Effects of reductive inorganics and NOM on the formation of chlorite in the chlorine dioxide disinfection of drinking water

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ABSTRACT

Chlorine dioxide (ClO_2) disinfection usually does not produce halogenated disinfection by-products, but the formation of the inorganic by-product chlorite (ClO_2^-) is a serious consideration. In this study, the ClO_2^- formation rule in the ClO_2 disinfection of drinking water was investigated in the presence of three representative reductive inorganics and four natural organic matters (NOMs), respectively. Fe^{2+} and S^{2-} mainly reduced ClO_2 to ClO_2^- at low concentrations. When ClO_2 was consumed, the ClO_2^- would be further reduced by Fe^{2+} and S^{2-}, leading to the decrease of ClO_2^-. The reaction efficiency of Mn^{2+} with ClO_2 was lower than that of Fe^{2+} and S^{2-}. It might be the case that MnO_2 generated by the reaction between Mn^{2+} and ClO_2 had adsorption and catalytic oxidation on Mn^{2+}. However, Mn^{2+} would not reduce ClO_2^-. Among the four NOMs, humic acid and fulvic acid reacted with ClO_2 actively, followed by bovine serum albumin, while sodium alginate had almost no reaction with ClO_2. The maximum ClO_2^- yields of reductive inorganics (70%) was higher than that of NOM (around 60%). The lower the concentration of reductive substances, the more ClO_2^- could be produced by per unit concentration of reductive substances. The results of the actual water samples showed that both reductive inorganics and NOM played an important role in the formation of ClO_2^- in disinfection.

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Introduction

Disinfection is the last and most important step in drinking water treatment, and chlorination is considered to be the most commonly and widely used step in disinfection process throughout the world. However, chlorination disinfection will inevitably produce highly toxic chlorine disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids and halogen acetonitrile. As a new alternative disinfectant, chlo-

rine dioxide (ClO_2) has been widely studied and applied in the past 30 years in order to reduce the formation of chlorine DBPs (Reckhow et al., 1990; Ramieri and Swietlik, 2010). During disinfection, ClO_2 reacts with organic matter in water through the oxidation-reduction reaction instead of the substitution reaction as chlorine, which limits the effective formation of organic halogenated DBPs. However, two inorganic DBPs, ClO_2^- and ClO_3^-, could be produced to satisfy the conservation of gain and loss electrons (Gordon et al., 1972). It has been reported that ClO_2^- can affect the human hematopoietic system at low concentrations, while an increase of methemoglobin can be caused at high concentrations. The toxicity of ClO_3^- has

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not been fully confirmed and is considered as a potential toxic substance (Abdel-Rahman et al., 1985; French et al., 1995). In contrast, water quality limits regarding ClO_2 have been much more strict and established in various countries. For example, the US EPA has issued the guideline for ClO_2^- of 1mg/L, while Italy and Germany have set 0.7 mg/L and 0.2 mg/L, respectively. The World Health Organization (WHO) and China set the guideline as 0.7mg/L for both ClO_2^- and ClO_3^-. Therefore, a serious challenge to the wide application of ClO_2 has been reported in terms of the disinfection of drinking water (Chang et al., 2000; Bond et al., 2009).

ClO_2 inorganic DBPs are mainly generated by ClO_2 decomposition and reaction with reductive substances in water (Baribeau et al., 2002), and approximately 60%–70% of consumed ClO_2 will be transformed into ClO_2^- (Sorlini et al., 2014). ClO_3^- is mainly derived from ClO_2 generators, and ClO_2 produces very little ClO_3^- directly (Veschetti et al., 2005). Therefore, compared with ClO_3^-, the formation of ClO_2^- is the main DBP in the ClO_2 disinfection process.

Humic substances are the main component of natural organic matter (NOM) in aquatic environments, accounting for around 50%–90% of the total organic matter and containing different ClO_2 reaction sites (Pomes et al., 1999; Swietlik et al., 2004). According to the different solubility in acid-based conditions, humic substances can be divided into humic acid (HA), fulvic acid (FA) and humin. The other part of NOM at a low level due to microbial decomposition includes some low molecular organics such as polysaccharides, proteins and amino acids (Bhatnagar et al., 2017), which vary depending on the water quality. In order to explore the influence of different pieces of NOM on the experiment, many researchers tend to use model organic compounds such as HA, FA, tannic acid, bovine serum albumin (BSA), sodium alginate (SA) and glucose to characterize various pieces of NOM in water (Katsoufidou et al., 2010; Choi et al., 2012; Gan et al., 2019). By studying the effect of NOM properties on ClO_2 disinfection, Yang et al. (2013) found that ClO_2 mainly destroyed the aromatic and conjugated structures of NOM and transformed the larger aromatic and long fatty chain organic structures into small, hydrophilic organic structures. Gan et al. (2019) proposed that ClO_2^- yields depend on the type of functional groups in the organic material. Amines and di- and tri-hydroxybenzenes can produce more ClO_2^- with ClO_2, while the olefins, thiols and benzoquinones have ClO_2^- yields less than 50%. However, the components of NOM in actual waters are too numerous to be identified individually, and thus are usually divided into species in order to investigate their effect on water quality. To explore the influence of NOM on the generation of ClO_2^-, the main pieces of NOM should be the major factor.

