

# Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies

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## Abstract

Coagulation process can be used to control natural organic matter (NOM) during drinking water production. The effectiveness of the coagulation process appeared to depend on the pH of coagulation rather than coagulant dosages. Jar tests conducted with depressed pH levels at different coagulation conditions removed more dissolved organic carbon (DOC) than those at moderate pH levels. For low DOC waters, like Omerli Lake Water (OLW), additional treatment would be necessary to achieve enhanced removal of NOM. In this study, three different coagulation techniques were used to remove disinfection by-products (DBP) precursors from three Istanbul surface water supplies. Jar test results indicate that optimize coagulation (OC) can enhance the removal of DBP precursors, and the removal of DOC could be improved from the current average of 15% to an average of 56% at the three sites tested. At lower pH, ferric coagulants generally performed better for removal of DBP precursors than did alum. © 2006 Elsevier B.V. All rights reserved.

*Keywords:* Enhanced coagulation; Organic matter removal; Trihalomethanes; Istanbul

## 1. Introduction

Drinking water in Istanbul is supplied mainly from three big surface water sources of Buyukcekmece, Terkos, and Omerli Lakes. The water is transferred to water treatment plants for treatment operations. In the treatment plants, source waters are treated to comply with European Union (EU) and Turkish water quality standards. Preoxidation of organic matters in source water occurred with chlorine in Buyukcekmece and Kagithane treatment plants, while Omerli treatment plants use ozone as a preoxidant agent. The final step of water purification of these treatment plants is disinfection with chlorine [1,2]. However, several studies reported that chlorination of organic matter in fresh water resulted in formation of disinfection by-products (DBP) [1,3–7]. Concerns regarding the potential health effects of DBP prompted several industrialized countries to develop a number of regulations [2,3,5]. The disinfectant/disinfection by-product (D/DBP) regulation in United States of America (USA) has set maximum contaminant levels for trihalomethanes (THM) and haloacetic acids (HAA) of 80 and 60 µg/l, respectively

[8]. On the other hand, EU regulated THM limit at a 100 µg/l [9]. Moreover, Turkish Government recently regulated 100 µg/l THM limit in drinking water to comply with EU regulations [1,10].

The USA regulation mandates water treatment plants using disinfectants to remove predetermined levels of total organic carbon (TOC) as a means of reducing DBP precursors [8,11] (Table 1). The US Environmental Protection Agency (EPA) has recognized either enhanced coagulation (EC) or granular activated carbon (GAC) as the best available technology (BAT) for controlling DBP precursors [8]. EC corresponds to the use of coagulant dosages effective for TOC removal. In USA, EC was selected as the Stage 1 treatment of choice because it was effective for the TOC removal and could be implemented at most water plants treating surface waters (Table 1) using existing treatment processes [12].

Natural organic matter (NOM) treatment through coagulation has been widely documented in the literature [13,14]. It was summarized by scientists that the major mechanisms by which NOM can be removed by coagulation involve charge neutralization of colloidal NOM, precipitation as humates or fulvates, and coprecipitation by adsorption on the metal hydroxide [13–15]. The coagulation of colloidal NOM can be caused by a compression of the double layer surrounding the charged colloid, by

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Table 1  
EPA alkalinity and total organic carbon (TOC) matrix for percent TOC removal goals by enhanced coagulation

TOC (mg/l)	Alkalinity (mg/l) as CaCO <sub>3</sub>		
	0–60.0 (%)	60.0–120.0 (%)	>120.0 (%)
2.0–4.0	35	25	15
4.0–8.0	45	35	25
>8.0	50	40	30

charge neutralization, and by bridging in the coagulant precipitate [13–15]. Precipitation of NOM refers to the formation of aluminum or iron humate with a lower solubility product. The degree of NOM removal by coagulation is affected by the nature and dosage of coagulants as well as the pH. The effectiveness of a given coagulant to remove NOM may vary with the active charge density, the floc surface area available for adsorption, and the nature of the bonds between the NOM and the metal hydroxide flocs [14–16]. On the other hand, the concept of EC involves a broadening of coagulation objectives from turbidity removal to include NOM removal. These dual objectives require modifying coagulation conditions. These conditions include coagulant type, coagulant dosage, and coagulation pH. The effects of higher dosage are readily apparent, providing more metal for complex formation. Lower pH reduces the charge density of NOM, making them more hydrophobic (absorbable). The practical definition of EC is to provide treatment conditions that still sustain effective turbidity removal while also increasing NOM removal. This work evaluated the effects of different coagulation conditions on the levels of organic matter removal at a bench scale for three raw water types in Istanbul.

## 2. Materials and methods

### 2.1. Source waters collection

The natural water sources used in this study were Terkos Lake Water (TLW), Buyukcekmece Lake Water (BLW), and Omerli Lake Water (OLW). Quality parameter of these raw waters over 15 month period is summarized in Table 2. Daily consumption of  $2 \times 10^6$  m<sup>3</sup> drinking water is supplied from these surface waters in Istanbul. Plant personnel collected raw water samples as grab samples, and they were shipped to

Istanbul Technical University (ITU) laboratory on the same day. When the samples were received at ITU Department of Environmental Engineering Laboratory, they were kept in the dark in a refrigerator at 4 °C to retard biological activity prior to use.

