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Original Paper

Effects of Combined Chlorine Dioxide and Chlorine Disinfection on the Formation of Disinfection Byproducts

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Abstract

To investigate the effects of combined chlorine dioxide (ClO_2) and chlorine disinfection on disinfection byproduct formation, this study controlled disinfection conditions (temperature, pH, dosing sequence) and organic matter types to analyze their influences on byproduct generation, and explored the practical application characteristics based on disinfection experiments of natural water samples. The results showed that combined disinfection could effectively reduce the formation of disinfection byproducts.The reaction rate of ClO_2 in the combined disinfectant was less affected by temperature than chlorine. The formation ratio of $CHCl_3$ increased with rising temperature, while that of ClO_2^- decreased. With increasing solution pH, the formation of ClO_2^- increased gradually, ClO_3^- first decreased and then increased, and $CHCl_3$ formation reached the maximum under neutral conditions and the minimum under acidic and alkaline conditions. Dosing ClO_2 first could effectively reduce the formation of the organic byproduct $CHCl_3$ and lower the compliance rate of generated byproducts. The reactivity order of combined disinfectants with organic matters was: TA > HA > BSA > SA. Fluorescence spectroscopy analysis before and after disinfection of natural water showed that the main precursors of combined disinfection were humic acid and fulvic acid-like substances.

Keywords

Chlorine, Chlorine dioxide, Combined disinfection, Disinfection byproducts, Natural organic matter

1. Introduction

Disinfection, as a critical step in drinking water treatment, plays an irreplaceable role in controlling the transmission of waterborne diseases (Zeng, Zhang, Zeng et al., 2009). Chlorine disinfection has been widely used worldwide since the early 20th century due to its advantages of low cost, simple operation,

and long-lasting disinfection efficacy. It has significantly reduced the incidence of waterborne diseases globally and remains the most extensively applied drinking water disinfection method both domestically and internationally (Feng, Yang, Wu et al., 2025). However, during chlorine disinfection, addition or substitution reactions occur between chlorine and natural organic matter (NOM) in water, leading to the formation of various chlorinated disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Sun, Cai, Song et al., 2026). A large number of studies have demonstrated that these byproducts possess potential health risks including carcinogenicity, teratogenicity, and mutagenicity, which may cause long-term harm to human health (Mzinyathi, Muthuraj, Ajala et al., 2025). Therefore, how to effectively control DBP formation while ensuring disinfection efficiency has become a crucial issue urgently requiring solution in the field of drinking water treatment.

To address the technical limitations of single disinfectants, the combined chlorine dioxide (ClO_2) and chlorine disinfection process has shown promising application prospects. This process can not only utilize the rapid sterilization ability of ClO_2 and its priority in oxidizing partial precursors to reduce the potential of organic DBP formation during subsequent chlorine disinfection (Prasert, Kurisu, & Phungsai, 2025), but also rely on the sustained bactericidal capacity of chlorine to maintain residual chlorine requirements in the water distribution network, while effectively controlling the residual concentrations of inorganic byproducts (Rougé, Lee, von Gunten et al., 2022). Nevertheless, as a novel disinfection technology, the mechanism underlying the impact of the combined ClO_2-chlorine disinfection process on DBP formation remains unclear, and a scientific and reasonable disinfectant matching method has not yet been established.

In view of this, targeting the problems of insufficient disinfection duration and the risk of exceeding the standard for inorganic DBPs during ClO_2 disinfection of drinking water, this study constructed a combined ClO_2-chlorine disinfection system to systematically analyze the formation patterns of DBPs ($CHCl_3$, ClO_2^-, and ClO_3^-) and optimize the combined disinfection process. This research aims to provide a theoretical basis for understanding the environmental behavior and stability of ClO_2 and chlorine during their combined disinfection of drinking water.

2. Materials and Methods

2.1 Experimental Materials

Sodium chlorate ($NaClO_3$), sodium chlorite ($NaClO_2$), and tannic acid (TA) were purchased from Aladdin Reagents. Sodium hypochlorite (NaClO) and humic acid (HA) were obtained from Sigma-Aldrich, while salicylic acid (SA) and bovine serum albumin (BSA) were supplied by Sinopharm Chemical Reagent Co., Ltd.The stock solution of chlorine dioxide (ClO_2) used in the experiments was prepared according to the method described in Chlorine Dioxide Technology for Drinking Water. HA, BSA, SA, and TA were dissolved in deionized water with stirring in the dark for 24 hours, followed by filtration through a 0.45 μm membrane filter. All prepared reagents were

hermetically sealed and stored in a refrigerator at 4℃ prior to use.

2.2 Combined Chlorine Dioxide and Chlorine Disinfection Experiments

The total available chlorine of the combined disinfectant was fixed at 5 mg/L, with a total organic carbon (TOC) concentration of 2 mg/L, pH of 7, and temperature (T) of 25℃. Combined disinfectants with different ClO_2/chlorine dosage ratios were prepared to investigate the effects of dosage ratio on chlorine consumption and the formation of ClO_2^-, ClO_3^-, and $CHCl_3$ during disinfection.