In addition to NOM, there are some reductive inorganics in natural water. For example, due to lack of oxygen, groundwater will contain relatively high concentrations of divalent iron and divalent manganese (Jusoh et al., 2005), while the exploitation of oil and natural gas will also produce a large amount of sulfide-containing wastewater. The WHO stipulates that Fe and Mn content in drinking water should be less than 0.3 mg/L and 0.1 mg/L, respectively, and that the limit of sulfide is 0.05 mg/L (WHO, 2017). The EPA stipulates that Mn content in drinking water should not exceed 0.05mg/L (US EPA, 2004). In groundwater, the concentrations of the two

elements are commonly up to 1.0 mg/L (Dorthel et al., 1998), while the content of S^{2-} usually depends on the production environment. During the water treatment process, ClO_2 is often used to remove Fe and Mn (Aieta and Berg, 1986). However, as a common reductive agent, Fe^{2+} can also reduce ClO_2. Mn has different valence states and certain catalytic ability, which is more complicated in the reaction with ClO_2. Nevertheless, few findings have been reported on the formation of the byproduct ClO_2^- to date. Csekö et al. (2018) studied the reaction mechanism between ClO_2 and sulfide in strong alkaline condition and found that ClO_2^- was first generated quickly, but that the middle reaction process was complex, while the final products were associated with reaction conditions. The content of reductive inorganics in actual water environments is lower than that in NOM, but the effect of reductive inorganics on some specific water bodies cannot be ignored, such as groundwater. At present, there are few reports on the influence of reductive inorganics in water on the formation of ClO_2^- in the process of ClO_2 disinfection. Therefore, determining whether the formation of ClO_2^- is influenced by both NOM and reductive inorganics needs to be further explored through experiments.

Above all, the focuses of this research are listed as follows: (1) study the law of ClO_2^- formation generated by the reaction between ClO_2 and three main reductive inorganics; (2) study the law of ClO_2^- formation generated by the reaction between ClO_2 and four main natural organic compounds; (3) compare the ClO_2^- generation potential of reductive inorganics with NOM in ClO_2 redox reaction; and (4) explore the factors affecting the ClO_2^- production in the ClO_2 disinfection process of an actual water samples.

1. Materials and methods

1.1. Chemicals

$NaClO_3$ (99.33%), $NaClO_2$ (81.10%), SA, BSA, $FeSO_4$, $MnSO_4$ and Na_2S were purchased from Macklin (China). HA and FA came from Sigma-Aldrich and Aladdin, respectively. XAD-4 resin was purchased from Sigma-Aldrich, and XAD-8 resin was purchased from Supelco.

The ClO_2 stock solution used in the experiment was prepared according to the standard method (APHA, 1998) by mixing diluted H_2SO_4 with sodium chlorite and then storing it in the refrigerator at 4°C away from light (**Appendix A Fig. S1**). The concentration of ClO_2 stock solution should be determined by iodometry before each experiment.

$FeSO_4$, $MnSO_4$ and Na_2S stock solution were all prepared by deionized water. HA, FA, SA and BSA were stirred and dissolved in deionized water for 24 hr without light, and then filtered through a 0.45 μm filter membrane. After the preparation, all the above reagents were sealed and kept in the refrigerator at 4°C.

1.2. ClO_2 oxidation experiment

Oxidation of ClO_2 with typical reductive substances in water was carried out in a 30 mL brown bottle without light. Inorganic samples were treated with NaOH and H_2SO_4 solution,

and organic samples were treated with 2 mmol/L phosphate buffer solution to adjust the pH. $FeSO_4$, $MnSO_4$ and Na_2S represented reductive inorganics, and were conducted at the set mass concentration when experimenting. HA and FA were selected to represent humus organics. SA and BSA represent sugars and proteins, respectively. The standard reserve liquid was prepared and its total organic carbon (TOC) concentration determined. NOM was added according to the required TOC concentration during the experiment.