### 2.2. Jar test coagulation procedure

#### 2.2.1. Baseline coagulation (BC)

Baseline coagulation (BC) is jar tests that simulated the water treatment plant conditions (coagulation dose) the day that the raw water sample was collected. Average coagulant dosage was found to be 40 mg/l in Istanbul water treatment plants. Thus, during BC, 40 mg/l was chosen as a coagulant dosage. The purposes of the baseline jar tests were to compare the jar test results with the full-scale plant data, and to serve as a point of comparison to the enhanced and optimized coagulation treatment conditions. Table 3 shows the operational parameters of these treatment plants.

#### 2.2.2. Enhanced coagulation (EC)

To determine EC conditions, a series of bench scale jar tests was used to identify the optimal coagulation dosage. All samples were brought to room temperature (21 °C) prior to jar testing. Experiments on 11 samples were performed using a multistage stirrer six paddle jar test apparatus. The reagent grade ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) and alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) doses were varied 20–140 mg/l. The standard jar test procedure consisted of a rapid mix at 150 rpm for 2 min, flocculation at 30 rpm for 30 min [1,15,17]. Then the floc was allowed to settle for 60 min prior to filtration through a 0.45 μm cellulose acetate membrane filter. The filtrate from each jar was used to perform DOC, UV<sub>254</sub>, SUVA, and THMFP studies.

#### 2.2.3. Optimized coagulation (OC)

Determination of optimized coagulation conditions required evaluation of both the optimum pH and coagulant dosage. To determine the optimum pH for a selected coagulant dose, jar tests were conducted using a constant coagulant dose and varied the pH of coagulation using sulfuric acid. The optimum pH of coagulation was identified as the highest pH at which there was maximum DOC removal. Other parameters including UV<sub>254</sub>, and THMFP removal were also considered in determining the

Table 2  
Raw water quality parameters for three surface water sources

Parameters	Unit	Terkos Lake Water (TLW)		Buyucekmece Lake Water (BLW)		Omerli Lake Water (OLW)	
		Range	Average	Range	Average	Range	Average
pH	–	7.40–8.10	7.78	7.60–8.50	8.00	6.80–7.60	7.15
Turbidity	NTU	1.3–3.2	2.5	1.2–3.6	2.8	1.8–2.8	2.4
Alkalinity	mg/l CaCO <sub>3</sub>	90–145	118	110–153	135	55–76	67
Br <sup>–</sup>	μg/l	80–460	280	70–530	370	24–120	60
Temperature	°C	15.3–24.8	19.2	14.9–23.2	21.3	15.0–24.2	20.4
DOC	mg/l	3.55–5.85	4.12	3.76–6.25	4.22	3.20–4.80	3.89
UV <sub>254</sub>	cm <sup>–1</sup>	0.0850–0.1650	0.1250	0.0760–0.1530	0.1310	0.0620–0.0980	0.0820
SUVA	l/(mg m)	2.25–3.64	3.03	2.02–3.76	3.10	1.60–2.80	2.11
THMFP	μg/l	235–412	295	176–345	255	128–245	203

Table 3  
Operational parameters of Istanbul water treatment plants

Water treatment plant	Source water	Applied Cl <sub>2</sub> dose range (mg/l)	Coagulant used	Coagulant dose range (mg/l)*	Flow rate (m <sup>3</sup> /day)	Treatment process
Kagithane	TLW	4–6	Alum	20–50 (40)	600,000	Pre-chlorination, coagulation, sedimentation, sand filtration, post-chlorination
Buyukcekmece	BLW	4–7	Alum	25–50 (40)	400,000	Pre-chlorination, coagulation, sedimentation, sand filtration, post-chlorination
Omerli	OLW	3–5	Alum and ferric chloride	20–40 (40)	1,200,000	Pre-ozonation, coagulation, sedimentation, sand filtration, post-chlorination

\* The number in parenthesis shows the average coagulant dosages. The mixing conditions for rapid and slow stages in all plants are 2 and 30 min, respectively.

optimum pH value. To determine the optimum coagulant dosage at the selected pH, coagulant concentrations were varied in each jar while the optimum pH value was maintained constant. This optimum pH/dose condition was defined as the optimized treatment. These series of tests were conducted using alum and ferric chloride.

### 2.3. Chlorination procedure

THM formation potential (THMFP) measurements were conducted in accordance with Standard Methods of 5710 B [18].

### 2.4. Analytical methods

DOC measurements were performed with a Shimadzu TOC-5000 analyzer equipped with an auto sampler [19], according to the combustion-infrared method as described in the Standard Methods 3510 B [18]. The sample is injected into a heated reaction chamber packed with a platinum-oxide catalyst oxidizer to oxidize organic carbon to CO<sub>2</sub> gas. Edzwald [20] suggested that DOC measurements were more representative than TOC for assessing the removal of dissolved DBP precursors by coagulation. Further, UV<sub>254</sub> absorbance measurements were performed in accordance with Standard Methods 5910 B [18] by a Shimadzu 1601 UV-vis spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell. The samples were first filtered through a prewashed 0.45 μm membrane filter to remove turbidity, which can interfere with this measurement, and distilled ultra filtered (DIUF) water was used as the background correction on the spectrophotometer. Besides, THM concentrations were determined with liquid-liquid extraction method according to Standard Methods 6232 B [18]. The sum of the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) mass concentrations was reported as TTHM in μg/l. A 35 ml THM samples were pipetted into a 40 ml vials, after that, 3 ml of pentane were transferred to each vial. The vials were then shaken vigorously for phase separation. The pentane extract was analyzed by a Agilent Gas Chromatography (6890 Series) with a micro electron capture detector (GC-μECD), auto sampler and capillary column

(J&W Science DB-1), 30 m × 0.32 mm i.d. × 1.0 μm film thicknesses.