The dosage ratio of the combined disinfectant was fixed at 1 (i.e., 2.5 mg/L ClO_2 + 2.5 mg/L chlorine, calculated as available chlorine), with TOC = 2 mg/L, pH = 7, and T = 25℃. Under the conditions of different reaction temperatures, pH values, and dosing sequences, the effects of these variables on chlorine consumption and the formation patterns of ClO_2^-, ClO_3^-, and $CHCl_3$ were explored respectively.

The formation ratio of byproducts was calculated using Equation (2-1), and the standard compliance rate was determined by Equation (2-2).

$$\eta = \frac{D}{C} \times 100\% \tag{2-1}$$

Where: η is the formation ratio of byproducts (%); D is the formation amount of byproducts (mg/L); C is the actual consumption of disinfectant (mg/L). The actual consumption of ClO_2 was calculated by dividing the measured ClO_2 consumption (expressed as available chlorine) by the conversion factor of 2.63.

$$\theta = \frac{D}{EL} \times 100\% \tag{2-2}$$

Where: θ is the standard compliance rate of byproducts (%); D is the formation amount of byproducts (mg/L); EL is the emission limit of byproducts (mg/L).

2.3 Experiments on the Reaction between Combined clo₂-chlorine Disinfectant and Natural Organic Matter

Typical organic substances commonly found in natural water bodies, including humic acid (HA), salicylic acid (SA), bovine serum albumin (BSA), and tannic acid (TA), were selected as disinfection precursors. Under the conditions of total organic carbon (TOC) = 4 mg/L, pH = 7, and temperature (T) = 25℃, the effects of different organic matter types on chlorine consumption and the formation patterns of ClO_2^-, ClO_3^-, and $CHCl_3$ during disinfection were investigated.

Actual natural water samples were collected, and fluorescence spectroscopy analysis was conducted before and after disinfection. The Fluorescence Regional Integration (FRI)[7] method was employed to obtain the integrated standard volume of different regions, which represents the relative content of organic matter corresponding to each region. This was used to analyze the reaction mechanism between the combined disinfectant and organic matter, and to identify the main precursor types of the combined disinfection process. The degradation rate R of organic matter was calculated using Equation (2-3).

$$R = \frac{\Phi_0 - \Phi_n}{\Phi_0} \times 100\% \quad (2\text{-}3)$$

Where: Φ_0 and Φ_n are the regional integration values of the original water and the water after disinfectant addition, respectively (a.u.•nm²).

2.4 Collection and Preservation of Actual Water Samples

Actual water samples used in the experiments were collected from an artificial lake located in Pukou District, Nanjing City. After collection, the samples were allowed to stand for 2 hours to remove large particulate sediment, followed by filtration through a 0.45 μm membrane filter. Water quality parameters were then determined immediately.

2.5 Analytical Methods

The concentration of ClO_2 was determined by the N,N-diethyl-p-phenylenediamine (DPD) method, and the available chlorine concentration was calculated using the indirect iodometric titration method (Cai, Fu, Li et al., 2009), as shown in Equation (2-4).

$$X = \frac{C \times V_{st} \times 0.03545}{V} \times 1000 \quad (2\text{-}4)$$

Where: X is the available chlorine concentration (g/L); C is the concentration of the standard sodium thiosulfate titrant (mol/L); V_{st} is the volume of the sodium thiosulfate solution used for titration (mL); V is the volume of the sample solution in the iodine flask (mL).

The concentrations of ClO_2^- and ClO_3^- were measured using a Dionex IC 2000 ion chromatography system equipped with an AS19 anion-exchange column and an AG-19 guard column. $CHCl_3$ was analyzed by headspace gas chromatography (HS-GC) with a DB-5 capillary column. TOC concentration was determined using a TOC analyzer. Three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy of natural water samples was conducted using a molecular fluorescence spectrophotometer.

3. Results and discussion

3.1 Effects of Disinfectant Dosage ratio on the Formation of Disinfection Byproducts

The variations of disinfection byproducts with the dosage ratio of ClO_2 to chlorine in the combined disinfection system are shown in Figure 1. As presented in Figure 1a, with the increase of ClO_2 dosage ratio, the consumption of ClO_2 increased linearly while the consumption of chlorine decreased correspondingly, indicating an obvious dose substitution relationship between the two disinfectants. The residual chlorine concentration first increased and then decreased with the increase of ClO_2 dosage ratio, reaching a peak of 1.58 mg/L at a dosage ratio of 0.25. This phenomenon is attributed to the high reaction activity and redox potential ($E° = 1.51$ V) of ClO_2, which enables it to rapidly degrade organic matter in water. At a low ClO_2 dosage ratio, ClO_2 quickly degrades some easily oxidizable organic matter, delaying the subsequent consumption of chlorine and thus leading to an increase in residual chlorine concentration. As the ClO_2 ratio continues to increase, its own consumption becomes dominant,

and no chloramine substances with sustained disinfection capacity are produced after the reaction, resulting in a decrease in residual chlorine levels.