During the oxidation experiment, the dosage of ClO_2 was fixed at 2 mg/L, and the content of ClO_2 in the reaction system was determined immediately after 1h of reaction, in which the reaction was almost complete (Appendix A **Fig. S2**). If ClO_2^- or ClO_3^- cannot be determined immediately, ethylenediamine (1 mL/L) should be added in the system after blowing off N_2 for 15 min and storing in the refrigerator at 4°C. The latest determination time should not exceed 6h.

1.3. Classification experiment of organic properties

In order to study the influence of organic properties, the HA solution was continuously passed through 100KDa, 10KDa and 1KDa molecular weight membranes by ultrafiltration device before and after ClO_2 treatment. Another HA solution was used for hydrophilic and hydrophobic classification through XAD-8 and XAD-4 resin according to the method of Aiken et al. (1992) before and after treatment. The trapped solution was collected between sections and the TOC measured.

1.4. Actual water sample oxidation experiment

The actual water samples used in the experiment were taken from a water source in the Nanjing section of the Yangtze river (Yangtze river water), an underground water source (groundwater) owned by an enterprise in Pukou district of Nanjing city, and micro-polluted pond water (pond water) in Pukou district of Nanjing city. After the water sample was retrieved, a 0.45 μm filter membrane was used to filter the water and then determine their water quality. Filtered water samples of 100 mL

were added with a certain amount of ClO_2 to the concentration required for the experiment, and the remaining content of ClO_2 and the production amount of ClO_2^- and ClO_3^- were determined immediately after 1 hr of disinfection.

1.5. Analytical methods

The concentration of NOM was determined by a TOC analyzer (Shimadzu, Japan), and UV_{254} was determined by an ultraviolet spectrophotometer (Shimadzu, Japan) at the wavelength of 254nm.

ClO_2^- and ClO_3^- were determined by a Dionex IC 2000 system equipped with an AS19 anionic column, and an AG-19 protective column (Dionex, USA). The content of ClO_2 was determined by the DPD method (US EPA). The turbidity of water samples was determined by a turbidity analyzer (Hach, USA).

The concentration of Fe^{2+} was determined by the phenanthroline spectrophotometric method. The concentration of Mn^{2+} was determined by an ICP-OES spectrometer (Thermo, America). The concentration of sulfide was determined by the methylene blue method.

2. Results and discussion

2.1. Influence of reductive inorganics

The consumption of ClO_2 and the production of ClO_2^- in the reaction of ClO_2 with three reductive inorganics are shown in **Fig. 1**. As seen in **Fig. 1**a, the consumption of ClO_2 increased with the rising concentration of reductive inorganics. As the concentration of S^{2-} and Fe^{2+} raised, ClO_2 consumption increased rapidly until ClO_2 was exhausted, and the reaction of S^{2-} was more significant. When Mn^{2+} was at low concentration, it was positively correlated with ClO_2 consumption. However, when Mn^{2+} was greater than 0.4 mg/L, the increase of ClO_2 consumption slowed. ClO_2 was not exhausted when the initial concentration of Mn^{2+} was added to 6 mg/L. As shown in **Fig. 1**b, the change in the production of ClO_2^- was basically
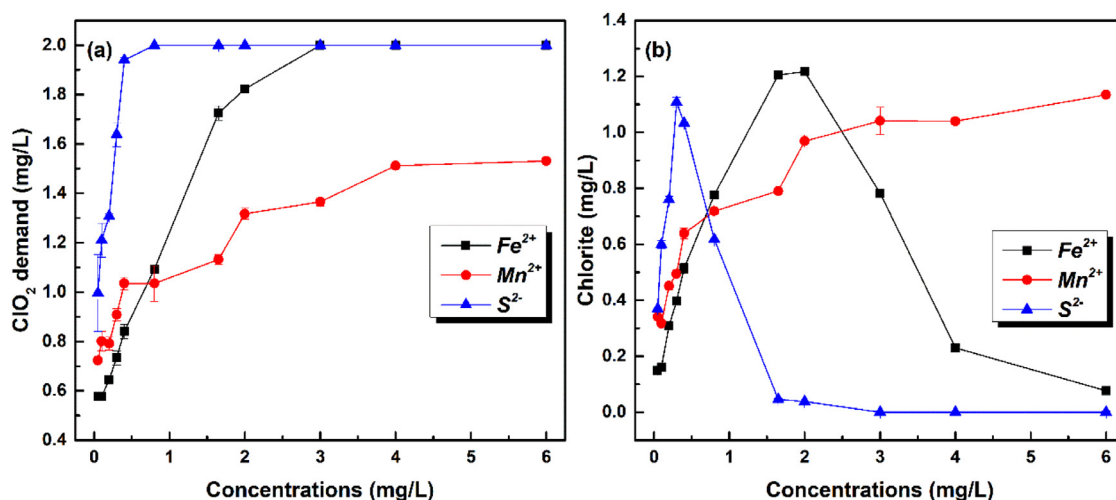

