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INVESTIGATION OF TRIHALOMETHANE FORMATION AFTER CHLORINE DIOXIDE PREEOXIDATION FOLLOWED BY CHLORINATION OF NATURAL ORGANIC MATTER

Chlorine dioxide (ClO_2) is widely used as powerful oxidant to remove taste, odor and pathogenic microorganisms with chlorine during water treatment. In this study, the formation of trihalomethanes (THMs) was investigated in sequential ClO_2 and chlorination processes. During the study, water samples were collected from Terkos Lake water (TLW) and Büyükçekmece Lake water (BLW) in Istanbul. To understand the relationship between the formation of THMs and the characteristics of natural organic matter (NOM), changes in the molecular weight (MW) of NOM fractions before and after ClO_2 oxidation were characterized with the ultrafiltration technique. The NOM fraction with MW <1 kDa is the dominant fraction among all the fractionated water samples. ClO_2 oxidized NOM to more hydrophilic and smaller organic fractions as seen in the NOM fraction with MWCO <1 kDa. ClO_2 preoxidation reduced THM concentrations but produced chlorite (ClO_2^-) and chlorate (ClO_3^-). The increase in ClO_2 doses enhanced the reduction percentages of THMs during subsequent chlorination in water samples without or with bromide application. Bromine incorporation was higher in ClO_2 preoxidized TLW and BLW samples. As a result, the findings of this study demonstrated that ClO_2 preoxidation prior to chlorination is an applicable strategy for control of THMs in water treatment.

1. INTRODUCTION

Chlorine dioxide (ClO_2) is a widely used chemical employed for disinfection during drinking water treatment since it is a powerful oxidizing agent for effective inactivation of viruses, bacteria, and waterborne pathogens [1, 2]. Also, it was used for taste and odor control, color removal, and removal of organics and inorganics from water. Although ClO_2 does not form significant levels of chlorination byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs), inorganic disinfection byproducts (DBPs) such as chlorite (ClO_2^-) and chlorate (ClO_3^-) occur as a result

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of ClO_2 disinfection [3, 4]. THMs represent a substantially greater fraction of chlorinated DBPs. Also, these products have adverse health effects on human beings and are considered to be potentially carcinogenic [5]. The USEPA has set maximum concentration levels of four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) to $80 \mu\text{g}/\text{dm}^3$. In Turkey, the THM limit is $100 \mu\text{g}/\text{dm}^3$ [6]. According to health concerns about chlorite and chlorate, the USEPA established a federal drinking water threshold level of $0.8 \text{ mg}/\text{dm}^3$ for ClO_2 and $1.0 \text{ mg}/\text{dm}^3$ for ClO_2^- ions [7].

Typically, up to 60% of the applied ClO_2 dose is reduced to ClO_2^- ions, and up to 10% is converted into ClO_3^- ions due to the presence of natural organic matter (NOM) in raw water sources [8]. To control the formation of various byproducts during the oxidation treatment of source water, it is of great importance to know the characteristics of the precursor in the source water. The characteristics of NOM are of great significance to the water treatment processes [9]. Not only the chemical but also the physical properties of NOM play major roles in disinfection processes with chlorine and chlorine dioxide [10]. Moreover, NOM is a major organic precursor for DBPs like THMs [11]. Therefore, NOM in raw water has to be characterized to understand its complexity. Some fractionation techniques, such as the resin adsorption process [10] and ultrafiltration [12], can be useful for NOM characterization. NOM is generally divided into hydrophobic, transphilic, and hydrophilic groups based on resin adsorption affinity [12]. To reduce the formation of DBPs, some water utilities are looking for alternative chemical biocides [13] such as ozone, chloramines, trichlorocyanuric acid, and ClO_2 . Among these biocides, ClO_2 has recently gained popularity, as it generates significantly less THMs and haloacetic acids (HAAs) [14] compared to other oxidants. ClO_2 oxidizes NOM and produces more hydrophilic and low molecular weight organic matter [15], which also affects the formation of DBPs during subsequent chlorination. Jang et al. [16] reported that HAAs formation potential increased in the order of transphilic > hydrophobic > hydrophilic NOM, suggesting HAAs yield formed during ClO_2 disinfection significantly depends on the characteristics of NOM.