As shown in Figure 1b, the formation amounts of ClO_2^- and ClO_3^- both increased with the increase of ClO_2 dosage ratio, and the formation amount of ClO_2^- was significantly higher than that of ClO_3^-. This indicates that the disproportionation reaction of ClO_2 during disinfection is the main pathway for the formation of its inorganic byproducts (Equation 3-1). Under neutral conditions (pH = 7), this disproportionation reaction becomes the dominant pathway for ClO_2 decomposition, and ClO_2^- accumulates in large quantities as the main primary product. In contrast, the formation of ClO_3^- may involve more complex secondary oxidation processes, leading to its relatively low formation amount. The formation amount of $CHCl_3$ decreased sharply with the increase of ClO_2 dosage ratio until it reached zero (Figure 1c). The formation of $CHCl_3$ during chlorine disinfection originates from the electrophilic substitution reaction of hypochlorous acid (HOCl) with electron-rich sites (such as phenolic and ketonic acid structures) in humic acid-like organic matter, which undergoes a series of processes including chlorination, hydrolysis, and cleavage to eventually form halogenated byproducts such as $CHCl_3$. In contrast, the reaction mechanism of ClO_2 is dominated by electron transfer, which can efficiently destroy the molecular structure of organic matter (e.g., breaking carbon-carbon double bonds, oxidizing phenols to quinones or small-molecule acids) without introducing chlorination reactions, thus avoiding the formation of $CHCl_3$ from the reaction pathway. In the combined disinfection system, increasing the ClO_2 ratio promotes the degradation of more organic matter through a “harmless” pathway, significantly reducing the content of precursors available for chlorination reactions, thereby inhibiting the formation of $CHCl_3$.

$$2ClO_2 + H_2O \rightleftharpoons 2H^+ + ClO_2^- + ClO_3^- \quad (3\text{-}1)$$

When ClO_2 was used alone for disinfection, the standard compliance rate of ClO_2^- increased sharply to 147.1%; when chlorine was used alone, the standard compliance rate of $CHCl_3$ was also as high as 158.6% (Figure 1d), both exceeding the standard limits with significant potential health risks. However, under the combined disinfection condition, the standard compliance rates of ClO_2^- and trihalomethanes could be reduced to a minimum of 21.4% and 20.1%, respectively. This indicates that by optimizing the dosage ratio of ClO_2 to chlorine, the formation of byproducts can be effectively controlled, and the risk of exceeding the standard can be significantly reduced.

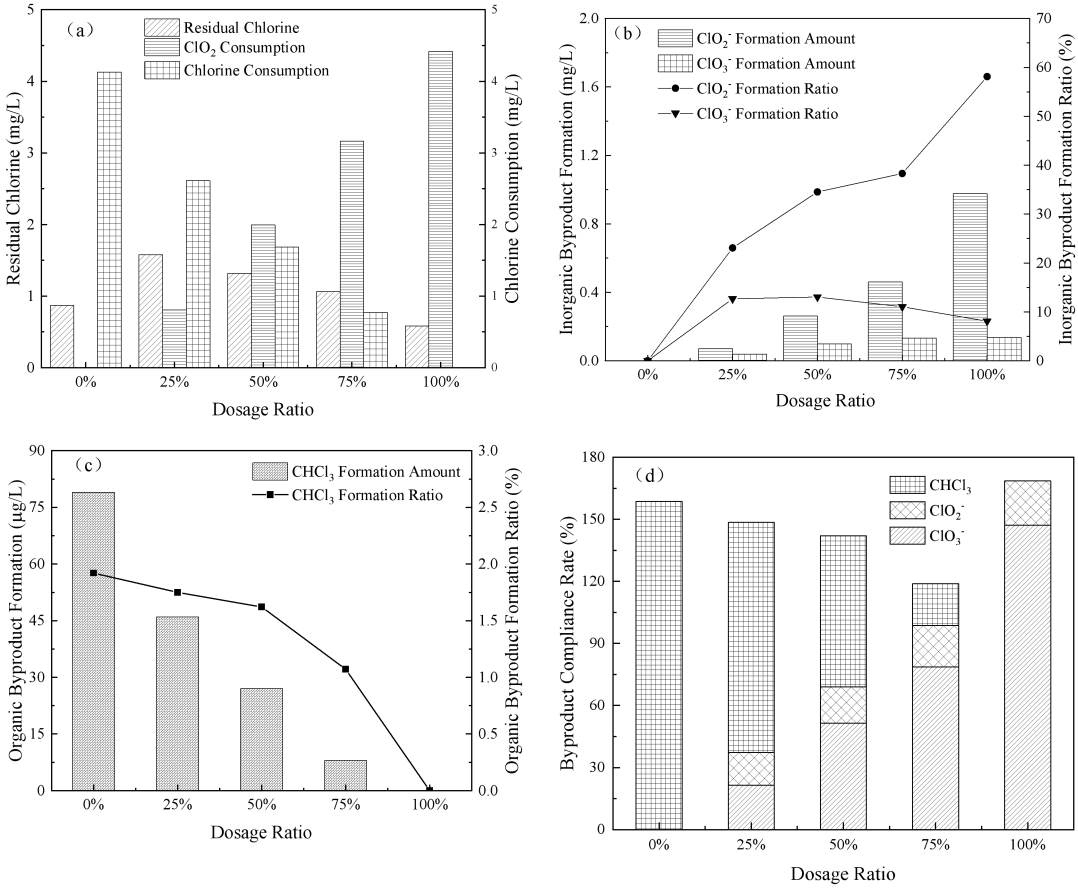

Figure 1. Effects of Disinfectant Dosage Ratio on the Formation of Disinfection Byproducts

3.2 Effects of Disinfection Conditions on Byproduct Formation

3.2.1 Temperature

The variations in disinfection byproducts with different reaction temperatures are shown in Figure 2. With increasing temperature, both disinfectant consumption and byproduct formation exhibited an increasing trend. This variation follows the Arrhenius law, i.e., elevated temperature increases the reaction rate constant, thereby accelerating the redox reaction between disinfectants and organic matter in water, significantly promoting the disproportionation of ClO_2, and leading to increased formation of ClO_2^- and ClO_3^-.