Fig. 1 – (a) ClO_2 consumption and (b) ClO_2^- production with the changes of reductive inorganics concentrations. ClO_2 2mg/L, pH 7, 25°C, 1hr.

consistent with the ClO_2 consumption in the Mn^{2+} reaction system. On the contrary, the production of ClO_2^- showed a trend of first increasing, and then decreasing in the Fe^{2+} and S^{2-} reaction system.

When ClO_2 was in excess, the products of ClO_2 oxidation of Fe^{2+} and S^{2-} were mainly ClO_2^- (Appendix A **Eqs. (S1) and (S2)**). Since ClO_2 will be over added in the disinfection process, the presence of Fe^{2+} and S^{2-} in water may lead to the formation of ClO_2^-. However, S^{2-} could be oxidized to SO_4^{2-} (Csekö et al., 2018) in the reaction process, while Fe^{2+} can only be oxidized to Fe^{3+}. The relative atomic weight of S is lower than that of Fe, and thus, the change of S^{2-} became more obvious. When the concentrations of Fe^{2+} and S^{2-} were excessive, ClO_2 was completely consumed and then the ClO_2^- concentration began to decrease. This is because the extra Fe^{2+} and S^{2-} will continue to reduce ClO_2^- (Appendix A **Eqs. (S3) and (S4)**).

The dosage of ClO_2 was fixed at 2mg/L in this experiment. According to the reaction equation, when the concentration of Fe^{2+} and S^{2-} was up to 1.65 mg/L and 0.12 mg/L, respectively, in theory, it could react with ClO_2 completely, and much lower than the concentration obtained in the experiment. However, within 1 hr of reaction time, the content of ClO_2^- generated by the self-decay of ClO_2 was observed to be very low (Appendix A **Fig. S3**). It was indicated that the reactions of Fe^{2+}, S^{2-} with ClO_2 and ClO_2^- are synchronized, thus causing the inflection point to move backward. However, in the presence of ClO_2, the reaction Appendix A **Eqs. (S1) and (S2)** dominated the main reaction process.

Fe and Mn are two adjacent transition metal elements in the periodic table with similar atomic weight. However, both ClO_2 consumption and ClO_2^- production at low concentration of Mn^{2+} were significantly higher than that of Fe^{2+}. This is because the product of Mn^{2+} after being oxidized by ClO_2 is MnO_2 (Appendix A **Eqs. (S5)**), while the Fe^{2+} maximum was oxidized to Fe^{3+}. Therefore, ClO_2 consumption of Mn^{2+} at the same mass concentration of ClO_2 was more than that of Fe^{2+}. Note that the growth of ClO_2 consumption and ClO_2^- production slowed as the Mn^{2+} concentration continued to increase, and a downward trend in ClO_2^- did not appear. Numerous researchers have reported that MnO_2 can have adsorption (Appendix A **Eqs. (S6)**) and catalytic oxidation (Appendix A **Eqs. (S7)**) on Mn^{2+} (Chen et al., 2016). With the increase of Mn^{2+} concentration, the amount of MnO_2 generated by ClO_2 oxidation increased, leading to enhance the capacity of adsorption and catalytic oxidation. The amount of Mn^{2+} that can react with ClO_2 was reduced, resulting in a slower growth rate of ClO_2 consumption and ClO_2^- production. At the same time, no obvious reaction between Mn^{2+} and ClO_2^- was reported (Steven, 2001), so excess Mn^{2+} cannot lead to a decrease in ClO_2^- production.

In addition, temperature (Appendix A **Fig. S5**) and pH (Appendix A **Fig. S6**) had a certain influence on the reaction of three reductive inorganics with ClO_2. The oxidation capacity of ClO_2 enhanced as the temperature rose, while the amount of ClO_2^- production increased. However, the ClO_2^- production quantity began to decrease when the temperature was greater than 35°C, as ClO_2 self -decay intensifies and ClO_2 consumption rises when the temperature is too high. As the loss of ClO_2 due to self-decay increased, the amount of ClO_2 that could react with the reductive substance decreased, leading to side reactions (Appendix A **Eqs. (S3), (S4), (S6), (S7)**) of ClO_2 that became obvious. Meanwhile, the decay of ClO_2 did not generate ClO_2^-, then the amount of ClO_2^- began to decrease. As the pH increased, Mn^{2+} and S^{2-} promoted the formation of ClO_2^-, while the amount of ClO_2^- produced by Fe^{2+} decreased. This is because Fe^{2+} will form $Fe(OH)_2$ with OH^- under alkaline conditions, reducing the reactivity of Fe^{2+} and ClO_2. No precipitation was observed in the experiment of Mn^{2+} and S^{2-}. Therefore, the influence of temperature and pH changes on ClO_2^- production is also a factor to be considered when ClO_2 disinfection is used in water plants.

