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Monitoring of Trihalomethanes Removal in Chlorinated Drinking Water Sources with Carbon Nanomaterials

Klorlanmış İçme Suyu Kaynaklarında Karbon Nanotüp Materyalleri ile Trihalometan Bileşiklerinin Gideriminin İzlenmesi

Kadir Özdemir*, Ömer Güngör

Department of Environmental Engineering, Bülent Ecevit University, Zonguldak, Turkey

Abstract

This study investigates trihalomethanes (THMs) removal from chlorinated drinking water sources with combined coagulation processes using single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Terkos Lake water (TLW), Büyükçekmece Lake water (BLW) and Ulutan Lake water (ULW) were used as drinking water source in this study. In the meantime, the chlorination of raw water samples within a reaction time of 168 hours was conducted in accordance with Standard Methods 5710 B. $CHCl_3$ was the dominant THM species removed by SWNCNTs doses (>75%) followed by $CHCl_2Br$ (>70%), $CHBr_2Cl$ (>60%) and $CHBr_3$ (>50%) for three chlorinated water sources. The results demonstrate that the combined coagulation processes is one of the most effective methods for THMs removal from various types of chlorinated water source waters.

Keywords: Carbon nanotubes, Chlorination, Combined-coagulation, Trihalomethanes

Öz

Bu çalışmada tek duvarlı (SWCNTs) ve çok duvarlı (MWCNTs) karbon nano tüpleri kullanılarak birleştirilmiş koagülasyon yöntemi ile klorlanmış içme suyu kaynaklarında meydana gelen trihalometan (THM) bileşiklerinin giderimi araştırılmıştır. Bu çalışmada içme suyu kaynağı olarak İstanbul İline içme suyu sağlayan Terkos Gölü ve Büyükçekmece Göl suyu ile birlikte Zonguldak İline içme suyu sağlayan Ulutan Baraj suları kullanılmıştır. Aynı zamanda 168 saatlik ham su örneklerinin klorlanması işlemi Standart Metotlar 5710-B'de belirtilen klorlama prosedürüne göre yapılmıştır. Yürütülen deneysel çalışmalarda en çok giderilen THM türü farklı SWCNT dozları kullanılarak koagüle edilen klorlanmış üç içme suyu kaynağında $CHCl_3$ (>%75) olduğu tespit edilirken, bunu sırası ile $CHBr_2Cl$ (>60%) ve $CHBr_3$ (>50%) takip etmektedir. Bu çalışmanın sonuçları farklı organik madde içeriğine sahip klorlu içme suyu kaynaklarında THM giderimi için kullanılan birleşik koagülasyon prosesinin en etkili yöntemlerden birisi olduğunu ortaya koymuştur.

Anahtar Kelimeler: Karbon nanotüpler, Klorlama, Birleşik koagülasyon, Trihalometanlar

1. Introduction

Chlorination has been widely used for disinfection in many countries to destroy waterborne pathogenic organisms (Elshorbagy et al. 2000, Rodriguez and Serodes 2001, Singer 1994). As the chlorine reacts with natural organic matter (NOM), disinfection byproducts (DBPs) form (Dickenson et al. 2008, Golfinopoulos 2000, Sadiq and Rodriguez 2004). Of the DBPs formed in chlorinated water, trihalomethanes (THMs) represent a significantly high fraction of these chlorination by-products. Also, these products may have adverse health effects on human beings and are considered potentially carcinogenic (Rook 1974, Bellar et al.1974, Krasner et al. 2002, Sharp et al. 2006, Ivancev et al. 2002, Dodds et al. 1999, Yang et al. 2000, Cedergen et al.2002). Therefore, many countries have established strict regulations to control these disinfection byproducts (Krasner et al. 2001, WHO 2000, Toroz and Uyak 2005, US EPA 2003). For instance, the United States Environmental Protection Agency (USEPA) has set a maximum contamination level of 80 µg/L for trihalomethanes and 60 µg/L for five haloacetic acids; and the European Community regulates the levels of four brominated/ chlorinated trihalomethanes (chloroform, dichlo-

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*Corresponding author: kadir.ozdemir@beun.edu.tr