Bromide exists naturally in raw waters of coastal cities due to seawater intrusion and ClO_2 is also a good primary disinfectant for water with high bromide levels. In other words, DBPs containing bromine, which are generally more toxic than their chlorinated counterparts [17], are generated as a result of chlorination and ozonation. Satpathy et al. [18] demonstrated that THMs have a greater tendency for bromine incorporation with the increase in the bromide level. Hong et al. [19] observed that species distribution shifted from the dominance of dichloro- and trichloro-HAAs on chlorination in the absence of excess bromide, to dibromo- and tribromo-HAAs in the presence of excess bromide as a result of the powerful substitution ability and high molecular weight of bromine. To reduce the toxic brominated DBPs amounts, disinfection processes in drinking water treatment systems were performed widely with only ClO_2 or a combination of chlorin-

ation. As such, the objective of this study is to investigate the changes in NOM properties with ClO₂ oxidation and the effects of ClO₂ oxidation on the formation of THMs in bromide-rich waters.

2. EXPERIMENTAL

Source water and sampling. Representative water samples were collected from Terkos Lake water (TLW) and Büyükçekmece Lake water (BLW) in Istanbul, Turkey. Samples were collected during the fall period (September–November). TLW and BLW are the main surface water sources for Istanbul, providing nearly 2 million m³ per day raw water to the drinking water treatment plants of Istanbul. Water samples were stored in 5 dm³ glass containers, transported to the laboratory, and filtered immediately using a Millipore membrane filter (0.45 µm). The samples were stored at 4 °C to retard microbial activity before use. The physicochemical characteristics of TLW and BLW based on 6 samples collected from the TLW and BLW during the fall period are given in Table 1.

Table 1

Physicochemical characteristics of TLW and BLW samples

Parameter	TLW		BLW	
	Range	Average	Range	Average
pH	7.35–8.11	7.69	7.97–8.43	8.13
Turbidity, NTU	3.4–8.7	4.3	1.8–7.7	3.2
Conductivity, µS/cm	285–596	411	311–687	533
Alkalinity, mg CaCO ₃ /dm ³	115–162	123	104–139	125
Total hardness, mg CaCO ₃ /dm ³	109–168	121	132–194	153
Temperature, °C	7.3–22.8	16.3	7.4–26.9	15.7
Chloride, mg/dm ³	38–63	51	63–125	76
Dissolved oxygen, mg/dm ³	6.98–8.12	7.85	6.21–7.88	7.23
Br ⁻ , mg/dm ³	83–310	120	140–280	210
DOC, mg/dm ³	3.79–7.69	4.73	3.32–5.89	4.05
UV ₂₅₄ , cm ⁻¹	0.07–0.155	0.13	0.06–0.14	0.11
SUVA, dm ³ /(mg·m)	2.03–4.09	2.77	1.84–3.21	2.52

Molecular size fractionation of NOM by ultrafiltration. The water samples containing NOM were taken from each surface water source. UF was carried out by using a stirred UF cell (Millipore 8200) with YM disc membrane made of regenerated cellulose (Amicon, USA). The molecular weight (MW) of the applied membranes was as follows: 1, 3, 5, 10, and 30 kDa. Each of the water samples was ultrafiltered sequentially through UF membranes with the MW equal to 30, 10, 5, 3, and 1 kDa. Before the fractionation process, the apparatus was cleaned according to the procedure of Zhao et al. [20].

Firstly, membranes were soaked several times (not less than three times) with deionized ultrapure water (DIUF) to remove glycerin which was added by the producers to the membrane to avoid drying during shipment. After soaking, the membrane was placed in the UF cell pressurized with nitrogen gas in the range from 20 to 35 kPa. DIUF was then passed through the UF cell with the membranes installed to remove any organic impurities. A transmembrane pressure of 0.35 MPa was applied for UF tests with surface water samples.