As shown in Figure 2b, the formation of $CHCl_3$ increased significantly from 12.454 μg L^{-1} to 37.793 μg L^{-1}, and its formation ratio also rose from 1.23% to 1.73%. $CHCl_3$ is mainly derived from the electrophilic substitution reaction between chlorine and reactive functional groups in humic acids (e.g., phenolic and enol structures). Higher temperature not only accelerates the decomposition rate of chlorine but may also enhance the formation potential of $CHCl_3$ by altering the conformation of organic matter and exposing more reactive sites. In the combined ClO_2^-chlorine disinfection system, a competitive reaction mechanism exists between the two disinfectants. ClO_2 can preferentially oxidize part of the organic matter and inhibit the formation of chlorinated byproducts to a certain extent.

However, at higher temperatures, the reactivity of chlorine is significantly enhanced, which may result in a remarkable increase in $CHCl_3$ formation. Therefore, temperature is a key factor regulating the formation of byproducts during combined disinfection.

Elevated temperature significantly increases the formation risk of ClO_2^-, ClO_3^-, and $CHCl_3$ by improving disinfectant reactivity and promoting side reaction pathways. Therefore, in practical drinking water treatment processes, especially in high-temperature seasons, disinfection temperature and dosing strategies should be carefully controlled to achieve a balance between disinfection efficiency and byproduct control.

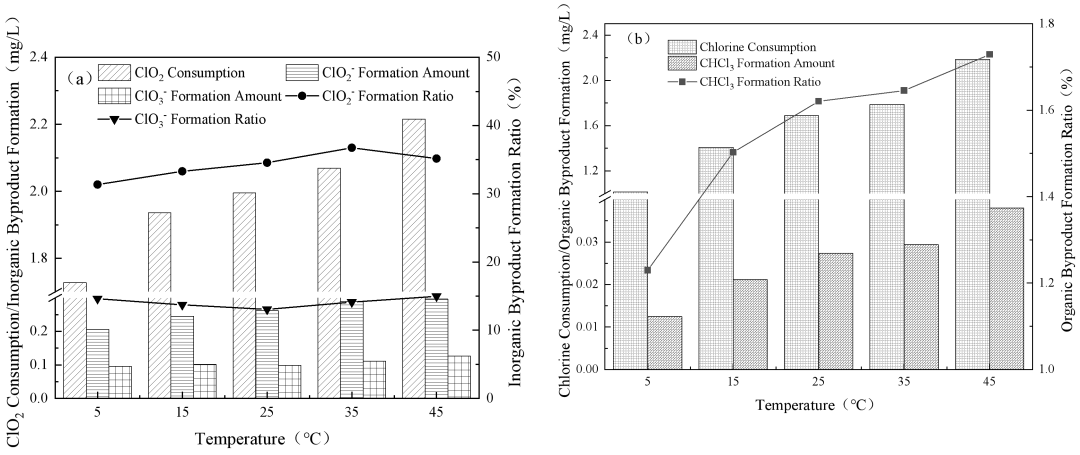

Figure 2. Effects of Temperature on the Formation of Disinfection Byproducts

3.2.2 pH

The variations in disinfection byproducts under different pH values are shown in Figure 3. As can be seen from Figure 3a, with increasing pH, ClO_2 consumption increased continuously from 1.52 mg/L to 2.38 mg/L. ClO_2 consumption was positively correlated with pH, mainly because phenolic and enol structures in humic acid are more easily deprotonated under alkaline conditions to form anionic species with stronger nucleophilicity, thereby promoting the single-electron transfer reaction with ClO_2 and improving the reaction rate. No ClO_2^- was detected under acidic conditions (pH=3), but 0.05 mg/L ClO_3^- was observed. This is because ClO_2^- formed via ClO_2 disproportionation was rapidly oxidized to ClO_3^- by high-concentration HOCl (Equation 3-2). With increasing pH, the concentration of HOCl decreased and this reaction pathway was inhibited, allowing ClO_2^- to accumulate. Its formation ratio increased from 33.5% at pH=5 to 42.8% at pH=11. The above results indicate that elevated pH significantly enhances the reactivity of ClO_2 and alters the distribution of inorganic byproducts. The reaction system gradually transforms from the co-action of chlorine and ClO_2 under neutral conditions to ClO_2-dominated oxidation under alkaline conditions.