Kadir Özdemir orcid.org/0000-0003-1464-7078
Ömer Güngör orcid.org/0000-0001-9554-0824

robromomethane, dibromochloromethane and bromoform) often called total trihalomethanes (TTHMs) at 100 µg/L (EC 1998). Furthermore, the trihalomethane limit in Turkey is 100 µg/L (as total trihalomethanes) (TMH 2005). Nanosorbents such as carbon nano tubes (CNTs), polymeric materials (e.g. dendrimers) and zeolites have exceptional adsorption properties; and are applied for the removal of heavy metals, organics and biological impurities (Savage and Diallo 2005). In other words, the applications of CNTs for NOM and removal of chlorinated organics have been developed to replace or enhance conventional treatment processes in recently. Further, CNTs strongly adsorb many of these polar organic compounds due to the diverse contaminant CNT interactions including hydrophobic effects, pep interactions, hydrogen bonding, covalent bonding, and electrostatic interactions (Yang and Xing 2010). Although many studies have focused on CNTs and their adsorption properties, there are a limited number of articles about the removal of halogenated compounds like THMs from the aquatic environment by using nanoparticles as adsorbent materials. For example; Long and Yang (2001) reported that significantly higher dioxin removal efficiency was found with CNTs than with activated carbon. Bina et al. (2012) determined that the removal efficiency for ethylbenzene using single-walled and multi-walled carbon nanotubes and hybrid carbon nanotubes and to rank their ethylbenzene removal abilities. Hu et al. (2012) investigated the adsorption process of roxarsone on multi-walled carbon nanotubes (MWCNTs), such as adsorption kinetics, thermodynamics, and the effects of various experimental parameters providing a potential solution to the roxarsone and other organometallic compounds in contaminated wastewater**.**

The present study is the first attempt in Turkey to investigate to the removal of THMs from chlorinated drinking water sources by a coagulation process using CNTs. Single – walled carbon nanotubes (SWCNTs) and Multı – walled carbon nanotubes (MWCNTs) will be used as CNTs for investigating to the removal efficiency of THMs in the coagulation process. Conventional coagulants (Alum + $FeCl_3$) will also be investigated for comparison. The novelty of this study is to remove THM compounds in chlorinated water sources by combined coagulation process using SWCNTs and MWCNTs as a coagulant matter.

2. Materials and Method

2.1. Source Water and Sampling

During this study, water samples were taken from Terkos Lake water (TLW) and Büyükçekmece Lake water (BLW) in Istanbul city and also Ulutan Lake water (ULW) in Zonguldak city, Turkey. The sampling was done in all four seasons from 2014 to 2015 (with seasons starting in September 2014, January 2015, May 2015, and August 2015). Raw water samples were collected as a grab sample, shipped to the laboratory on the same day and kept in the dark in a refrigerator at 4 °C to retard biological activity prior to use.

2.2. Coagulation Procedure

Prior to the jar test, stock solutions containing 5,000 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. Coagulation of TLW, BLW and ULW was carried out by using a Phipps and Bird six-paddle jar test apparatus. The jars were round beakers with 1L capacity. Rapid mixing was at 150 rpm for 2 min; flocculation was carried out at 40 rpm for 30 min. The ferric chloride and alum was consistently used for THMs removal at similar dosages as coagulant. On the other hand, the coagulant dose was varied in accordance with the NOM content of the source water, related to hydrophobicity. Once the jar tests were completed, the treated water samples were collected and passed through 0.45 µm-membrane filters for DOC and THM analysis.

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_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 the 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 procedure for purifying CNTs has been used by other researchers in previous CNT studies (Chungsying et al. 2005).

2.4. Chlorination Procedure

Chlorination of raw water samples was conducted in accordance with Standard Methods 5710 B (APHA 2005). Before chlorination, sample pH values were adjusted to 7 by addition of HCl or NaOH solution as appropriate. The chlorinated samples were placed into 125 mL amber glass bottles with polypropylene screw caps and TFE faced septa. The chlorination process was conducted for a given chlorine dosage (10 mg/L), fixed pH (pH 7), and room temperature (20 °C). After chlorination, the water samples were incubated at 20 °C for the desired contact time (168 h). At the end of the reaction period, a quenching agent (sodium sulfite solution) was added to each of the chlorinated water samples for the analysis of THM formation.

