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Removal of UV254 in Drinking Water Sources using Carbon Nanomaterials by a Combined Coagulation Process

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Abstract. The objective of this study is to investigate the ultraviolet absorbance at 254 nm (UV254) 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 (FeCl3) was also conducted using Ulutan Lake water (ULW) samples collected in four seasons. The proposed process was more effective than using alum and FeCl3. UV254 was always removed to a greater extent than dissolved organic carbon (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 UV254 removal changed with increasing doses of alum + SWCNTs in winter, higher removal percentages of UV254 were determined with the application of MWCNTs and conventional coagulants. Further, the greatest percentage of UV254 removal was determined in spring (95.87%) with the addition of FeCl3 doses greater than 50 mg/L. The results explain that the combined coagulation process is more effective than the conventional coagulants alone in different seasons for UV254 removal in ULW.[1]

Keywords: UV254, 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 (UV254) 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]-[9]. Coagulation is one of the most common methods for removing NOM in water [10], [11]. Multivalent salts such as aluminum sulfate (alum) and FeCl3 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 UV254 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

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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 m3 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 ULW 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	mgCaCO3/L	127	142	130	150
Temperature	0C	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
UV254	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. 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_2SO_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].

2.3. Coagulation Procedure

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 FeCl3 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.

2.4. Analytical Methods

DOC analyses were performed with a Shimadzu TOC-5000 analyzer equipped with an auto sampler 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 CO2 gas. UV254 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. UV254 Removal with Coagulation using SWCNTs

UV_{254} is a surrogate organic parameter for defining the aromatic content of NOM in water. Figure 1 compares the removal of UV_{254} when increasing the doses of SWCNTs with the addition of alum and $FeCl_3$ coagulants for four seasons. The percent removal of UV_{254} using only SWCNTs was about 82%, 76%, 71%, and 65% for winter, spring, fall, and summer, respectively (Figure 1). High UV_{254} 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_{254} removal was observed with of $FeCl_3$ + SWCNT than with alum. The greatest UV_{254} removal was determined in winter using $FeCl_3$ + SWCNT as 96.14%. The other UV_{254} removals by $FeCl_3$ + 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 [13], [17], [18].

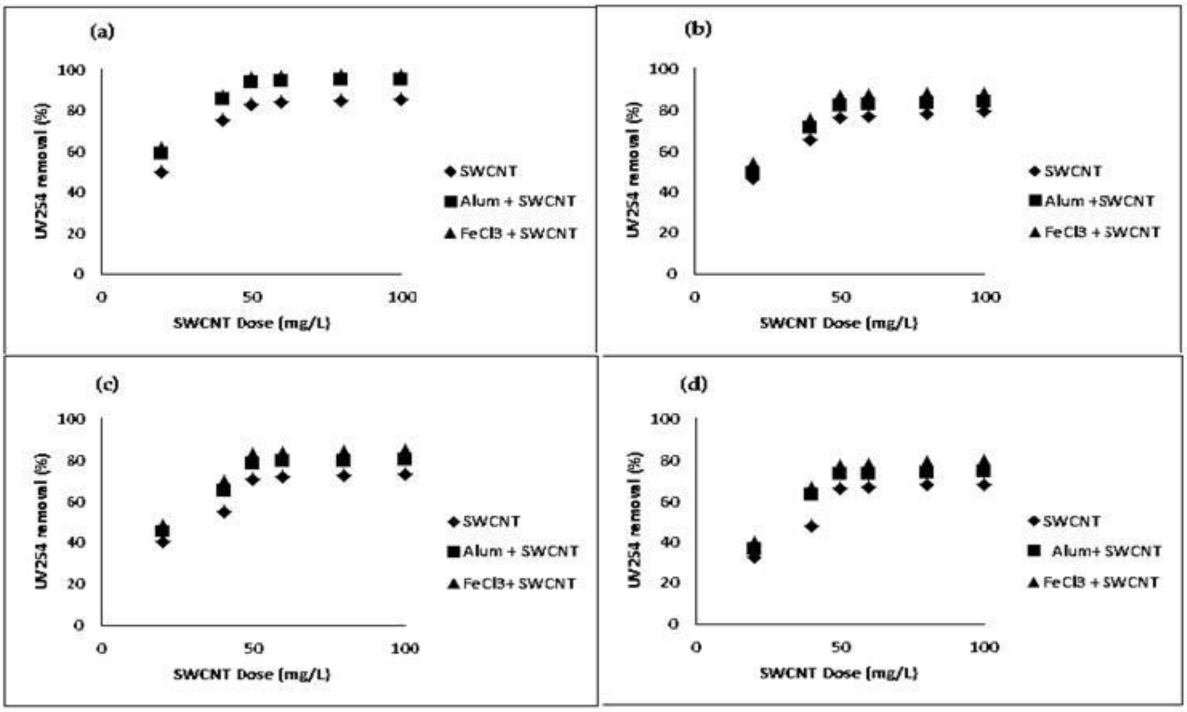

Fig. 1: Removal of UV254 by SWCNTs and combined coagulation using jar test from (a) winter, (b) spring, (c) fall, and (d) summer. Optimum coagulant dose = 50 mg /l.