$$ClO_2 + HOCl \rightarrow ClO_3^- + Cl^- + H^+ \quad (3\text{-}2)$$

Chlorine consumption first increased and then decreased with increasing pH, reaching the maximum

value of 1.688 mg/L at pH=7. The variation trend of $CHCl_3$ formation was consistent with that of Cl_2 consumption, also peaking at pH=7 (27.4 μg/L) and being relatively low under acidic and alkaline conditions (<17.5 μg/L) (Figure 3b). Both chlorine consumption and $CHCl_3$ formation reached maximum values under near-neutral conditions, which is closely related to the hydrolysis species distribution of chlorine (pKa ≈ 7.5). When pH < 7.5, HOCl dominates the system and exhibits strong electrophilic reactivity, which can attack electron-rich sites in humic acid. When pH > 7.5, OCl^- becomes the main species with weak oxidation capacity, resulting in reduced chlorine consumption. $CHCl_3$ formation is mainly determined by HOCl-driven electrophilic chlorination, and the vicinity of pH=7 is the optimal range for HOCl content and reactivity. Therefore, chlorine consumption and corresponding $CHCl_3$ formation strongly depend on the pH-regulated distribution of active chlorine species and show maximum values under near-neutral conditions.

By regulating the species and reactivity of disinfectants, pH significantly affects disinfectant consumption and byproduct formation pathways during ClO_2/chlorine combined disinfection. Alkaline conditions favor ClO_2^-dominated oxidation and ClO_2^- accumulation, while near-neutral conditions are most conducive to chlorine disinfection and $CHCl_3$ formation. The results demonstrate that by optimizing pH conditions, the ClO_2/chlorine combined disinfection process can exhibit significant advantages in controlling organic and inorganic byproducts.

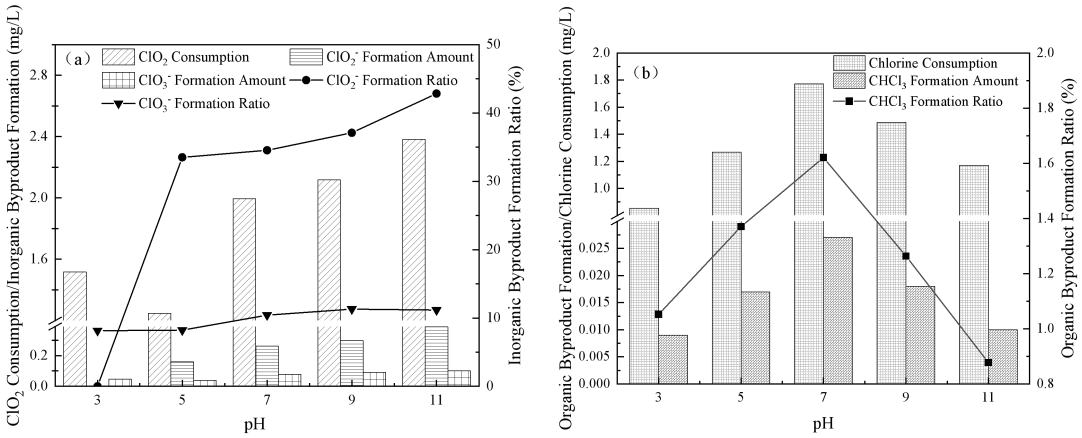

Figure 3. Effects of pH on the Formation of Disinfection Byproducts

3.2.3 Dosing Sequence

The effect of dosing sequence on disinfection byproducts is shown in Figure 4. The consumption of ClO_2 was positively correlated with the formation of inorganic byproducts. Under the condition of **ClO_2 first dosing**, ClO_2 preferentially reacted with organic matter in water and was consumed via reduction pathways, mainly converted into ClO_2^- and ClO_3^-. Therefore, the highest concentration of inorganic byproducts was observed under this sequence.

The formation of $CHCl_3$ showed a clear synergistic trend with chlorine consumption. When chlorine was dosed first, HOCl preferentially underwent electrophilic substitution with organic matter such as

humic acid, and the available chlorine was largely consumed, thereby significantly promoting the formation of organic byproducts. The subsequently dosed ClO_2 exerted limited oxidation effect on the already formed $CHCl_3$, resulting in a persistently high concentration.

The distribution of DBPs under different dosing sequences indicated that there existed competition and sequence effects in the reaction between disinfectants and organic matter. The first-dosed disinfectant tended to dominate the initial reaction pathway and determine the type of main byproducts. When ClO_2 was added first, its strong oxidizability preferentially consumed some reactive organic sites and altered the subsequent reactivity of organic matter, thereby inhibiting the potential of the subsequently dosed chlorine to form $CHCl_3$ to a certain extent.

Conversely, if chlorine was added first, it preferentially bound to highly reactive organic sites and efficiently formed organic halogenated byproducts, while the later-dosed ClO_2 mainly contributed to the formation of inorganic byproducts. In the simultaneous dosing mode, complex competitive interactions occurred between the two disinfectants, leading to the formation of both types of byproducts being between those of the two sequential dosing conditions.