2.5. Analytical Procedure

All water samples were analyzed based on procedures described in the Standard Methods (APHA 2005). All standard solutions were prepared in ultra pure water (Sartorius Co., Germany). Further, raw water samples were filtered using 0.45 μm cellulose acetate filters before analyses and chlorination. DOC analysis was conducted by the high temperature combustion method according to 3510B using a Shimadzu-5000A TOC analyzer equipped with an auto-sampler (APHA 2005).The minimum quantification limit of the analyzer was 0.1 mg/l. UV254 absorbance readings were carried out by a Shimadzu 1601 UV Visible spectrophotometer at a wavelength of 254 nm (APHA 2005). THM measurement was conducted using EPA Method 551.1 of liquid–liquid extraction (LLE) with pentane (US EPA 2003). THM calibration standards were prepared using certified commercial mix solutions (AccuStandard, Inc., purity N99%). The four THM species were chloroform, bromodichloromethane, dibromochloromethane, and bromoform. THM analyses were performed with the HP 6890 Series II Gas Chromatograph equipped with a micro Electron Capture Detector (GC-μECD). A capillary column of DB-1 (30 m×0.32 mm I.D.×1.0 μm, J&W Science) was used. Injections of samples were made in split/splitless mode, with helium as carrier gas and nitrogen as makeup gas.

3. Results and Discussion

3.1. Removal of THMs by SWCNTs

Figure 1 compares the removal of THM species by increasing doses of SWCNTs for three chlorinated water sources within a jar-testing procedure. As can be seen in Figure 1, among the chlorinated water samples, the $CHCl_3$ was the dominant THM species removed by SWNCNTs doses (>75%) followed by $CHCl_2Br$ (>70%), $CHBr_2Cl$ (>60%) and $CHBr_3$ (>50%) for three chlorinated water