## 3. Results and discussion

Removal of organic precursors by coagulation process is impacted by many factors such as coagulation conditions, characteristics of NOM, nature and concentrations of inorganic compounds, and the design and operation of the treatment plant [21]. Therefore, the removal of organic matter from water with coagulation process varies widely, generally between 10 and 90% [1,13]. The aim of this study was to evaluate how different coagulation conditions impact DBP precursors levels in treated water. Organic precursors removal by BC, EC, and OC treatment techniques were assessed by monitoring raw and coagulated water DOC, UV<sub>254</sub>, SUVA, and THMFP value. The effects of coagulation pH, coagulant dosage and type, and raw water characteristics were also successively assessed.

As shown in Figs. 1–3, coagulation of TLW, BLW, and OLW samples data indicated that as both coagulant dosages increased further, the amount of DOC removal also increased gradually. Ferric chloride reduced the DOC level to 2.08, 2.00,

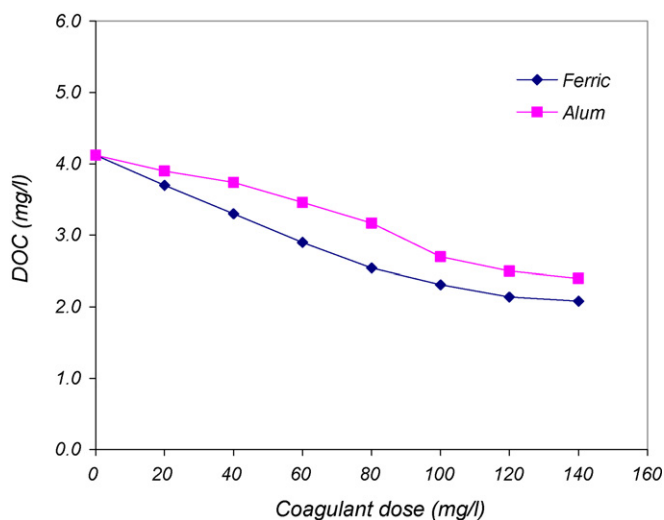


Fig. 1. DOC Removal with ferric and alum for TLW.

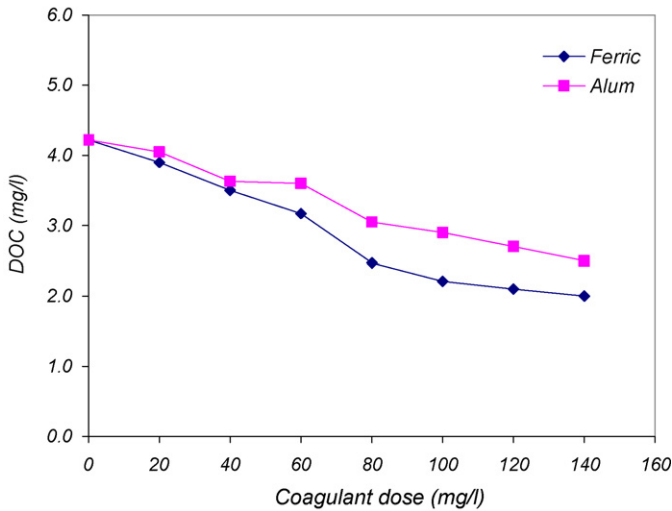


Fig. 2. DOC Removal with ferric and alum for BLW.

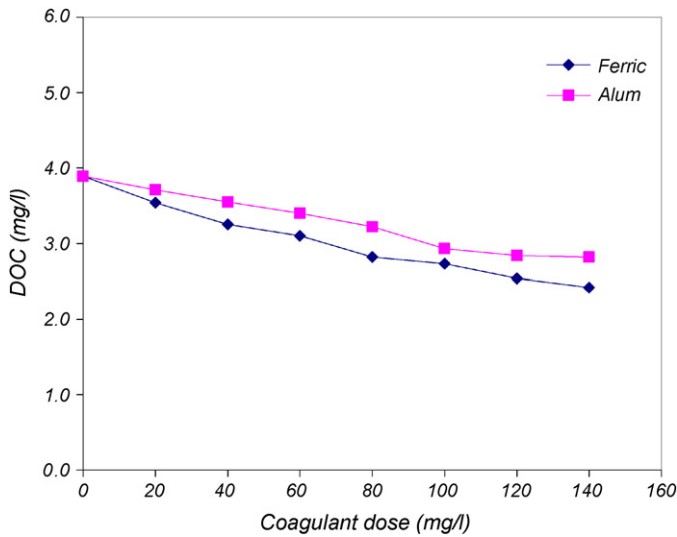


Fig. 3. DOC Removal with ferric and alum for OLW.

and 2.42 mg/l with the dosage of 140 mg/l for TWL, BLW, and OLW, respectively. While, 140 mg/l aluminum sulfate coagulation resulted in a DOC level of 2.40, 2.50, and 2.82 mg/l in TWL, BLW, and OLW, respectively. As observed in three sur-

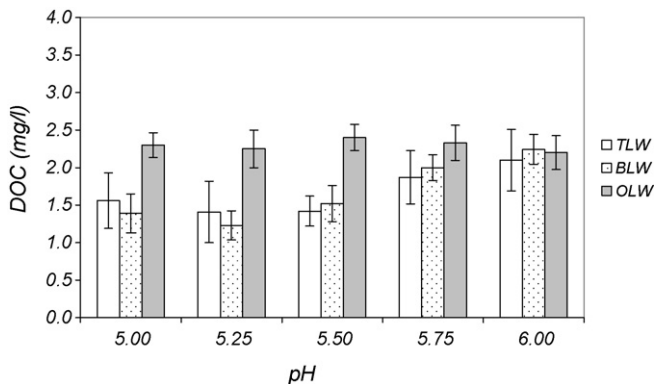


Fig. 4. Ferric coagulation of pH scans on DOC reduction for three water samples.