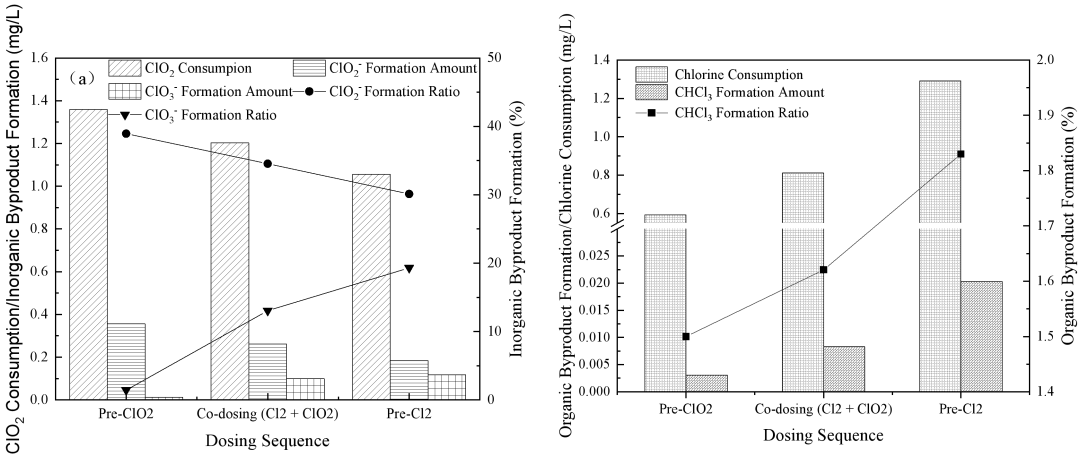

Figure 4. Effects of Dosing Sequence on the Formation of Disinfection Byproducts

3.2.4 Organic Matter

The variations in chlorine consumption and disinfection byproduct formation after reaction with the four organic substances are shown in Figure 5. As shown in Figure 5a, the order of ClO_2 consumption in different organic systems was: TA ≈ HA > BSA > SA. In TA and HA systems, the dosed ClO_2 (2.5 mg/L) was completely consumed, whereas only 0.18 mg/L was consumed in the SA system, showing obvious chemical inertness. This difference can be explained from the perspective of molecular structure: TA and HA are rich in phenolic hydroxyl groups and aromatic structures, which easily act as electron donors to participate in the single-electron reduction process of chlorine dioxide, generating a large amount of chlorite. The extremely high chlorite formation ratio in the TA system further confirms the high reactivity of polyphenolic structures. In contrast, as a polysaccharide substance, SA mainly consists of aliphatic chains and glycosidic bonds, lacking highly reactive sites susceptible to oxidation

or substitution, thus exhibiting low reactivity toward ClO_2. In addition, the chlorate formation ratio in all systems was below 13%, indicating that chlorate was not the main inorganic byproduct under this combined disinfection condition, which is consistent with the results of Sorhini et al.

The variations in chlorine consumption and organic byproduct formation were similar to those of chlorine dioxide (Figure 5b). TA and HA showed the highest chlorine consumption and chloroform formation, again demonstrating that aromatic substances are key precursors of DBPs during chlorination disinfection. The high chloroform formation potential of TA is particularly prominent, further proving that polyphenolic structures exhibit extremely high activity in electrophilic chlorination reactions, which is consistent with the study of Bond et al. Chloroform generated by BSA may originate from the halogenation of amino acid residues such as tyrosine and tryptophan in its structure. Due to its molecular inertness, SA still barely participates in the chlorination process, and its chloroform formation is negligible, consistent with the consensus of low reactivity of polysaccharides during disinfection.

In the ClO_2/chlorine combined disinfection system, the molecular structure of organic matter is the core factor determining disinfectant consumption behavior and byproduct formation potential. Organic substances rich in phenolic hydroxyl groups and aromatic structures (TA, HA) not only significantly promote the conversion of chlorine dioxide to chlorite but also serve as the main precursors for chloroform formation via chlorination, thus becoming the key targets for controlling combined disinfection byproducts. In practical water treatment processes, enhanced removal of such highly reactive organic matter should be prioritized to synergistically control the formation risks of inorganic and organic disinfection byproducts.

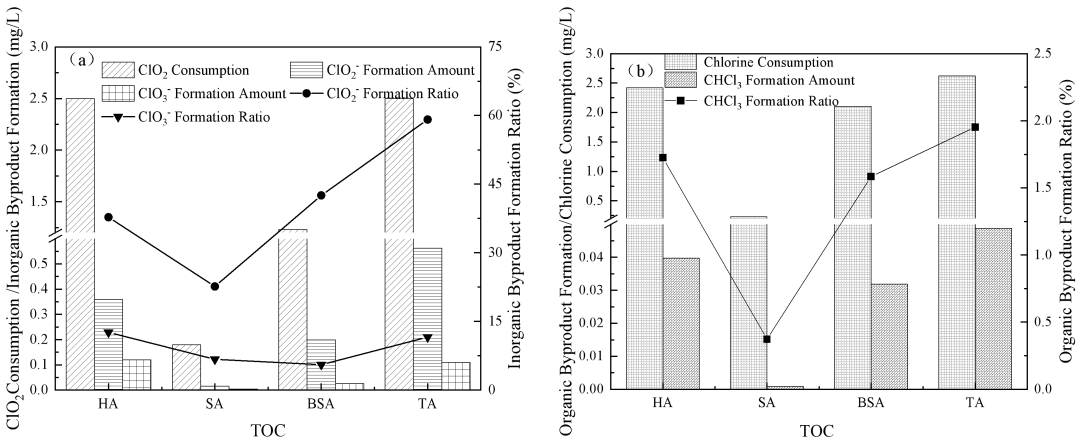

Figure 5. Effects of Organic Matter Type on the Formation of Disinfection Byproducts

