winter, (b) spring, (c) fall, and (d) summer. Optimum coagulant dose = 50 mg/L. UV<sub>254</sub>: ultraviolet absorbance at 254 nm; SWCNT: single-walled carbon nanotube.

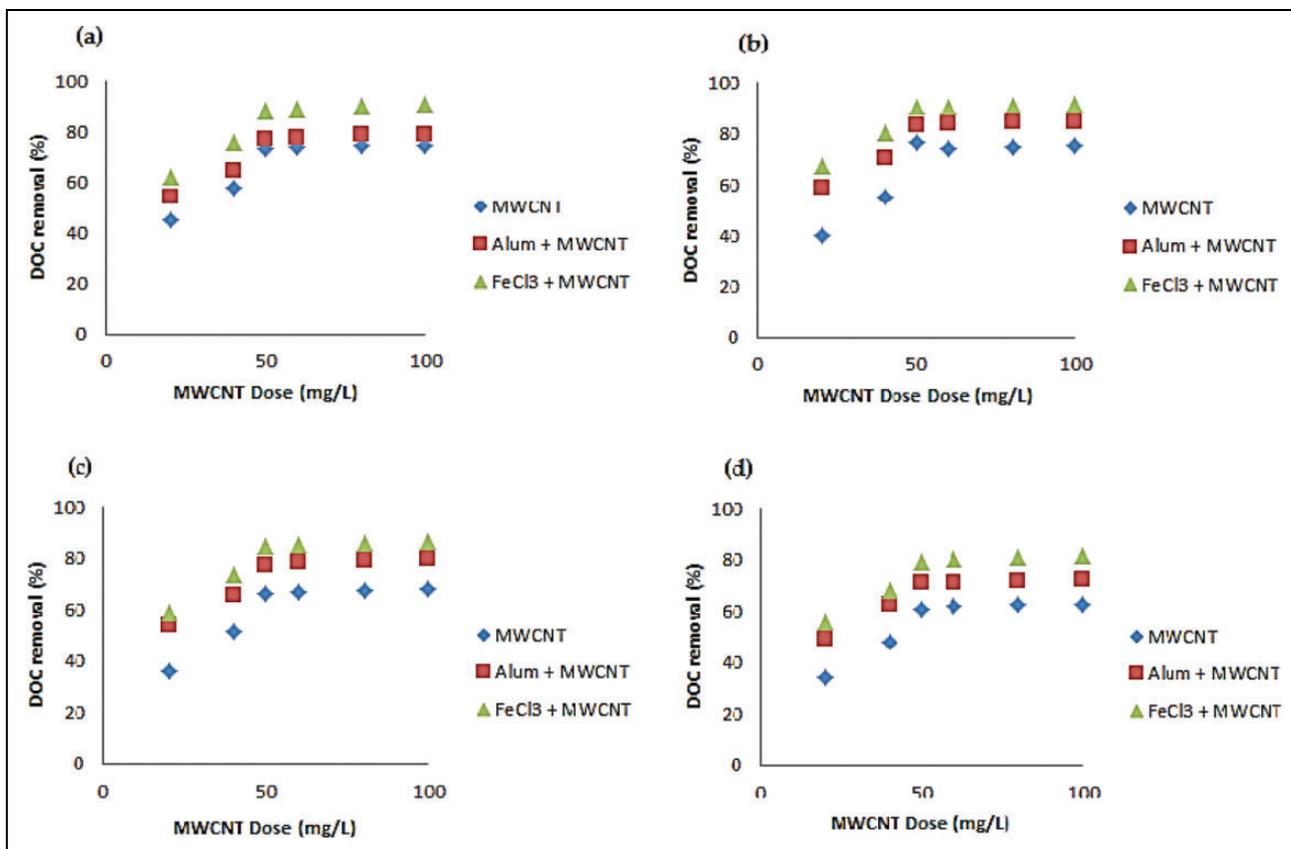
removal percentage of DOC was slightly lower in winter when using only MWCNTs (73.4%) than when using SWCNTs (81.13%), the remaining seasons experienced relatively high levels of NOM removal using only MWCNTs, with removal percentages of 76.54%, 66.44%, and 61% for spring, fall, and summer, respectively (Figure 3). 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  $\mu\text{S}/\text{cm}$ ) is higher than that of spring (conductivity = 611  $\mu\text{S}/\text{cm}$ ), fall (conductivity = 593  $\mu\text{S}/\text{cm}$ ), and winter (conductivity = 511  $\mu\text{S}/\text{cm}$ ). 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. These observations are consistent with other studies on removal of NOM.<sup>4,22,27,28</sup> 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.