face water samples, at similar coagulant dosages, ferric chloride consistently outperformed alum for DOC removal. As a comparison, our results are consistent with other studies [12,20]. In this study, 40 mg/l coagulant dosage was chosen for BC conditions. Moreover, even though 140 mg/l coagulant dosage resulted in maximum DOC removal in three surface waters coagulation, because of economical and engineering point of view and considerations, 80 mg/l coagulant dosages was selected for EC and OC studies.

### 3.1. Effects of coagulation conditions on DOC removal

#### 3.1.1. Coagulation pH

Literature findings reported that the pH of coagulation was dependent on the coagulant type and treated water sample [21]. Numerous researchers have identified coagulation pH as the parameter having a great effect on achieving optimal organic precursors removal by coagulation process [13,22,23]. The results of our study support these findings, indicating that the pH of coagulation rather than the coagulant dosage was the determinant factor for DOC removal. Fig. 4 shows ferric chloride coagulation of pH scans conducted for TLW, BLW, and OLW with varying DOC and alkalinity levels. Each curve was created with an 80 mg/l coagulant dosage while the pH of coagulation was varied by addition of H<sub>2</sub>SO<sub>4</sub>. These data show that the optimal pH was 5.25 for three water sources and DOC removals were varied with pH. For example, for BLW with an alkalinity of 135mg/l, the optimal pH was 5.25 with 71% DOC removal. For TLW, an optimal pH of 5.25 value resulted in 66% DOC reduction with an alkalinity of 125 mg/l. Finally, in OLW, the optimal coagulation efficiency was 43% at optimal pH of 5.25 with a 67 mg/l alkalinity. It can be concluded that the DOC removal efficiency with ferric chloride was increasing with increased DOC levels.

As shown in Fig. 5, the optimal pH for alum coagulation was obtained at 5.50 for TLW and BLW, while, in OLW the optimal pH was 5.25 as in the case for ferric chloride. Optimized conditions with alum removed 52, 67% DOC from TLW and BLW, respectively. For OLW samples, lowering the pH to 5.25 with sulfuric acid led to 34% DOC treatment. As a comparison, Chowdhury et al. [24] reported that baseline plant conditions removed 9% of the TOC (TOC = 2.4 mg/l), but TOC removals

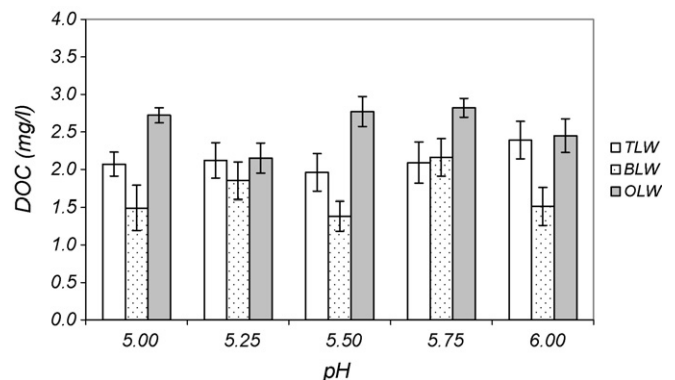


Fig. 5. Alum coagulation of pH scans on DOC reduction for three water samples.

increased to 25% when carbon dioxide was added to lower the pH from 8.0 to 7.0. Lind [25] also found that TOC removal was improved at lower pH values with alum and ferric chloride coagulation. For our study, the best precipitation pH for DOC substances has been obtained at 5.25 with ferric chloride and at 5.50 with alum coagulation. As mentioned in literature, the lower pH, by increasing the protonation of the NOM and increasing the positive charge of the coagulating species, reduces the coagulant demand and favors the adsorption of humics onto metal hydroxides [26].

### 3.1.2. Coagulant type

The choice of coagulant was also a factor in the performance of coagulation conditions. The performance of ferric chloride for removal of DOC was compared to alum (Figs. 1–3). Ferric chloride resulted in better DOC removal than alum. As shown in Tables 4 and 5, BC with ferric chloride removed on average 0.26 mg/l more DOC than alum, while EC with ferric treatment removal resulted in 0.55 mg/l more DOC than alum, and finally OC conditions with ferric chloride removed 0.34 mg/l more DOC than alum. Mainly due to more favorable pH, iron salts typically resulted in greater removal of DOC. Studies reported in the literature are similar, suggesting that the performance of a particular coagulant is dependent upon the specific characteristics of the NOM and the test conditions [21]. Some investigators have reported that iron was superior to alum salts [15,27,28]. For example, in experiments performed on the TLW previously, the average TOC removal was 49% with alum and 69% with ferric chloride [2]. Besides, Crozes et al. [22] observed higher removals of DOC when using ferric chloride compared to alum.