3.3 Fluorescence Spectral Analysis of Actual Water Samples before and after Disinfection

The fluorescence spectra of water samples before and after disinfection are shown in Figure 6. The corresponding standardized fluorescence regional integration volumes were obtained by integrating the fluorescence data of actual water samples before and after disinfection, as shown in Figure 6e. The

fluorescence regional integration (FRI) method established by Chen et al. was used for quantitative analysis of the three-dimensional fluorescence spectra of water samples before and after disinfection, and the spectra were divided into five representative regions: Region I: Ex/Em = 200–250 nm/280–325 nm, Region II: Ex/Em = 200–250 nm/325–375 nm, Region III: Ex/Em = 200–250 nm/375–550 nm, Region IV: Ex/Em = 250–450 nm/280–375 nm, Region V: Ex/Em = 250–450 nm/375–550 nm. Fluorescent substances in Regions I, II and IV were related to protein-like materials, while those in Regions III and V were associated with humus-like substances.

As shown in Figure 6e, humus-like fluorescence dominated in raw water, with the highest fluorescence intensity in Region V, followed by Region III. Together, they accounted for 77% of the total fluorescence intensity, indicating that humic acid and fulvic acid were the main components of natural organic matter in the water. After disinfection, the fluorescence intensity in all regions decreased. The apparent removal rates of organic matter were calculated based on changes in the standardized fluorescence regional integration volumes (Figure 6f). Chlorine disinfection achieved the highest total removal rate (38.4%), with regional removal rates as follows: Region I 2.8%, Region II 31.6%, Region III 44.5%, Region IV 32.8%, Region V 40.3%. The total removal rate of ClO_2 disinfection was 23.8%, with regional rates of 1.1%, 9.6%, 23.3%, 16.8% and 30.2%, respectively. Combined disinfection showed the lowest total removal rate of 19.7%, with regional rates of 1.0%, 13.0%, 18.4%, 9.5% and 25.9%, respectively.

The difference in disinfection efficiency was mainly attributed to the properties of disinfectants and their interactions. Chlorine (Cl_2/HOCl) had a high standard redox potential ($E° = 1.49$ V) at neutral pH, exhibiting strong non-selective oxidation and efficient degradation of various organic substances. Although ClO_2 had a lower redox potential ($E° = 0.95$ V), it showed high selectivity toward electron-rich groups (e.g., phenolic structures) due to its single-electron transfer mechanism [4]. In the combined disinfection system, rapid reactions occurred between ClO_2 and HOCl, converting some effective components into less oxidative chlorate and chloride ions, thus significantly reducing the effective concentration for organic oxidation and resulting in a lower overall removal rate than single disinfectants.

Regardless of the disinfection method, the removal rates of humus-like regions (Regions III and V) were consistently higher than those of protein-like regions. This was mainly due to the special molecular structure of humic acid and fulvic acid: complex macromolecules linked by aromatic rings, polyphenols, quinone groups, carboxyl groups and other bridges, rich in highly reactive electron-rich functional groups (e.g., phenolic hydroxyl groups). Such structures were prone to electrophilic substitution by electrophilic reagents (e.g., HOCl) and electron transfer reactions with single-electron oxidants (e.g., ClO_2), leading to rapid destruction of conjugated chromophores and significant fluorescence quenching. In contrast, protein-like substances had relatively few and concentrated reaction sites, showing low reactivity with ClO_2.

Within the same reaction time, the consumption of humus-like substances by combined disinfection

was significantly lower than that by single disinfection, meaning less precursors were oxidized and decomposed, which may be an important reason for the relatively low formation of disinfection byproducts under this process.