Cl₂ and ClO₂ oxidation. Oxidation of water samples by Cl₂ and ClO₂ was carried out in a 500 cm³ amber-color glass bottle. TLW and BLW samples were buffered to pH 7.5 with 5 mM phosphate buffer. Cl₂ stock (1000 mg/dm³) and working standard (5 mg/dm³) solutions were prepared using commercial 4% NaOCl and standardized by iodometric titration (accuracy ±0.18 mg/dm³). It is essential that ClO₂ solutions used for the study be devoid of chlorine for accurate comparison of THM formation during both biocide treatment conditions. The chlorine-free ClO₂ solution was generated by acidifying sodium chlorite with 1 M H₂SO₄, followed by stripping the ClO₂ with nitrogen over sodium chlorite solution and dissolving the ClO₂ gas in chilled Millipore Type-I water (18 MΩ·cm). Water samples were treated with Cl₂ dose of 5 mg/dm³ and ClO₂ working standard solutions to obtain initial oxidant ClO₂ doses of 2–10 mg/dm³ to investigate the dose effect of ClO₂ on THM formation within 24 hours. To evaluate the effect of bromide concentrations, 10 mg/dm³ KBr stock solution was prepared and various bromide concentrations (Br⁻ concentrations; 0.5, 1 and 2 mg/dm³) were added to water samples together with oxidants.

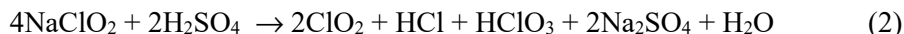
Calculation of bromine incorporation factor. To assess bromine substitution during THM formation, the percentage of molar bromine incorporation (BIP) is used generally and it was calculated according to [34]:

$$BIP = \frac{[\text{THM-Br}]}{[\text{THMs}]} \times 100\% \quad (1)$$

where [THM-Br] is the sum of the molar concentrations of the bromine-containing THM species and THMs represents the sum of the molar concentrations of the bromine THMs species with chloroform (CHCl₃).

Analytical procedure. All water samples were analyzed based on procedures described in the Standard Methods (SM) [21]. Dissolved organic carbon (DOC) analyses were performed with a Shimadzu TOC-5000 analyzer equipped with an autosampler, by the high-temperature combustion method according to SM-3510B. A UV-1608 Shimadzu spectrophotometer was used for measurements of UV absorbance at 254 nm. Specific UV absorbance (SUVA) was calculated as the UV₂₅₄ absorbance divided by the DOC concentrations. THM analyses were conducted by the EPA method 551.1 for

liquid–liquid extraction (LLE) with pentane and gas chromatography with electron-capture detection [22]. According to mass balance for each NOM fraction, DOC recovery rates for TLW and BLW samples were found to be 100 ± 6.2 and $100\pm 4.4\%$, respectively. ClO_2 was generated according to



The concentration of ClO_2 was determined by $\text{Na}_2\text{S}_2\text{O}_3$ titration similar to chlorine analysis. Residual oxidant concentration at various intervals was measured by the DPD-colorimetric method [21].

THMs analyses were performed with the HP 7890 Series II gas chromatograph equipped with a micro electron capture detector (GC- μ ECD) and the analytical detection limit was $0.1\pm 0.0001 \mu\text{g}/\text{dm}^3$. A capillary column of DB-1 (30 m \times 0.32 mm I.D. \times 1.0 μm , J&W Scientific) was used. Injections of samples were made in split/splitless mode, with helium as carrier gas and nitrogen as makeup gas. The four THM species were chloroform (CHCl_3), dichlorobromomethane (CHCl_2Br), dibromochloromethane (CHBr_2Cl), and bromoform (CHBr_3). Analyses of Br^- , ClO_2^- , and ClO_3^- in the water samples were carried out using the Dionex IC 3000 system (USA) equipped with an AS-19 analytical column and an AG-19 guard column as per USEPA method 300.1 [23] and the analytical detection limit was $0.001\pm 0.0001 \text{ mg}/\text{dm}^3$.

3. RESULTS AND DISCUSSION

3.1. NOM SIZE DISTRIBUTION IN WATER SOURCES

The MW of most NOM in TLW and BLW samples was <1 kDa and its percentage was determined as 46.09 and 57.78% for TLW and BLW samples, respectively (Fig. 1).