### 3.1.3. Coagulant dose

Coagulant dose under BC conditions was 40 mg/l, and EC used 80 mg/l dosage without pH adjustment. Besides, a coagulant dosage of 80 mg/l also was used at selected pH for OC conditions. For all water samples, increasing the coagulant dosage led to an increase in DOC removal. As shown in Table 4, BC of 40 mg/l ferric chloride removed 20, 17, and 16% of the DOC on TLW, BLW, and OLW, respectively. While EC with 80 mg/l of ferric chloride yielded a DOC reduction of 38, 41, and 28%

for TLW, BLW, and OLW, respectively. Furthermore, OC of TLW, BLW, and OLW with 80 mg/l iron salt at pH value of 5.25 resulted in 66, 71, and 43% DOC reduction, respectively. Table 5 also shows that 40 mg/l dosage of alum with BC removed 12, 14, and 9% of DOC on TLW, BLW, and OLW, respectively. Moreover, alum treatment with EC resulted in 23, 28, and 17% DOC removal for TLW, BLW, and OLW, respectively. Finally, the amount of DOC removal with alum OC was 52, 67, and 34% for TLW, BLW, and OLW, respectively. The results of the study show that at similar coagulant dosages and coagulation techniques, ferric chloride consistently outperformed alum in terms of DOC removal from water samples. Uyak and Toroz [15] reported that ferric hydroxide floc has a greater affinity of a fraction of NOM than for aluminum hydroxide floc. This difference in adsorption capacity is likely due to more active adsorption sites on the ferric hydroxide floc [22]. Furthermore, ferric chloride presents roughly two times more active positive charges than does aluminum sulfate [22]. Therefore, colloid destabilization and the formation of humates can both be expected to be achieved with ferric chloride more effectively than alum.

### 3.2. Effect of source water characteristics on organic matter removal

Natural organic content and alkalinity level of source water affect the coagulation performance. Usually higher DOC content increases the coagulation efficiency. For this study, moderate variations in organic matter removal were observed between the tested water samples (Tables 4 and 5). Overall, removal of DOC ranged between 9 and 71%. The removal of humic materials, determined by monitoring the reduction in UV absorbance at 254 nm, ranged between 17 and 84%. THMFP removal amount was in the range of 24 and 79%. Organic precursors are composed of a mixture of compounds varying in size, structure and composition. It was reported that the chemical characteristics of the DOC, as well as other physicochemical properties of the raw water, will determine the degree of removal by coagulation [21]. Analysis of raw water DOC and alkalinity levels showed that quantity of DOC and alkalinity influenced treatment efficiency. Higher NOM removal was observed for BLW with average DOC

Table 4  
THM precursors removal with ferric chloride coagulation under three different coagulation conditions

Source water	Coagulation techniques	pH	Ferric (mg/l)	DOC (mg/l)	UV <sub>254</sub> (cm <sup>-1</sup> )	SUVA (l/(mg m))	THMFP (µg/l)	DOC (%)	UV <sub>254</sub> (%)	SUVA (%)	THMFP (%)
TLW	Raw water	7.78	0	4.12	0.1250	3.03	295	0	0	0	0
	BC	6.94	40	3.30	0.0717	2.17	202	20	43	28	32
	EC	6.57	80	2.54	0.0487	1.92	134	38	61	37	55
	OC	5.25	80	1.41	0.0201	1.43	62	66	84	53	79
BLW	Raw water	8.00	0	4.22	0.1310	3.10	255	0	0	0	0
	BC	7.10	40	3.50	0.0850	2.43	162	17	35	22	36
	EC	6.72	80	2.47	0.0590	2.39	146	41	55	23	43
	OC	5.25	80	1.23	0.0250	2.03	73	71	81	34	71
OLW	Raw water	7.15	0	3.89	0.0820	2.11	203	0	0	0	0
	BC	6.89	40	3.25	0.0670	2.06	141	16	18	2	31
	EC	6.30	80	2.82	0.0560	1.99	112	28	32	6	45
	OC	5.25	80	2.23	0.0438	1.96	83	43	47	7	59

Table 5  
THM precursors removal with alum coagulation under three different coagulation conditions

Source water	Coagulation techniques	pH	Alum (mg/l)	DOC (mg/l)	UV <sub>254</sub> (cm <sup>-1</sup> )	SUVA (l/(mg m))	THMFP (μg/l)	DOC (%)	UV <sub>254</sub> (%)	SUVA (%)	THMFP (%)
TLW	Raw water	7.78	0	4.12	0.1250	3.03	295	0	0	0	0
	BC	6.86	40	3.64	0.0747	2.05	200	12	40	32	32
	EC	6.35	80	3.17	0.0517	1.63	156	23	59	46	47
	OC	5.50	80	1.96	0.0348	1.78	94	52	72	41	68
BLW	Raw water	8.00	0	4.22	0.1310	3.10	255	0	0	0	0
	BC	7.10	40	3.63	0.0932	2.57	195	14	29	17	24
	EC	6.72	80	3.05	0.0804	2.64	167	28	39	15	35
	OC	5.50	80	1.38	0.0406	2.94	82	67	69	5	68
OLW	Raw water	7.15	0	3.89	0.0820	2.11	203	0	0	0	0
	BC	6.92	40	3.55	0.0680	1.92	140	9	17	9	31
	EC	6.40	80	3.22	0.0580	1.80	137	17	29	15	33
	OC	5.25	80	2.55	0.0365	1.43	97	34	55	32	52

value of 4.22 mg/l with a 135 mg/l alkalinity (Tables 4 and 5). On average, water sample of TLW with 4.12 mg/l DOC and 118 mg/l alkalinity exhibited DOC removals of 41, and 29% for ferric and alum coagulation, respectively. DOC removal of OLW samples with DOC levels below 4 and 67 mg/l alkalinity resulted in 29 and 20% for ferric and alum coagulants, respectively. Numerous researchers have reported that specific physical and chemical properties of NOM including the molecular weight of organic constituents, the solubility of organic compounds, the charge density of molecules, or the functional group composition, all impact the removal of NOM during coagulation [20,29–34].