3.2. UV254 Removal with Coagulation using MWCNTs

Figure 2 shows the removal of UV_{254} in all four seasons in ULW samples during the combined coagulation experiments. The percentage removal of UV_{254} using only MWCNTs was 72.2% in winter and 68.29% in summer. The highest UV_{254} removal using only MWCNTs was recorded in spring (80.2%), followed by fall (76.61%). It was concluded that the coagulation process was more effective on NOM that includes a greater amount of UV absorbing sites or activated functional groups in aromatic compounds.

As shown in Figure 2, 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 has shown that while the increases in UV_{254} removal changed with increasing doses of alum + SWCNTs in winter, the higher removal percentages of UV_{254} were determined with the application of MWCNTs and conventional coagulants. Moreover, the greatest percentage of UV_{254} removal was observed in spring (95.87%) with the addition of $FeCl_3$ doses greater than 50 mg/L.

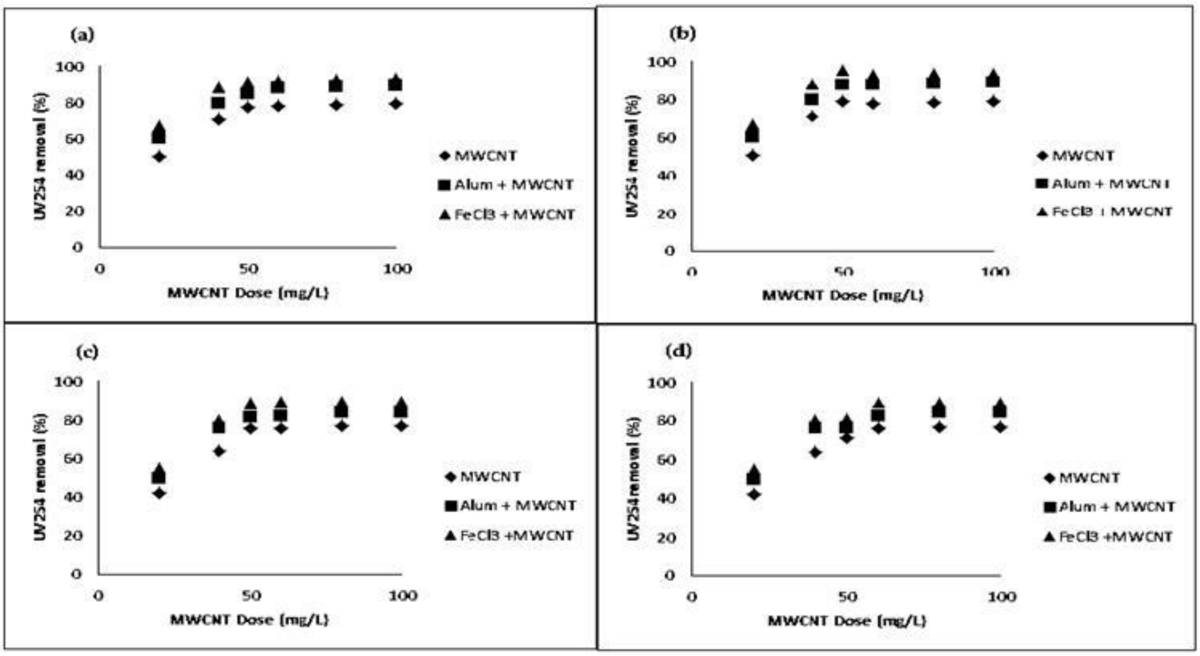

Fig. 2: Removal of UV254 by MWCNTs and combined coagulation using jar test for (a) winter, (b) spring, (c) fall, and (d) summer. Optimum coagulant dose = 50 mg /l.

4. Conclusion

The coagulation experiments showed that SWCNTs were generally more powerful than MWCNTs for UV_{254} removal in winter because of the larger surface area of the SWCNTs. Combined coagulation treatment generally resulted in higher removal of UV_{254} in ULW samples. UV_{254} removal was nearly 82% with only the use of SWCNTs in winter, whereas the removal ratio increased by about 10% with the combined use of $FeCl_3$ and SWCNTs. The removals were lower when using only MWCNTs in spring and fall, while the highest was recorded with $FeCl_3$ and CNTs. Furthermore, among the other seasons, using $FeCl_3$ and MWCNTs produced the largest amount of UV_{254} (95.87%) removal in spring.

The combined coagulation treatment using carbon nanomaterials was more efficient than the conventional coagulant in the removal of UV_{254} 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 UV_{254} removal when using the combined coagulation process. This finding has been confirmed by many studies [19]-[21]. Therefore, the combined coagulation process can be used in water treatment plants instead of conventional coagulation in order to remove natural organic matter effectively in the future studies.

5. References

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