2.2. Influence of NOM

The consumption of ClO_2 and the formation of ClO_2^- after the reaction with the four NOMs are shown in Fig. 2.

Among the four NOMs, HA and FA have similar properties. As the initial concentration of the two organics increased, ClO_2 consumption gradually increased. When the TOC was approximately 4 mg/L, ClO_2 was exhausted and the produc-
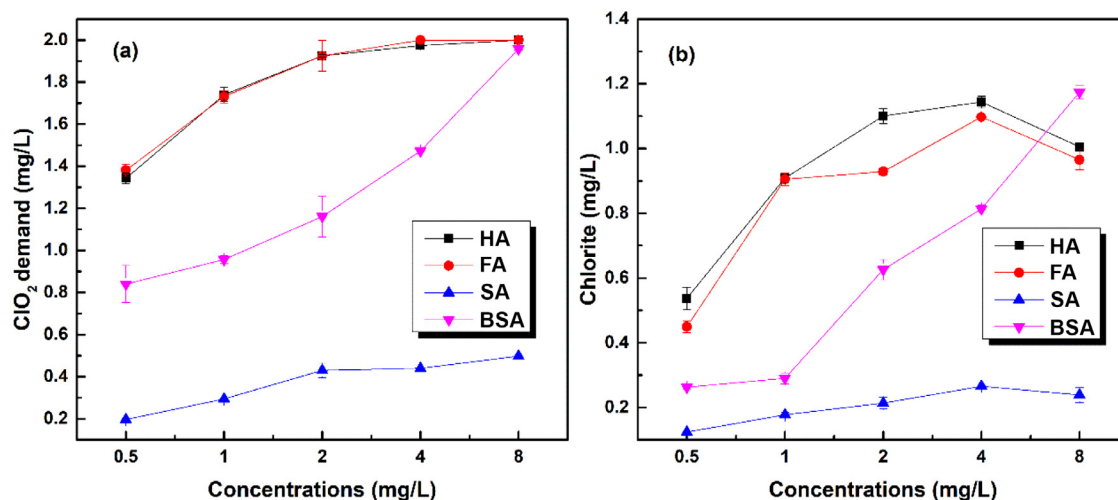
Fig. 2 – (a) ClO_2 consumption and (b) ClO_2^- production with the changes of NOM concentrations. pH=7, 25°C, 1 hr.

tion of ClO_2^- reached the maximum. When the SA dosage was 8 mg/L, the production amount of ClO_2^- was only 0.24 mg/L. It can be considered that the presence of SA in the water cannot lead to the excess of ClO_2^-. The amount of ClO_2^- generated by BSA increased with the increase of TOC concentration, while ClO_2 consumption and ClO_2^- production at low concentration were far lower than that of HA and FA. When the BSA concentration was up to 8 mg/L, ClO_2 was exhausted completely and the highest ClO_2^- production was similar to that of HA and FA.

HA and FA are both humic substances with hydrophobicity (Bhatnagar et al., 2017), and the molecular weight of HA is higher than that of FA (Hiradate et al., 2006; Qin et al., 2015). From the molecular weight and hydrophilic classification experiment on HA water distribution (Appendix A **Fig. S4**), it was indicated that the proportion of strong hydrophobic substances decreased after the oxidation of ClO_2, while that of weak hydrophobic substances and hydrophilic substances was opposite. The proportion of organic matter with molecular weight of >100KDa decreased, while the proportion of organic matter with molecular weight of 10–100KDa, 1–10KDa and <1KDa all increased. This indicated that the reaction between ClO_2 and humus will convert large molecular weight organic matters into small molecular weight organic matters, and hydrophobic organic matters into hydrophilic organic matters, which is also consistent with the conclusion of Yang et al. (2013). However, the ClO_2^- produced by both of them began to decrease slightly with the increase of organic matter concentration in the case of excessive HA and FA, which may be due to the fact that ClO_2^- also has oxidation to a certain extent and will continue to react with the excess organic matter. As a polysaccharide, SA had the lowest reaction activity with ClO_2 among the four NOMs, indicating that the presence of polysaccharide in water will not cause the increase of ClO_2^-. BSA is a globulin in bovine serum containing 582 amino acid residues and is generally used as a representative substance of proteins. However, ClO_2 only modifies tyrosine and tryptophan residues, and cannot react with most amino acids. Therefore, the ClO_2^- produced by BSA at the same TOC concentration was lower than HA and FA (Ogata, 2007; Zhang et al., 2008).