### 3.3. THM precursors removal

#### 3.3.1. UV<sub>254</sub>

UV<sub>254</sub> is an instrumental parameter identifying the aromatic content of water. Figs. 6 and 7 shows the reduction of UV<sub>254</sub> levels in TLW, BLW, and OLW with ferric and alum coagulation, respectively. The percent removal of UV<sub>254</sub> with ferric chloride for TLW, BLW, and OLW samples was about 73, 73, and 49%, respectively. On the other hand, the maximum UV<sub>254</sub> removals with alum coagulation were 69, 60, and 44% for TLW, BLW, and OLW, respectively. It was concluded that ferric chloride was

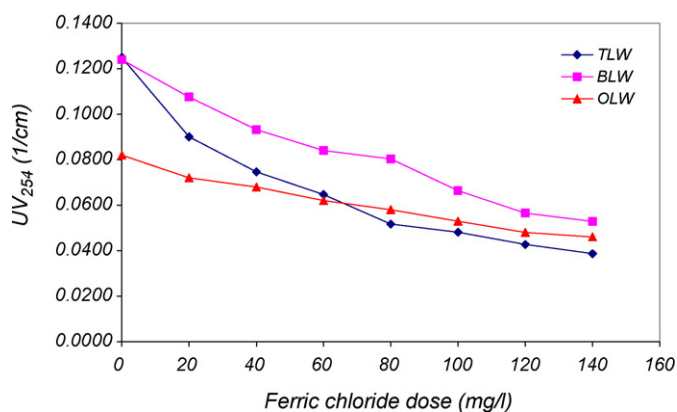


Fig. 6. UV<sub>254</sub> removal with ferric for three water samples.

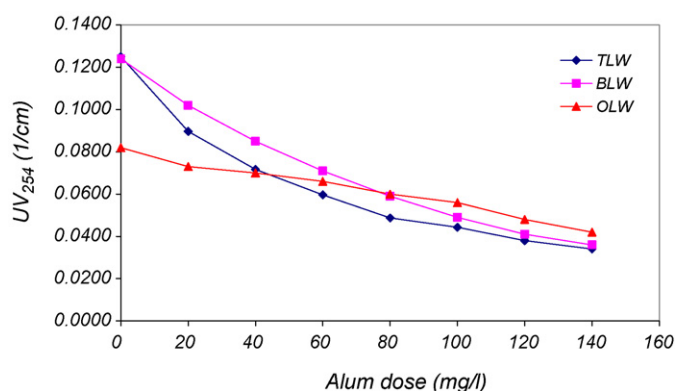


Fig. 7. UV<sub>254</sub> removal with alum for three water samples.

found to be more effective than alum in terms of UV<sub>254</sub> removals. In this study, the UV<sub>254</sub> material was always removed to a greater extent than DOC. In Fig. 8, a comparison of DOC versus UV<sub>254</sub> removal is shown. The optimal curve is also shown, and points on this curve indicate equivalent removal of DOC and UV<sub>254</sub> for three surface water samples. Points above this curve indicate that

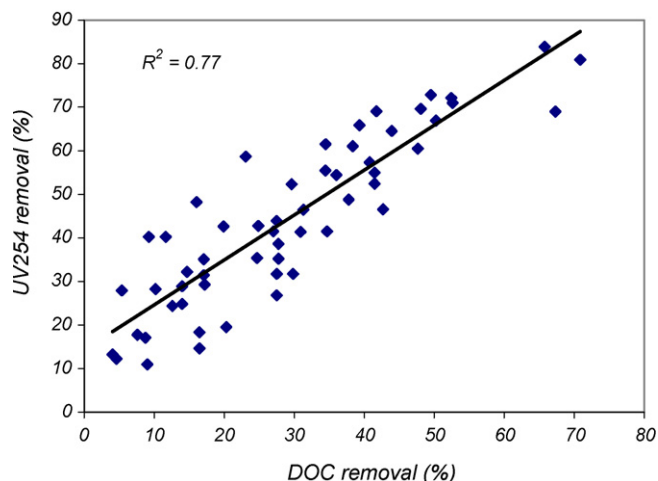


Fig. 8. Comparison of DOC removal vs. UV<sub>254</sub> removal for three water sources studied under three different coagulation conditions.

the percent removal of UV<sub>254</sub> was higher than the percent DOC removal, whereas the reverse is true for points below the line. As shown in Tables 4 and 5, the average DOC removal for BC was 15% compared with 30% for removal of UV<sub>254</sub>. For EC, DOC removals averaged 29%, whereas UV<sub>254</sub> removal increased to 46%, indicating good removal of aromatic compounds. Finally, in OC conditions, the DOC removal amount increased to 56%, while the average UV<sub>254</sub> removal was 68% with optimal pH values. As a result, when compared UV<sub>254</sub> to DOC removal, the percentages of UV<sub>254</sub> reduction were from 1.22- to 1.99-fold higher than DOC reduction, suggesting that coagulation was more effective in removing UV<sub>254</sub> absorbing materials than DOC [15,16,35,36].