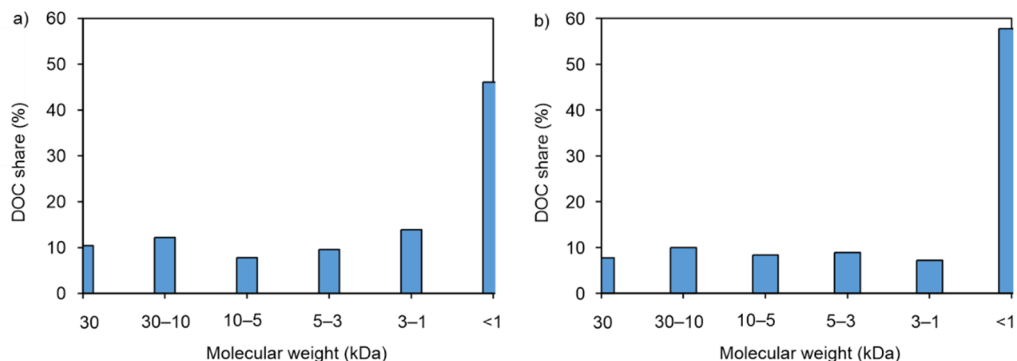


Fig. 1. Fraction mass distribution of water samples from: a) TLW, b) BLW

The NOM fractions with MW >30, 30–10, 10–5, 5–3, and 3–1 kDa in TLW and BLW samples were 10.44 and 7.78, 12.17 and 8.33, 7.83 and 8.33, 9.56% and 8.89, 13.91 and 7.22%, respectively, based on the DOC concentration calculations. The results of this part of the study show that organic carbon of NOM in TLW and BLW consists of hydrophilic fractions which are characterized by aliphatic carbon and nitrogenous compounds such as carbohydrates, sugars, and amino acids [24]. Our results confirm the findings by Wei et al. [10] that the fraction of MW less than 1 kDa comprises the largest part of DOC content in all water samples. Also, molecules with low molecular weight and small size are relatively hydrophilic and not effectively removed by coagulation or adsorption [25]. As the major fraction of NOM in TLW and BLW was <1 kDa, NOM in source waters would not be removed effectively by the conventional drinking water treatment process.

3.2. EFFECT OF ClO₂ OXIDATION ON NOM

Figure 2 illustrates NOM fractions in water samples with and without ClO₂ oxidation to provide information about the MW distribution and hydrophobicity of NOM in TLW and BLW samples.

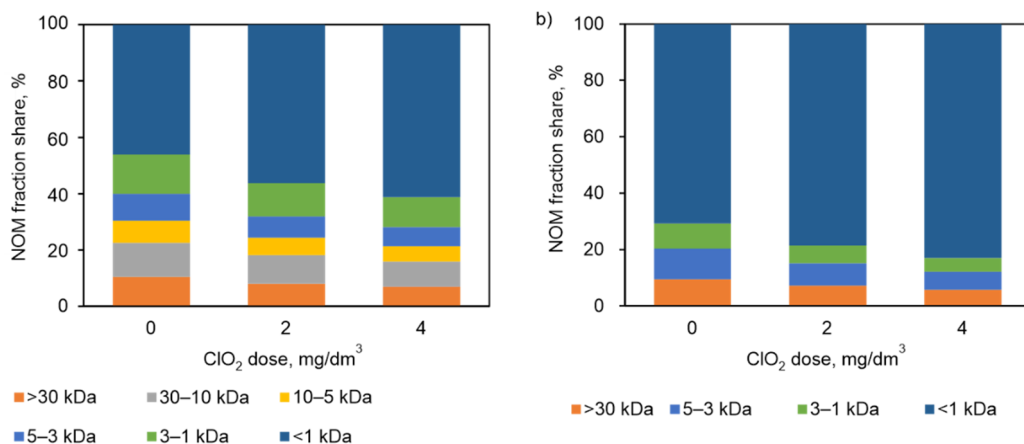


Fig. 2. NOM fractions in TLW (a) and BLW (b) samples without and with ClO₂ oxidation