The amount of ClO_2^- generated in the reaction of ClO_2 with HA increased initially, and then decreased with a rise of temperature, while the ClO_2^- generated by FA only decreased. The increase of temperature promoted the reaction between BSA and ClO_2. Due to the weak reaction between SA and ClO_2, the influence of temperature on SA was mainly from the self-decay of ClO_2 at high temperature (Appendix A **Fig. S7**). Alkaline conditions facilitated the formation of ClO_2^- in the reactions of FA and SA with ClO_2, while the maximum ClO_2^- generation of HA and BSA were at neutral conditions. In general, the formation of ClO_2^- was inhibited under acidic conditions when ClO_2 reacted with NOM. The effect of pH on NOM was less obvious than that of reductive inorganics (Appendix A **Fig. S8**).

2.3. Comparison of ClO_2^- formation potential

The ratio of ClO_2^- production to ClO_2 consumption is defined as ClO_2^- yields in order to imply the ability of reductive substances to reduce ClO_2 to ClO_2^-.

However, this parameter was not suitable when the reductive substances were at low concentrations. The self-decay of ClO_2 cannot be ignored when ClO_2 is excessive, and the self-decay barely generated ClO_2^- (Appendix A **Fig. S2**), leading to the low ClO_2^- yields. By comparing the maximum ClO_2^- yields of reductive inorganics and NOM (**Fig. 3**a, **3**b), the reductive inorganics were significantly higher than NOM. The maximum ClO_2^- yield of reductive inorganics was more than 70%, while that of NOM was approximately 60%. Gan et al. (2019) selected 10 different HAs and measured their ClO_2^- yields, where most of them were around 60%, which is consistent with the conclusions obtained in this experiment. The yields of ClO_2^- were lower than that of NOM when Fe^{2+} and S^{2-} was excessive, because Fe^{2+} and S^{2-} could continue to reduce ClO_2^- after ClO_2 was exhausted. Although SA had the highest ClO_2^- yields at low concentrations, its reactivity with ClO_2 was weak. Therefore, the significance of this indicator was still limited.

Fig. 3c and **3**d represent the ratio of the production amount of ClO_2^- to the mass concentration of the reductive substance with the change of concentration, which can reflect the ClO_2^- generating potential of the reductive substance per unit concentration. At low concentrations, the unit NOM and the reductive inorganics can produce more ClO_2^-. In the actual water plant disinfection process, ClO_2 would be over added to ensure the persistence of disinfection. Meanwhile, the WHO sets the maximum level of Fe and Mn at 0.3 and 0.1 mg/L, respectively, in drinking water, and the limit of sulfide is 0.05 mg/L (WHO, 2017). The limits of reductive inorganics are all at the low level in order to ensure that the reaction between reductive inorganics and ClO_2 is dominated by ClO_2^- generation. According to the limits of Fe^{2+} (0.3 mg/L), Mn^{2+} (0.1 mg/L) and S^{2-} (0.05 mg/L) in this experiment, it can be estimated from **Fig. 2**b that the production of ClO_2^- was approximately 0.40 mg/L, 0.32 mg/L and 0.37 mg/L, accounting for 57.1%, 45.7% and 52.9% of the effluent limit of ClO_2^- (0.7 mg/L), respectively. Therefore, the effect of reductive inorganics in water cannot be ignored. If the content of reductive inorganics was high, the level of inorganic DBPs of ClO_2 may exceed the standard limits.

2.4. Effect of ClO_2 disinfection on actual water samples

The effect of ClO_2 disinfection on actual water samples under the conditions of 1.5 and 2.5 mg/L dosage of ClO_2 are shown in **Fig. 4**.