As shown in Figure 3, the addition of alum increases DOC levels in all four seasons. The removal of DOC also remained constant at MWCNT 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<sub>3</sub>, 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 (Table 3).

**UV<sub>254</sub> removal with coagulation using MWCNTs.** Figure 4 shows the removal of UV<sub>254</sub> in all four seasons in ULW samples during the combined coagulation experiments. The percentage removal of UV<sub>254</sub> using only MWCNTs was 72.2% in winter and 68.29% in summer. The highest UV<sub>254</sub> removal using only MWCNTs was recorded in spring (80.2%), followed by fall (76.61%). It was concluded that the coagulation process was more



**Figure 3.** 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. DOC: dissolved organic carbon; MWCNT: multiwalled carbon nanotube.

**Table 3.** The highest DOC removals from ULW with combined coagulation.

Season	DOC removal (%)			
	Alum + SWCNT	Alum + MWCNT	FeCl <sub>3</sub> + SWCNT	FeCl <sub>3</sub> + MWCNT
Winter	88.70	77.21	94.13	88.06
Spring	79.2	83.1	83.0	90
Fall	72	79.98	76.41	84.63
Summer	67.11	71.1	72.64	79.1

DOC: dissolved organic carbon; ULW: Ulutan Lake water; SWCNT: single-walled carbon nanotube; MWCNT: multiwalled carbon nanotube.

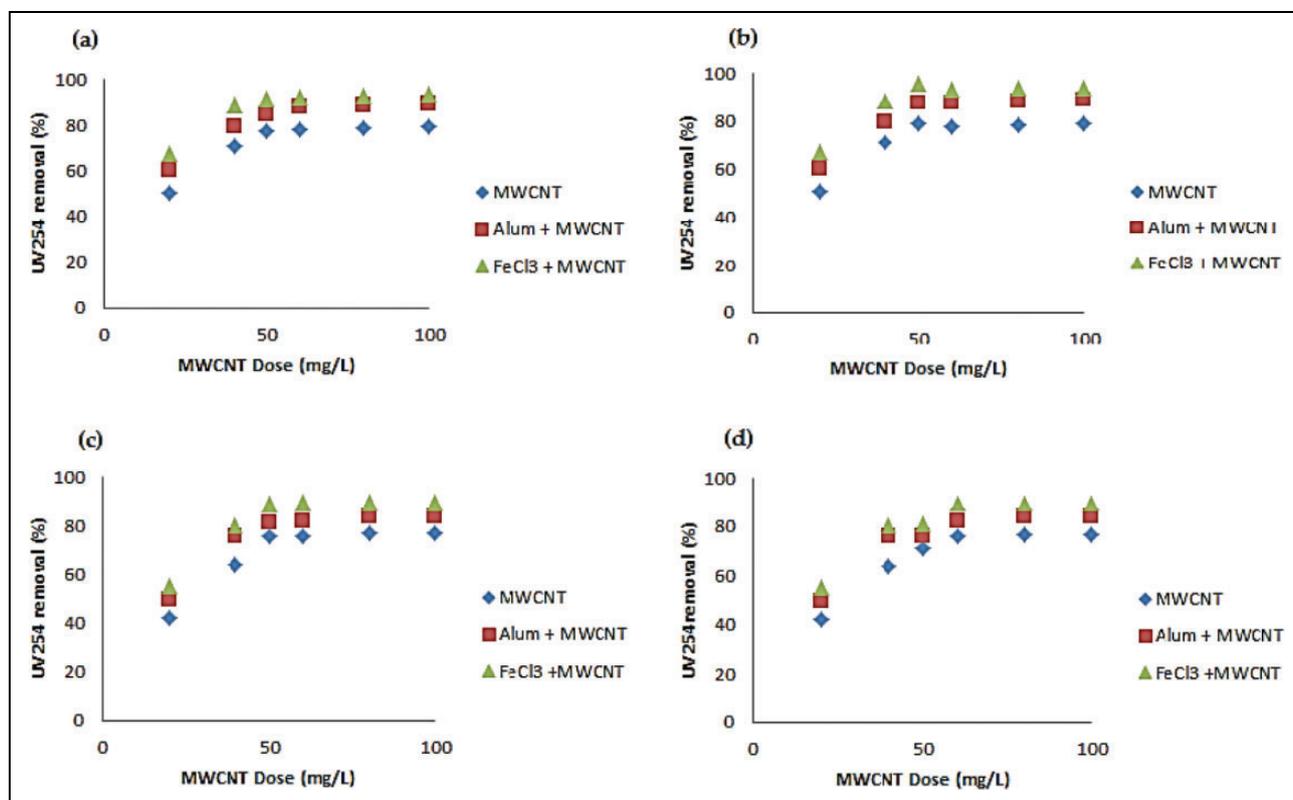
effective on NOM that includes a greater amount of UV absorbing sites or activated functional groups in aromatic compounds.