### 3.3.2. SUVA

Edzwald [20] found that SUVA values higher than 3 describe a relatively hydrophobic DOC, mainly containing aquatic humic material of high molecular weight which is likely to be effectively removed during coagulation. On the contrary, SUVA values of less than 3 indicate that the DOC is hydrophilic, low in molecular weight, low in charge density, and only slightly affected by coagulation. For the three water samples studied, SUVA values decreased significantly after coagulation (Tables 4 and 5). The highest DOC removal of 71% was observed for the BLW sample with the highest SUVA (SUVA = 3.10 l/(mg m)) treated with ferric chloride. Alternatively, the lowest DOC reduction was observed (9–43%) for sample OLW, with a SUVA of 2.11 and a raw water DOC concentration of 3.89 mg/l. The average removal of DOC for TLW sample with SUVA value of 3.03 was 41% with ferric chloride coagulation. Several studies have shown that humic substances are preferentially targeted during coagulation [13,20,23,29,34]. For example, the comparison of <sup>13</sup>C NMR spectra of water samples before and after chemical coagulation demonstrated that aromatic carbon was preferentially removed [31]. Furthermore, the nature of humic substances also impacts their removal. The removal rates of hydrophobic compounds were found to be higher than those of hydrophilic compounds [37,38]. Huang and Yeh reported that coagulation removed 50 and 35% of humic and fulvic acids present in colored waters, respectively [32].

### 3.3.3. THMFP

Uyak and Toroz reported that THMFP reduction is attributed to removal of THM precursors [15]. Tables 4 and 5 show the results of jar testing of BC, EC, and OC treatments. Overall, EC and OC resulted in improved 7 day THMFP removals compared with the corresponding BC treatments. THMFP values decreased significantly after coagulation (Tables 4 and 5). The highest THMFP removal of 79% was observed for the TLW sample in OC conditions with ferric chloride. Moreover, the moderate THMFP reduction of 55% was observed with EC on TLW sample. It is likely that the improved reductions in THMFP were related to the lower pH of coagulation as well as the increased DOC removal. The average improvement with OC for three waters over BC conditions for removal of THMFP was 53%. The jar tests results indicate that ferric chloride was

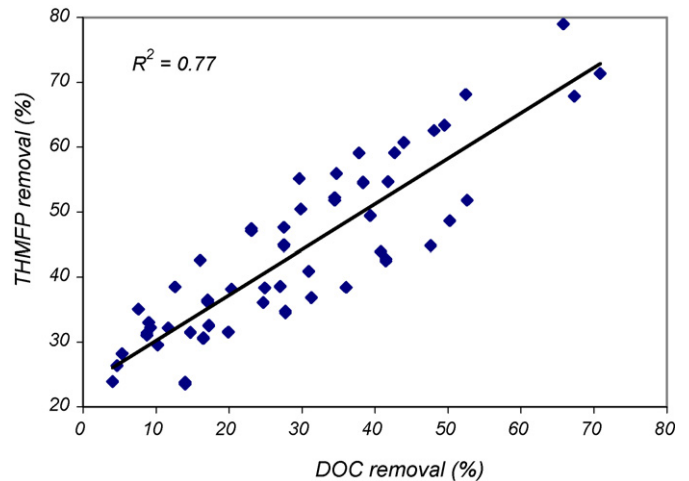


Fig. 9. Comparison of DOC removal vs. THMFP removal for three water sources studied under three different coagulation conditions.

found to be more effective again than alum in terms of THMFP removals. Studies conducted by Uyak and Toroz [15] reported that the difference between ferric chloride and alum reduction levels of THMFP is attributed to a greater affinity of a fraction of NOM for ferric hydroxide floc than for aluminum hydroxide floc. Moreover, the reduction in THMFP increased with increasing both coagulant dosages and decreasing pH values.

As many people have reported, DOC removal appeared to be a conservative indicator for treatment of THMFP with precursors preferentially removed by OC [38]. The correlation between DOC removal and THMFP removal was moderate with a  $R^2$  value of 0.77 (Fig. 9). On the other hand, the relationship between THMFP and UV<sub>254</sub> absorbing compounds was slightly higher, with a correlation coefficient of 0.80 (Fig. 10). These results indicate that waters higher in UV<sub>254</sub> tend to exert a higher chlorine demand and the higher concentrations of chlorine applied to satisfy that demand may have resulted in greater THM formation [39].

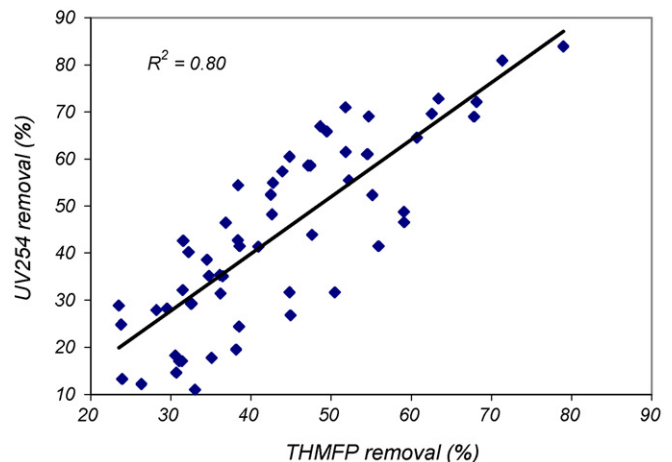


Fig. 10. Comparison of THMFP removal vs. UV<sub>254</sub> removal for three water sources studied under three different coagulation conditions.