When the ClO_2 dosage was 1.5 mg/L, the ClO_2 residue of the Yangtze river water, groundwater and pond water was 0.58 mg/L, 0.83 mg/L and under the detection limit, and the ClO_2^- content was 0.49 mg/L, 0.53 mg/L and 0.95 mg/L, respectively. ClO_2^- production of the pond water was higher than the relevant standard, and the reaction was not complete. When the ClO_2 dosage increased to 2.5 mg/L, the ClO_2 residue of the pond water reached 0.67 mg/L, and the ClO_2^- concentration was up to 1.10mg/L, which was much higher than the ClO_2^- production of the Yangtze river water and groundwater. However, the concentration of ClO_2^- in the Yangtze river water and groundwater only increased by 0.02 mg/L and 0.06 mg/L, respectively, indicating that increasing the amount of ClO_2 continuously will not lead to an obvious increase of ClO_2^- when ClO_2 is excessive. Thus, the amount of reducing substance in
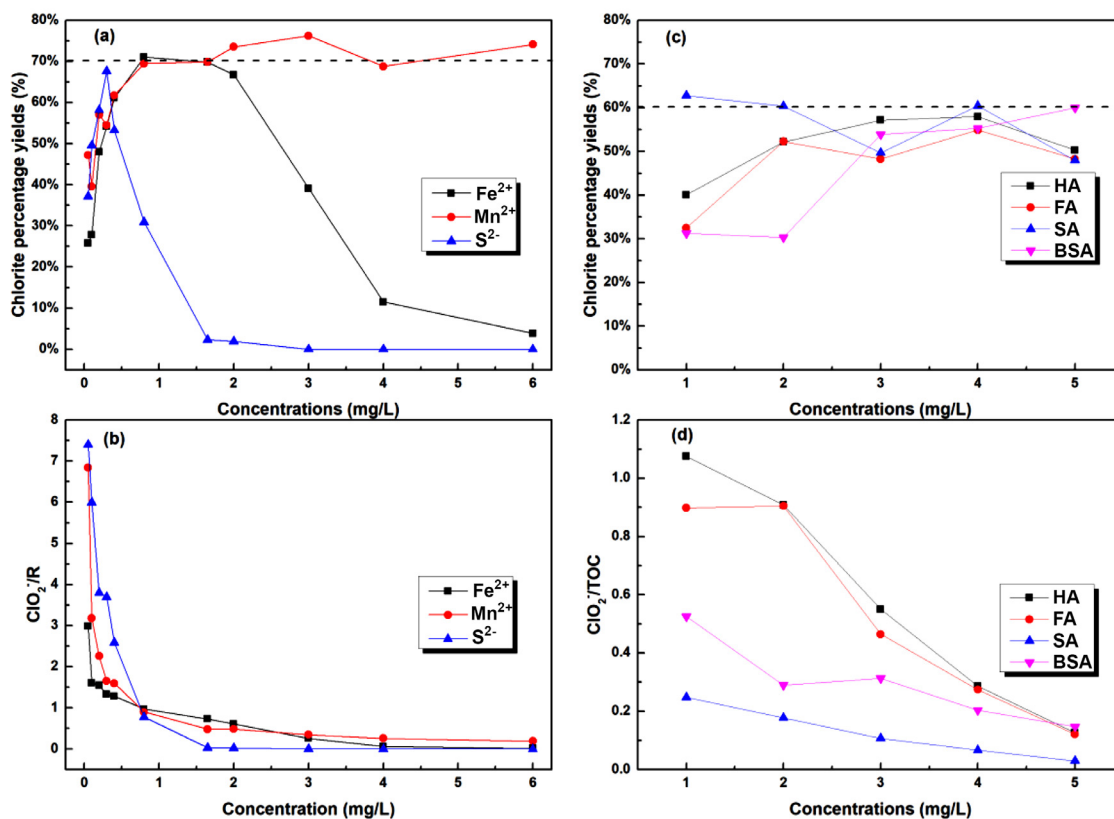
Fig. 3 – Trend of ClO_2^- yields with concentration for (a) reductive inorganics and (c) NOM; The amount of ClO_2^- produced by (b) reductive inorganics and (d) NOM at unit concentration. pH=7, 25°C, 1hr.
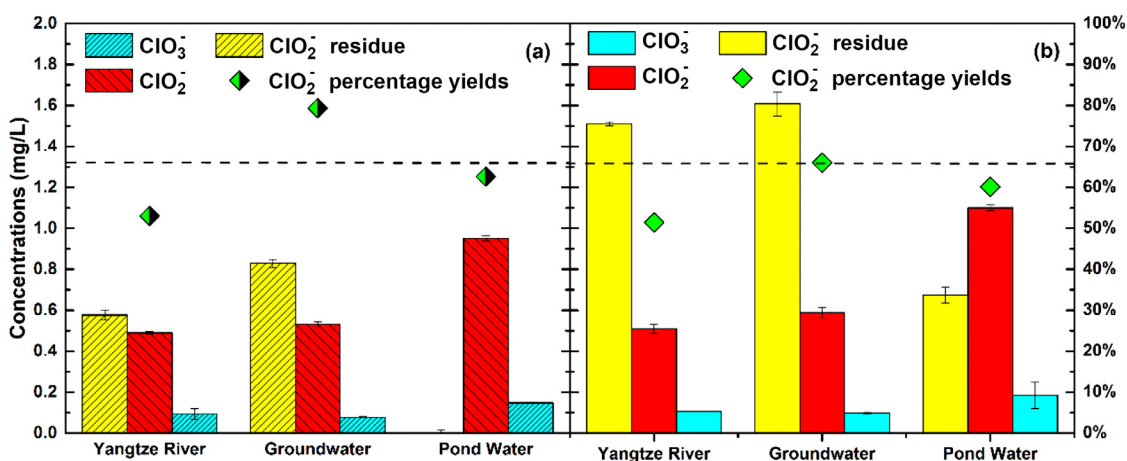