As shown in Figure 4, UV<sub>254</sub> was always removed to a greater extent than DOC. The application of alum + MWCNT doses greater than 50 mg/L was similar to that observed with SWCNTs, with 77.35% removal in winter, 81.12% in fall, 87.76% in spring, and 76.23% in summer. This result shows that while the increases in UV<sub>254</sub> removal changed with increasing doses of alum + SWCNTs in winter, higher removal percentages of UV<sub>254</sub> were determined with the application of MWCNTs

and conventional coagulants. Moreover, the greatest percentage of UV<sub>254</sub> removal was observed in spring (95.87%) with the addition of FeCl<sub>3</sub> doses greater than 50 mg/L. As a result, the combined coagulation was more effective at removing UV<sub>254</sub>-absorbing materials than DOC (Table 4).

**Comparison between only conventional coagulation (alum and FeCl<sub>3</sub>) and combined coagulation process**

Figures 5 and 6 compare the removal percentages of DOC and UV<sub>254</sub> using only conventional and combined coagulation processes. In winter, high DOC and UV<sub>254</sub> removal percentages (>80%) were determined when using the combined coagulation. When using only alum, the DOC and UV<sub>254</sub> removals were 51.65% and 59.78%, respectively. Higher DOC and UV<sub>254</sub> removals were observed when using only FeCl<sub>3</sub> (63.05% and 69.57%) than with alum. A significant increase was seen when FeCl<sub>3</sub> was combined with SWCNTs compared to the use of only FeCl<sub>3</sub>. For all seasons, DOC and UV<sub>254</sub> removals were low for both alum and FeCl<sub>3</sub> alone, while high DOC and UV<sub>254</sub> removals were observed with combined coagulation. The highest DOC (94.13%) and UV<sub>254</sub> (96.14%) removals were obtained by combining coagulation with FeCl<sub>3</sub> +



**Figure 4.** Removal of UV<sub>254</sub> by MWCNTs and combined coagulation using jar test for (a) winter, (b) spring, (c) fall, and (d) summer. Optimum coagulant dose = 50 mg/L. UV<sub>254</sub>: ultraviolet absorbance at 254 nm; MWCNT: multiwalled carbon nanotube.

**Table 4.** The highest UV<sub>254</sub> removals from ULW with combined coagulation.

Season	UV <sub>254</sub> removal (%)			
	Alum + SWCNT	Alum + MWCNT	FeCl <sub>3</sub> + SWCNT	FeCl <sub>3</sub> + MWCNT
Winter	93.74	77.35	96.14	91.42
Spring	81.6	87.76	86.6	95.87
Fall	78.32	81.12	83.21	88.8
Summer	71.87	76.23	77.68	80.8

UV<sub>254</sub>: ultraviolet absorbance at 254 nm; SWCNT: single-walled carbon nanotube; MWCNT: multiwalled carbon nanotube.