The highest contribution was from the fraction with MW lower than 1 kDa for TLW and BLW. With ClO₂ oxidation with 2 mg/dm³ at the contact time of 24 h, the size distribution of NOM changed, and the individual fractions of NOM with MW from <1 kDa, 3 to >30 kDa for TLW were 61.1, 12.9, 8.2, 6.8, 11.1 and 8.6%, respectively. A similar trend was observed in BLW samples. For instance, as the organic matter with MW less than 1 kDa formed 57.8% of the DOC concentration in BLW samples without ClO₂ oxidization, this ratio increased to 74.6, and 86.8% in BLW samples oxidized with 2 and 4 mg/dm³ of ClO₂. Also, the highest percentage of DOC was obtained for the

fraction of MW <1 kDa (86.8%) among the other fractions in BLW samples oxidized with the highest dose of ClO_2 . On the contrary, after being oxidized with doses of 2 and 4 mg/dm^3 of ClO_2 , a slight decrease was observed in the ratio of DOC concentrations for the other NOM fractions in TLW and BLW samples (Fig. 2). The results indicate that ClO_2 converted large organic fractions of NOM to small organic fractions, especially to MW <1 kDa.

3.3. FORMATION OF ClO_2^- AND ClO_3^- AND THE EFFECT OF ClO_2 PREOXIDATION ON THE CHLORINATION PROCESS

ClO_2^- and ClO_3^- are inorganic by-products that are formed during ClO_2 oxidation of water [26]. Figure 3 shows the concentrations of ClO_2^- and ClO_3^- in TLW and BLW samples with the application of 2–10 mg/dm^3 ClO_2 .

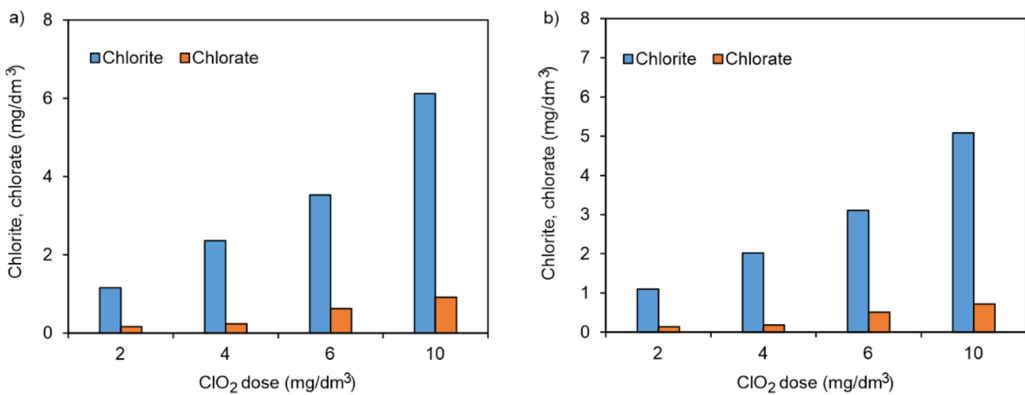


Fig. 3. Formation of chlorite and chlorate in TLW (a) and BLW (b) water samples after treatment with various doses of ClO_2 ; pH 7 and reaction time 24 h

The ClO_2^- concentration levels varied from 1.14 to 6.12 mg/dm^3 and from 1.1 to 5.08 mg/dm^3 with the applied ClO_2 for TLW and BLW samples, respectively (for 2–10 mg/dm^3 of ClO_2). The level of ClO_2^- ion formed in BLW samples was lower than in TLW samples, which may be due to the presence of slightly higher chloride content (56 mg/dm^3) in BLW. On the other hand, ClO_3^- concentrations varied from 0.16 to 0.91 and 0.14 to 0.72 mg/dm^3 of the applied ClO_2 concentration for the TLW and BLW samples, respectively. These findings indicate that up to approximately 60% reduction in the conversion of ClO_2 to ClO_2^- was observed by increasing the dose from 2 to 10 mg/dm^3 . Furthermore, as ClO_2 doses raised to 2 mg/dm^3 or higher, the ClO_2^- concentrations were higher than 1 mg/dm^3 , the maximum contaminant level in the U.S.D/DBP rules [23]. Therefore, ClO_2 should be applied at doses lower than 2 mg/dm^3 to meet the regulations [27–29].

Figure 4 shows the formation of THMs in TLW and BLW samples during chlorination as well as during chlorination preceded by dosing with ClO_2 at 2 mg/dm^3 . Approximately 50% of THMs were produced within the contact time of 1 h.