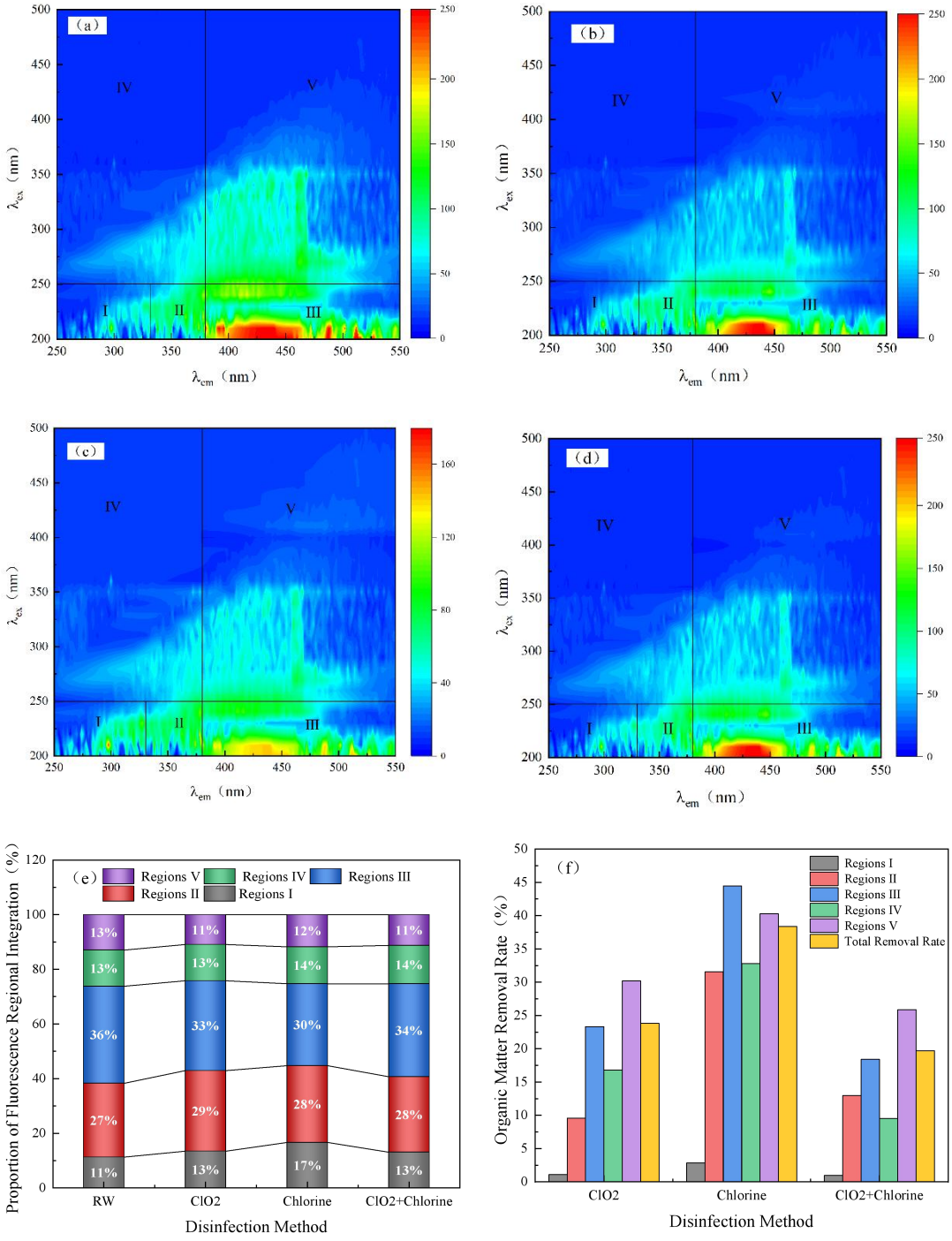

Figure 6. Fluorescence Spectra of Water Samples before and after Disinfection: (a) Raw Water; (b) ClO_2 Disinfection; (c) Chlorine Disinfection; (d) Combined Disinfection; (e) Percentage of each Fluorescence Regional Integration Volume to the Total Integration Volume; (f) Organic Matter Removal Rate

4. Conclusion

(1) Compared with single disinfectant, combined disinfection can reduce the formation of disinfection byproducts and significantly meet the drinking water standards for DBPs. With the increase in the proportion of ClO_2 in the combined disinfectant, the formation of ClO_2^- increases continuously, while that of $CHCl_3$ decreases gradually. An appropriate dosing ratio can not only improve residual chlorine and disinfection efficiency but also reduce the formation of DBPs.

(2) Temperature affects the reaction rate during combined disinfection. Higher temperature accelerates the reaction rate, increases the consumption of ClO_2 and chlorine, and continuously raises the formation amount and formation ratio of ClO_2^- and $CHCl_3$, while the formation of ClO_3^- increases slightly.

(3) At pH = 3, no ClO_2^- is formed. The formation ratio of ClO_2^- increases gradually with rising pH, while that of $CHCl_3$ first increases and then decreases. Under alkaline conditions, the reaction between ClO_2 and OH^- is intensified, leading to a significant increase in ClO_2^- and ClO_3^-, whereas $CHCl_3$ decreases due to the reduced proportion of HClO.

(4) Dosing ClO_2 first results in the highest chlorine consumption and the highest formation amount and ratio of ClO_2^- and ClO_3^-, but the lowest formation of $CHCl_3$. Dosing chlorine first leads to the highest $CHCl_3$ formation and the lowest ClO_2^- formation. Simultaneous dosing yields intermediate formation levels of both byproducts.

(5) Among the four NOM fractions, HA and TA show high reactivity toward both ClO_2 and chlorine, with high formation of inorganic and organic byproducts. BSA exhibits high reactivity toward ClO_2 but low reactivity toward chlorine. SA has extremely low reactivity with both disinfectants.

(6) Fluorescence spectral analysis shows that organic matter in water samples is dominated by humus-like substances. In terms of total fluorescence intensity removal rate, single chlorine disinfection is the strongest, followed by single ClO_2 disinfection, and combined disinfection is the weakest. Combined disinfection achieves optimal byproduct control by transforming organic precursors into less reactive substances, and its mechanism lies in selective transformation rather than total removal.

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