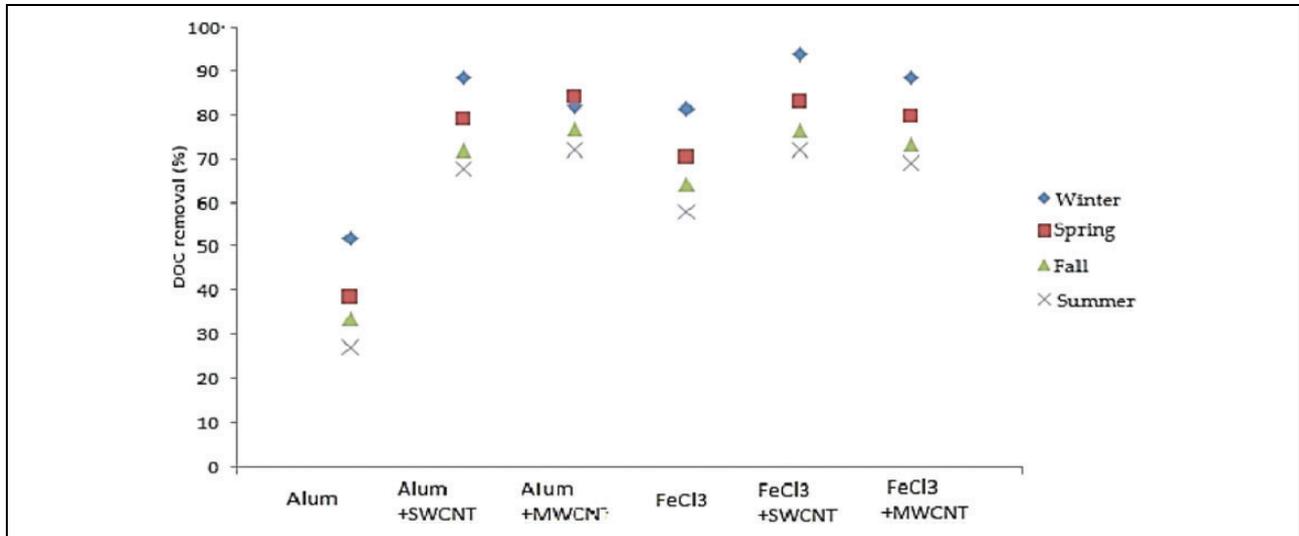
SWCNTs. DOC and UV<sub>254</sub> removals in summer were lower than in other seasons with removal percentages of 27.29% and 32.5% when alum was used, while they were 40.15% and 46.83% when FeCl<sub>3</sub> was used. The use of FeCl<sub>3</sub> with CNTs provided the highest removal percentage of DOC and UV<sub>254</sub> in spring (90% and 95.87%), followed by the fall (84.69% and 88.80%). Another trend was observed for DOC and UV<sub>254</sub> removal using alum, which produced the highest DOC and UV<sub>254</sub> removal alone and combined with SWCNTs (88.7% and 93.74%) in winter.

Higher NOM removal percentage was observed in winter using SWCNTs with conventional coagulants compared

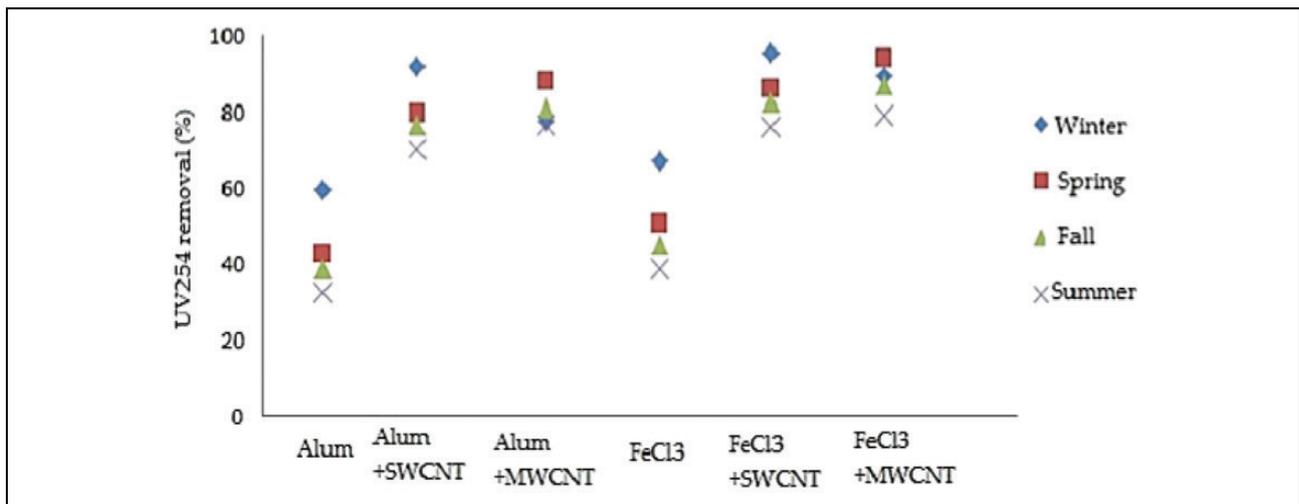
with other seasons, which was expected because of the larger molecular size and increased hydrophobicity of the NOM. However, NOM removal in fall, spring, and summer was higher when using MWCNTs and conventional coagulants. This result could be explained by the hydrophilic portion of NOM. The removal of hydrophilic NOM by combined coagulation is more difficult than hydrophobic NOM removal.