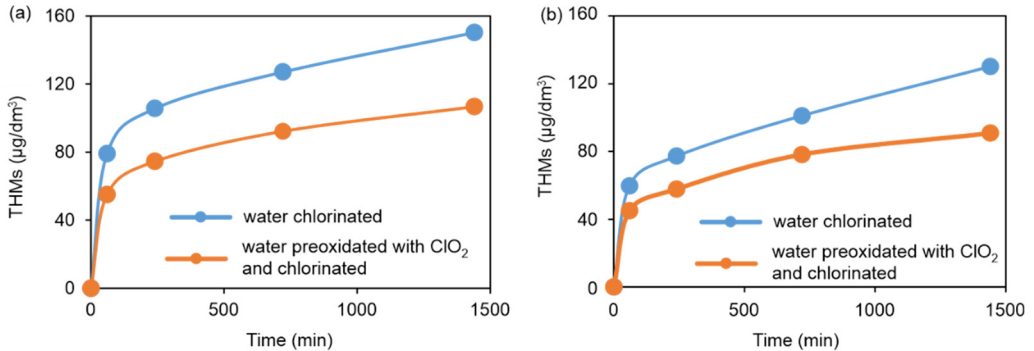


Fig. 4. Formation of THMs during chlorination and chlorination with ClO_2 preoxidation for TLW (a) and BLW (b) samples; $[\text{Cl}_2]$ 5 mg/dm^3 , $[\text{ClO}_2]$ 2 mg/dm^3 , pH 7, reaction time 24 h

The results up to 24 h reaction time showed that the highest THMs concentrations were observed in chlorinated TLW due to high organic matter content, followed by BLW. With the application of 2 mg/dm^3 ClO_2 before chlorination, the concentrations of THMs in TLW and BLW were reduced by around 30% and 25%, respectively. In other words, with chlorination, at a contact time of 24 h, the levels of THMs were recorded as 135.17 µg/dm^3 and 97.26 µg/dm^3 for TLW and BLW samples with a chlorine dose of 5 mg/dm^3 , whereas THM concentrations were determined as 97.26 µg/dm^3 and 72.91 µg/dm^3 with the application of 2 mg/dm^3 ClO_2 oxidation at the reaction time of 24 h. These findings demonstrate that ClO_2 preoxidation reduced the formation of THM during subsequent chlorination. Similar observations have been reported by some authors [30, 31].

3.4. EFFECT OF BROMIDE ON THM FORMATION

Figure 5 presents the formation of THMs during chlorination of TLW and BLW samples in the presence of various bromide concentrations with and without ClO_2 preoxidation. CHCl_3 was the dominant species among the four THMs (CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3) compounds without ClO_2 preoxidation. In the presence of bromide, the concentrations of brominated THM species increased quickly in chlorinated TLW and BLW samples within the reaction time of 24 h. On chlorination, with reaction time of 24 h, the concentrations of CHBr_2Cl and CHBr_3 varied from 33.04 µg/dm^3 and 14.66 µg/dm^3 (TLW) and 45.06 µg/dm^3 and 21.36 µg/dm^3 (BLW) for a bromide dose of 0.5 mg/dm^3 to 50.47 µg/dm^3 and 25.97 µg/dm^3 (TLW) and 59.14 µg/dm^3 and 32.56 µg/dm^3 (BLW) for a bromide dose of 1 mg/dm^3 , whereas the concentrations of CHCl_3 varied from 50.52 µg/dm^3 (TLW) and 49.23 µg/dm^3 (BLW) to 36.26 µg/dm^3 (TLW)

and $32.87 \mu\text{g}/\text{dm}^3$ (BLW) for the same conditions. This observation indicates that the concentration of brominated THMs gradually increased by increasing the bromide concentration for the bromide doses studied ($0.5, 1,$ and $2 \text{ mg}/\text{dm}^3$).