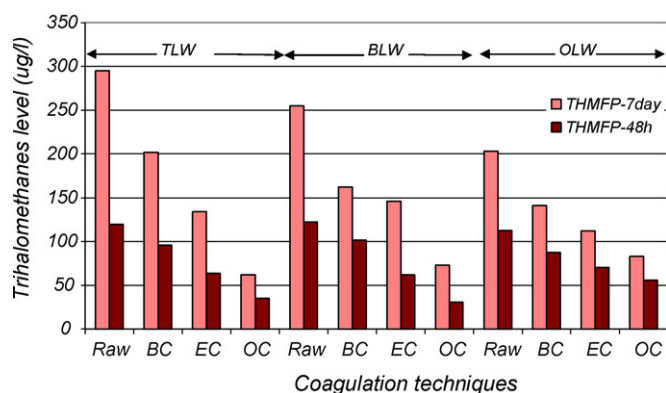


Fig. 11. Comparison of THMFP<sub>48h</sub> with THMFP<sub>7day</sub> for ferric chloride coagulation.

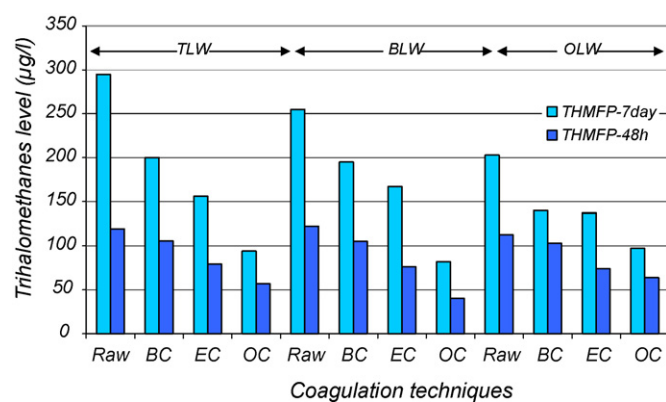


Fig. 12. Comparison of THMFP<sub>48h</sub> with THMFP<sub>7day</sub> for alum coagulation.

### 3.4. Enhanced and optimized coagulation benefits

EC and OC can be an economical alternative for improved NOM removal from raw water in comparison to GAC adsorption, and membrane filtration processes. Further, Table 6 gives us a qualitative summary of three treatment options in terms of the efficiency of each process in removing NOM, the complexity of the process in relation to operation and maintenance, and total annualized cost of the technology [40]. Optimized coagulation is the least costly option among them. Many water treatment plants try to comply with new DBP regulations by using existing facilities and enhancing the coagulation process.

It was concluded, EC and OC techniques can be able to meet the EPA and EU THM limits of 80 and 100 µg/l, respectively. Furthermore, Figs. 11 and 12 present the 48 h THMFP results for evaluation of THM levels in distribution systems of Istanbul. OC led to higher removal of DOC than did the BC. For THMFP-48 h, under OC and EC conditions with ferric chloride and alum,

Table 6  
Qualitative summary of selected aspects of NOM removal technologies [40]

NOM removal processes	Removal efficiency	Process complexity	Process cost
Optimized coagulation	Good	Low–medium	Low
GAC adsorption	Very good	Medium–high	Medium
Membrane filtration	Excellent	Medium	Medium–high

all water sources meet the both EPA and EU THM limits, respectively. However, under BC conditions with ferric treatment, just TLW and OLW meet the EU THM limit of 100 µg/l, whereas with alum coagulation, none of three surface water supplies meet the required THM limit of EPA and EU, respectively.

The reductions in THMFP for 7 day concentrations under OC conditions were between 52 and 79% (average THMFP reduction of 66%); while DOC removals under OC conditions ranged from 34 to 71% (average DOC removal of 56%) (Tables 4 and 5) for three surface water. EC and OC would result in an additional DOC removal of 50 and 74%, respectively. This improvement in DOC removal was significant. As a comparison, Amy [29] reported that EC was capable of achieving DOC removals of 50%. Depending on the source water, Bell et al. [38] observed that organic removal could reach 60–80% by OC with ferric chloride. Overall, EC and OC proved to be beneficial for waters of varying water quality. The results indicated that benefits of OC were site specific. To determine how effective EC and OC treatments are under certain conditions, it is necessary to conduct bench scale, pilot or full-scale experiments.

## 4. Conclusions

This investigation included jar tests using three raw water supplies in Istanbul, Turkey. Organic precursors such as, DOC, UV<sub>254</sub>, SUVA, and THMFP removals were used to identify the BC, EC, and OC treatments. During this study, variations in NOM removal were observed that could be attributable to the coagulation conditions, and the raw waters SUVA values. Compared to conventional treatment practices of BC, EC led to an additional removal of 50% for DOC, 34% UV<sub>254</sub>, 21% SUVA, and 28% for THMFP. Moreover, OC conditions resulted in extra treatment of 74% for DOC, 55% UV<sub>254</sub>, 36% SUVA, and 53% for THMFP. OC can be an efficient and inexpensive tool in comparison to GAC adsorption, and membrane filtration to control NOM in Istanbul water supplies. Overall, when OC was implemented in jar tests, the effectiveness of the treatment program appeared to depend on the pH of coagulation. Jar tests conducted with depressed pH levels at OC conditions removed more DOC than those at moderate pH levels at EC. For low DOC waters, like OLW, additional treatment would be necessary to achieve enhanced removal of NOM. The effectiveness of the treatment process may be different for DOC, UV<sub>254</sub>, and THMFP. Reduction in one of these parameters does not guarantee that other fractions have been equally affected. It is important, therefore, to monitor each of these fractions to ensure reductions in DBP formation levels.

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