## Discussion

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 the conventional coagulant, the majority of hydrophilic NOM was removed by using MWCNTs and FeCl<sub>3</sub> in summer. Combined coagulation treatment generally resulted in higher removal of DOC and UV<sub>254</sub> in ULW samples. DOC and UV<sub>254</sub> removals were 63.05% and 68.75% with the use of only FeCl<sub>3</sub> in winter, whereas the removal ratio increased by about 30% with the combined use of FeCl<sub>3</sub> and SWCNTs. The removals were lower when using only conventional coagulants in spring and fall, while the highest was recorded with FeCl<sub>3</sub> and CNTs. For example, the DOC removal with only FeCl<sub>3</sub> was about 50% in



**Figure 5.** Comparison of DOC removal using conventional coagulation (only alum and FeCl<sub>3</sub>) and combined coagulation processes. Optimum alum and FeCl<sub>3</sub> dose = 80 mg/L and combined coagulant dose = 50 mg/L. DOC: dissolved organic carbon.



**Figure 6.** Comparison of UV<sub>254</sub> removal using conventional coagulation (only alum and FeCl<sub>3</sub>) and combined coagulation processes. Optimum alum and FeCl<sub>3</sub> dose = 80 mg/L and optimum combined coagulant dose = 50 mg/L. UV<sub>254</sub>: ultraviolet absorbance at 254 nm.

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<sub>3</sub> and MWCNTs produced the largest amount of DOC (80.5%) and UV<sub>254</sub> (84.6%) removal in summer.

Along with the potential changes in the physical characteristics of the CNTs, the change in content of the water source due to seasonal changes may also contribute to the NOM removal with a dependence on the type of CNTs. For instance, the pH value in summer (pH 8.11) is higher than that in winter (pH 7.43) with the coagulation using MWCNTs. Compared to SWCNTs, the removal of DOC and UV<sub>254</sub> is significantly higher in summer with coagulation using MWCNTs. Figures 5 and 6 compare the removal percentages of DOC and UV<sub>254</sub> using coagulation only and combined coagulation. In winter, DOC and UV<sub>254</sub>

removals were higher than 80% when using combined coagulation. However, the removal percentages were around 50–70% when using alum or FeCl<sub>3</sub> only. For all seasons, the highest DOC and UV<sub>254</sub> removals were 94.13% and 96.14% when using FeCl<sub>3</sub> and SWCNTs, respectively (Table 4). As shown in Table 3, the lowest DOC and UV<sub>254</sub> removals were determined when using only alum as 27.29% and 32.5% in summer, followed by FeCl<sub>3</sub> (40.15% and 46.83%).

Another important water quality parameter that affects NOM removal is the ionic strength. The outcomes demonstrate that increases in ionic strength are caused by the increased DOC and UV<sub>254</sub> removal due to the chemical and physical structure of NOM in ULW in all four seasons. Similar observations were determined by previous studies on CNTs and NOM removal.<sup>42,73,74</sup>

The combined coagulation treatment using carbon nano-materials 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  $\text{FeCl}_3$ , but the removal increases significantly with the combined coagulation. This phenomenon may result from the CNTs having  $\pi$ - $\pi$  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.<sup>25,26,41,42</sup> Because of the harmful effects on human health and the environment, the CNT waste was transported to solid waste incinerators with other hazardous wastes from the laboratory after purifying, where they can completely oxidize at above  $500^\circ\text{C}$  through pyrolysis.<sup>66</sup> 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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