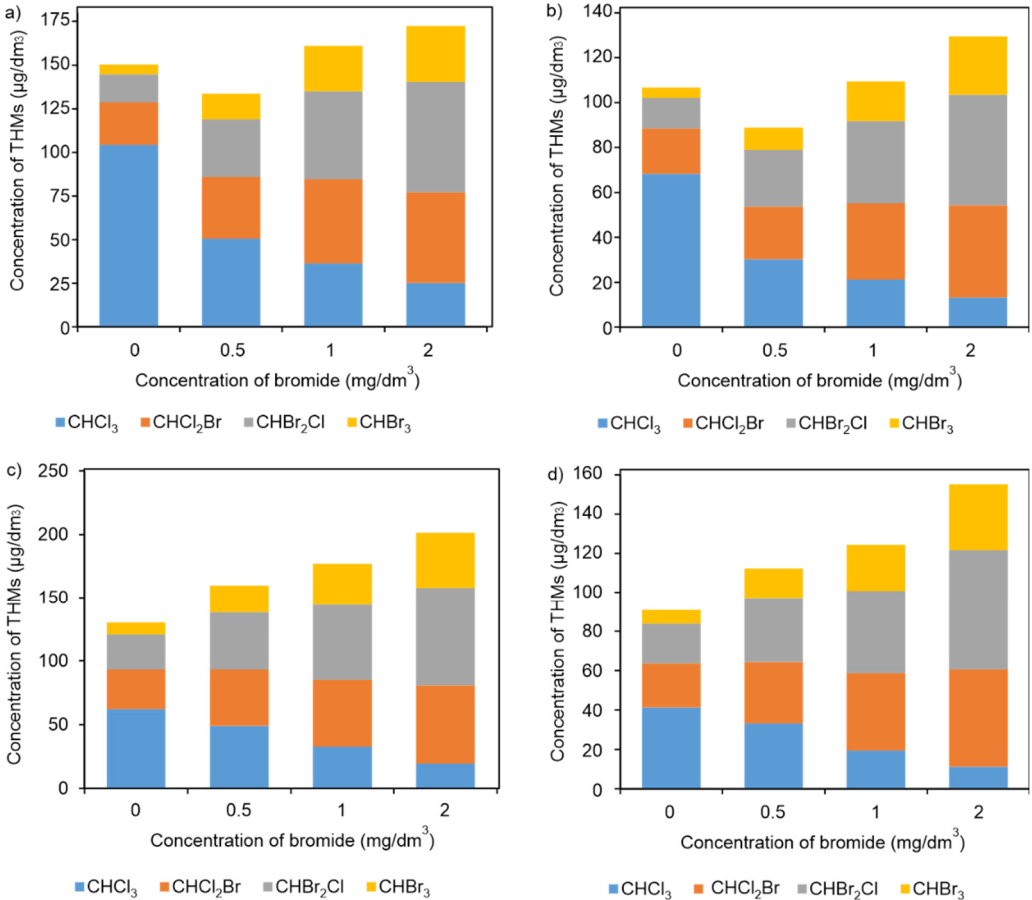


Fig. 5. Effect of bromide concentration on the formation of THMs during chlorination of TLW (a) and BLW (c) samples; pH 7, reaction time 24 h; Effect of bromide concentration on the formation of THMs during chlorination and preoxidation with ClO_2 ($2 \text{ mg}/\text{dm}^3$) for TLW (b) and BLW (d) samples; pH 7, reaction time 24 h

Furthermore, the chlorination of high levels of bromide-containing water modifies the chlorination process, i.e., bromide is rapidly oxidized to bromine and directly affects the formation and distribution of THM species. These results are confirmed by several studies [32, 33]. However, it should be noted that the application of ClO_2 preoxidation reduced the levels of THMs. The results also showed that ClO_2 preoxidation with the dose of $2 \text{ mg}/\text{dm}^3$ was followed by an approximately 30% reduction in brominated THM

species within 24 h for 0.5, 1 and 2 mg/dm³ applied bromide doses in TLW and BLW samples. For example; after ClO₂ preoxidation with a dose of 2 mg/dm³, CHBr₃ concentration in TLW and BLW decreased from 25.97 µg/dm³ (TLW) and 32.56 µg/dm³ (BLW) to 17.71 µg/dm³ (TLW) and 23.76 µg/dm³ (BLW) for bromide dose of 1 mg/dm³. A similar trend was determined for the other THM species under the same conditions. The presence of bromide not only enhanced THM generation but also shifted THMs to more brominated species. The ratio of bromine incorporation (BIP) was used to evaluate bromine substitutions during THM formation in this study.