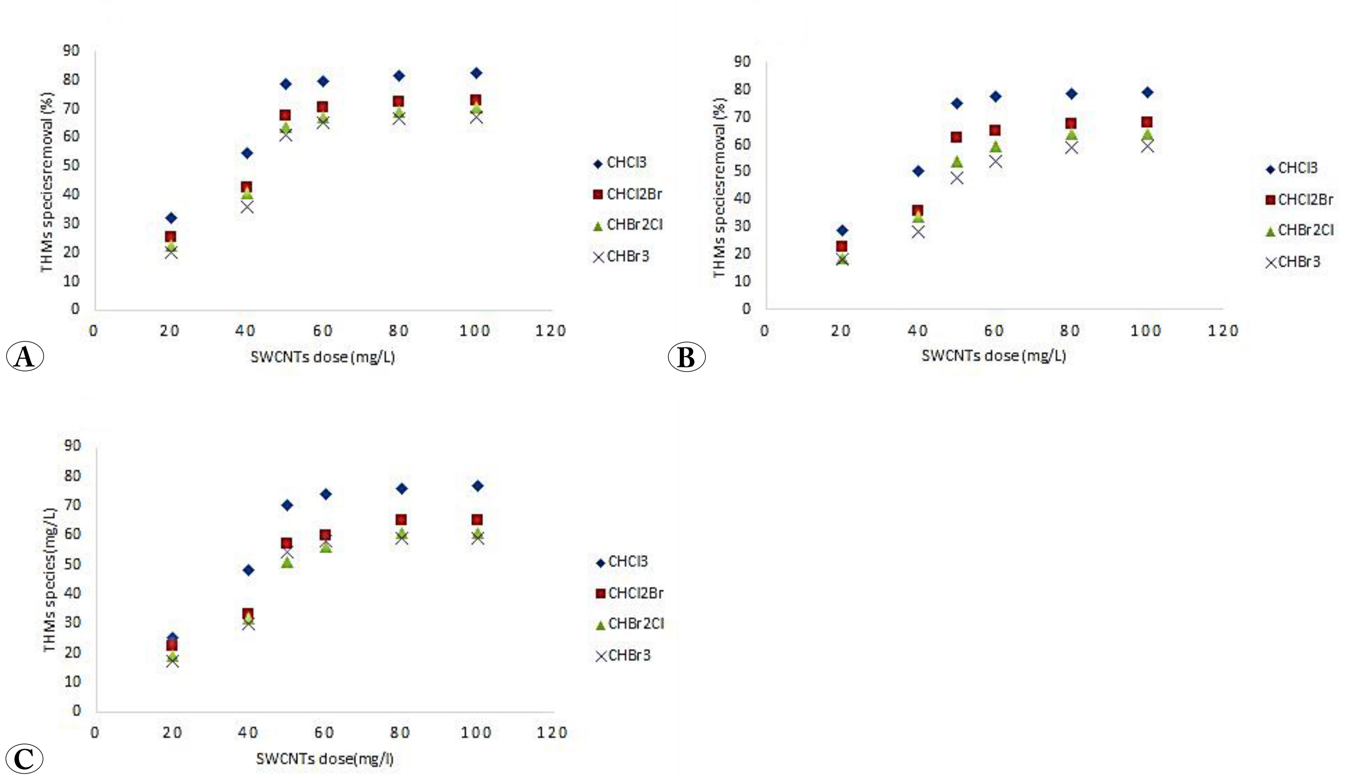

Figure 1. Removal of THM species by SWCNTs using jar test for **(A)** TLW, **(B)** BLW, **(C)** ULW. Optimum coagulant dose = 50 mg /L.

sources within the reaction time of 168 hours. The highest $CHCl_3$ removal of 79% was accounted for by the optimum SWCNTs dose of 50 mg/L in chlorinated TLW water.. For example; the removal percentage of $CHCl_2Br$, $CHBrCl_2$ and $CHBr_3$ were recorded as 68%, 64% and 60%, respectively. This trend was similar to ULW and BLW. This finding is explained that since the surface tension of $CHCl_3$ is much lower than the other THM species and also the polarity of $CHCl_3$ is thus the highest, followed by $CHBrCl_2$, $CHBr_2Cl$ and then $CHBr_3$, the adsorption of $CHCl_3$ onto the CNTs is much easier (Chungsying et al. 2005).

3.2. Removal of THMs by MWCNTs

Figure 2 shows the removal of THM species by increasing doses of MWCNTs, with conventional coagulants during jar-testing. Similar to that determined with SWCNTs, the highest percentage removal among to the THMs species using only MWCNTs was observed as $CHCl_3$ (74.12%) in three chlorinated water sources. However, the removal of brominated species ($CHCl_2Br$, $CHBr_2Cl$ and $CHBr_3$) was significantly higher in BLW using MWCNTs than that of using SWCNTs. Among the brominated spices, the maximum removal was recorded to $CHBr_2Cl$ as 68%, followed by $CHCl_2Br$ (64%) and $CHBr_3$ (58%) in chlorinated BLW. For ULW, the maximum $CHCl_3$ removal was similar for both MWCNTs (67%) and SWCNTs (66%). On the other hand, the removal of brominated THM species using only MWCNTs was determined higher levels than that of SWCNTs, with removal percentage of 62%, 65% and 60% for chlorinated ULW samples.

4. Conclusion

In this study, coagulation experiments demonstrated that SWCNTs were more effective than MWCNTs in removing THM species from TLW containing hydrophobic organic matters. On the other hand, $CHCl_3$ was the dominant species among the four THM compounds. Although the maximum $CHCl_3$ removal ratio was found in chlorinated TLW samples due to using SWCNTs. This is due to the two reasons: one of them is noted that the smallest molecule, $CHCl_3$, is the most preferentially removed by coagulation onto CNTs, followed by $CHCl_2Br$, $CHBr_2Cl$ and then $CHBr_3$. Second, the polarity of $CHCl_3$ is the highest, followed by $CHCl_2Br$, $CHBr_2Cl$ and then $CHBr_3$, which