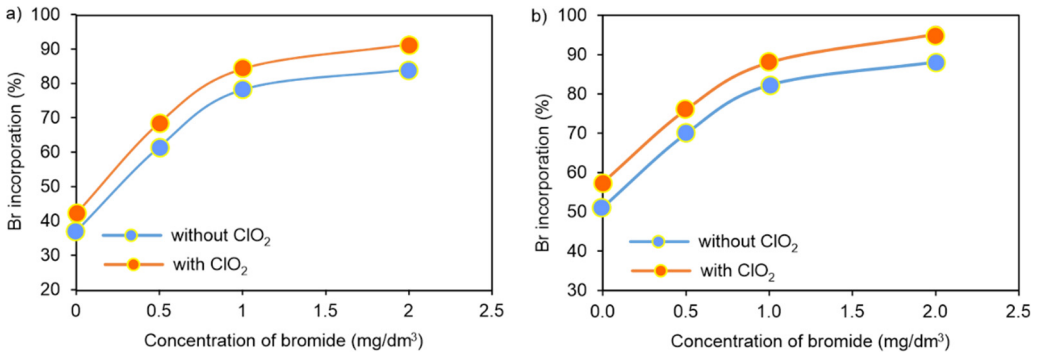


Fig. 6. Effect of bromine incorporation in THMs generated due to chlorination and chlorination preceded by ClO₂ preoxidation for: (a) TLW, b) BLW samples

The effect of bromine incorporation rates with and without ClO₂ preoxidation of TLW and BLW samples is shown in Fig. 6. The bromine incorporation rate increased with the increase in the concentration of bromide. For example, bromine incorporation rates in TLW and BLW were 61.57 and 69.86% at a bromide concentration of 0.5 mg/dm³, and they were equal to 84.07 and 88.13% at a bromide concentration of 2 mg/dm³, respectively. The percentages of bromine incorporation in ClO₂ preoxidation water samples were higher than for water samples subjected only to chlorination. While the highest bromine incorporation ratio was found for ClO₂ preoxidated BLW samples (95.21%) at a dose of 2 mg/dm³ for a reaction time of 24 h, the lowest ratio was determined for only chlorinated TLW (36.98%) samples at the lowest bromide dose (0.5 mg/dm³) within the reaction time of 24 h. Meanwhile, this result demonstrated more bromine incorporation in THM formation after ClO₂ preoxidation. More bromine was incorporated into THMs by the hydrophilic fraction because bromine is more reactive with aliphatic precursors than with aromatic precursors [24].

4. CONCLUSION

The formation and distribution of THMs in sequential ClO₂ and chlorination processes were systematically examined for Terkos Lake water (TLW) and Büyüçekmece

Lake water (BLW) samples containing NOM. The changes in NOM properties were characterized with UF technique and the fraction with MW <1 kDa was the predominant organic matter fraction among all NOM fractions, following the results of mass balance on DOC. As the NOM fractions in TLW and BLW were oxidized with ClO₂, the share of NOM fractions <1 kDa increased in TLW and BLW. It was concluded that ClO₂ tended to form more hydrophilic and low-molecular-weight NOM fractions. It was also reported that ClO₂⁻ and ClO₃⁻ concentrations increased due to increasing ClO₂ doses and generally up to 60% of the applied ClO₂ dose was reduced to chlorite ion, and 8–10% was converted to ClO₃⁻ ion. On the other hand, the ClO₂ preoxidation reduced the formation of THMs by around 25–30% in TLW and BLW samples during subsequent chlorination. The other finding in this study was that the content of brominated THM species increased with increasing bromide concentrations and bromine was very reactive in the substitution and addition reactions that formed THMs. Further, the ClO₂ preoxidation reduced the brominated THM concentrations resulting from the application of bromide doses of 0.5–2 mg/dm³. Bromine incorporation was used to indicate the degree of bromine substitution in THMs. Bromine incorporation in THMs exhibited higher values in ClO₂ preoxidized TLW and BLW samples than for water samples subjected to chlorination only. This indicated more bromine incorporation in THM formation after ClO₂ preoxidation. In other words, the increased bromide incorporation due to ClO₂ oxidation of the source water with moderate bromide concentrations may be an important parameter to consider when changing water treatment from Cl₂ to ClO₂.

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