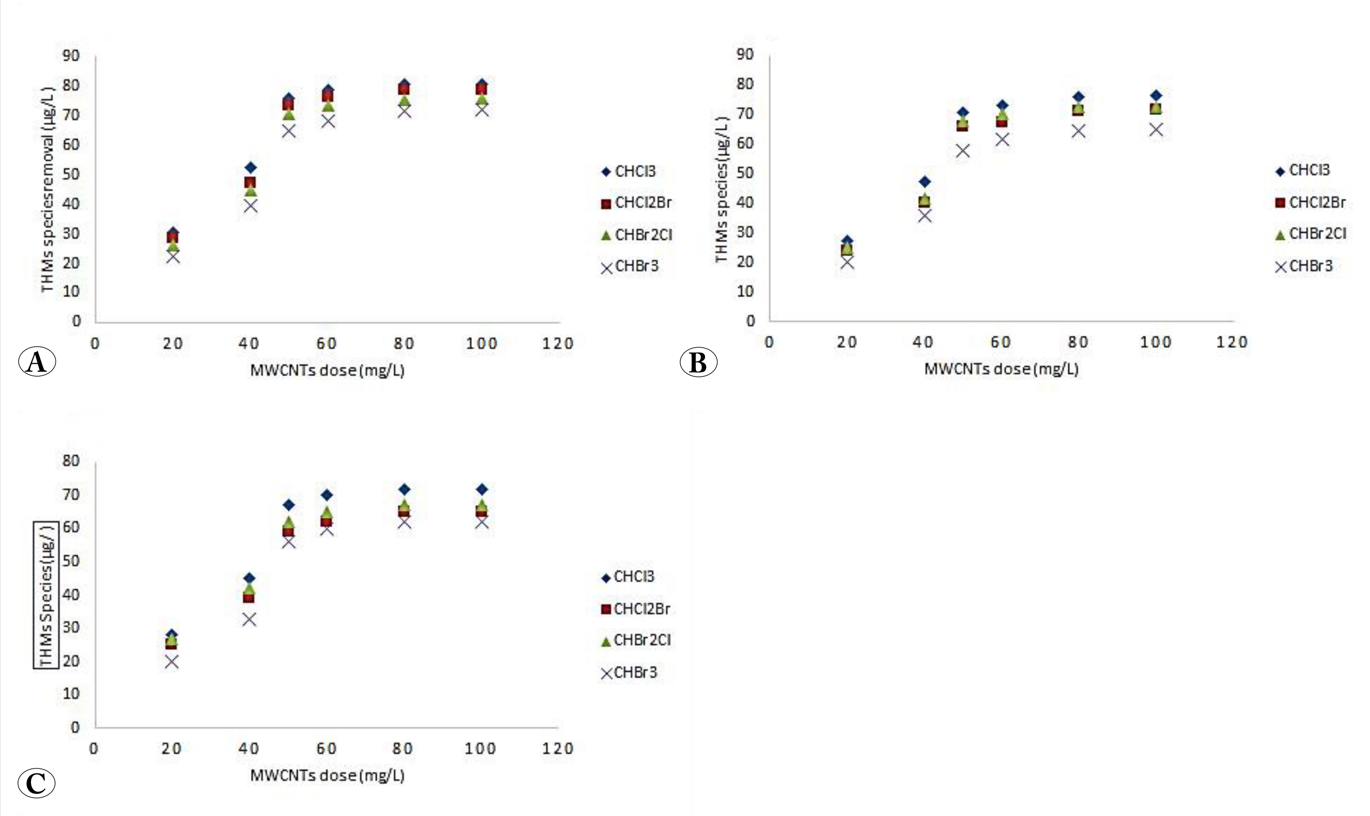

Figure 2. Removal of THM species by MWCNTs using jar test for **(A)** TLW, **(B)** BLW, **(C)** ULW. Optimum coagulant dose = 50 mg /L.

made removal of $CHCl_3$ onto CNTs much easier. This result is confirmed by previous studies (Chungsying et al. 2005). For brominated THM compounds, maximum THM removal as $CHCl_2Br$ (64%), $CHBr_2Cl$ (68%) and $CHBr_3$ (58%) was observed in BLW using MWCNTs. This outcome is attributed to the chlorination of high levels of bromide-containing water, which modifies the chlorination process and thus bromide affects the formation and distribution of THM species.

Results from this investigation show that coagulation using carbon nanomaterials can be effective in the removal of THMs from various types of chlorinated source waters.

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