Fig. 4 – Trend of ClO_2 residue, ClO_2^-, ClO_3^- and ClO_2^- yields during disinfection of Yangtze River water, groundwater and pond water when ClO_2 dosage was (a) 1.5 mg/L and (b) 2.5 mg/L respectively.

the water determined the formation of ClO_2^-. According to the three-dimensional fluorescence spectrum (Appendix A **Fig. S9**), the fluorescence peaks of dissolved organic substances in pond water were mainly in the range of Ex=200–250nm and Em=400–450nm, belonging to the category of FAs. Some fluorescence peaks fell between Ex=250–280nm and Em=450–550nm, belonging to HAs (Chen et al., 2003; Leenheer and

Croué, 2003). It was indicated that NOM was mainly composed of HA and FA in the pond water. Water quality analysis (Appendix A **Table S1**) showed that the pond water contained high levels of NOM and Mn^{2+}. When the ClO_2 was used to disinfect water, it led to the formation of ClO_2^- in large quantities. The organic components of Yangtze river water were similar to the pond water, but the TOC concentration was ob-

served to be only half of the pond water. Moreover, the Fe^{2+} and Mn^{2+} concentrations of Yangtze river water were at a low level, so the formation of inorganic DBPs was markedly lower than the pond water. Although the TOC content in groundwater was only 0.30mg/L, its ClO_2^- production was similar to the Yangtze river water due to the high content of Mn^{2+}. Therefore, the ClO_2^- of groundwater mainly came from the reaction of ClO_2 with the reductive inorganics, among which Mn^{2+} played an important role. To compare the ClO_2^- yields of the three water samples, the groundwater was the highest, followed by the pond water and then the Yangtze river water. The research results confirmed that the reductive inorganics had stronger ClO_2^- formation potential than NOM. In addition, the ClO_2^- yields of groundwater were significantly reduced after increasing the amount of ClO_2. This was because the higher the concentration of ClO_2, the more ClO_2 was consumed through self-decay (Appendix A **Fig. S3**), which declined the conversion ratio of ClO_2 to ClO_2^-. However, since the Fe^{2+} and S^{2-} content in the water samples of the Yangtze river were higher than the groundwater, this can only highlight the role of Mn^{2+}. In order to confirm the role of Fe^{2+} and S^{2-}, 0.05mg/L reductive inorganics were added into the Yangtze river water samples, respectively. The result (Appendix A **Fig. S10**) showed that S^{2-} generated the most ClO_2^-, while the least was Fe^{2+} at the same increment. In addition, the ClO_2^- yields of samples were all improved after adding the reductive inorganics, proving the effect of reductive inorganics on inducing ClO_2^- formation. Based on the analysis of three kinds of water samples of DBPs' formation, both NOM and reductive inorganics played an important role in the process of formation of ClO_2^-. The incidence of NOM and reductive inorganics on ClO_2^- formation needs to be further studied.

3.   Conclusion

The main conclusions are as follows: (1) Fe^{2+} and S^{2-} mainly react with ClO_2 to generate ClO_2^- at low concentration, and ClO_2^- is further reduced with the increase of concentration. The increase of Mn^{2+} concentration will promote the formation of ClO_2^-. Meanwhile, the product MnO_2 has adsorption and catalytic oxidation on Mn^{2+}, which reduces the reaction efficiency of Mn^{2+} and ClO_2, and Mn^{2+} with ClO_2^-. (2) Among the four NOMs, HA, FA have the highest reactive activity with ClO_2, followed by BSA, while SA hardly reacts with ClO_2. (3) The maximum ClO_2^- yield of the three reductive inorganics is greater than 70%. The maximum ClO_2^- yield of NOM is about 60%, lower than that of reductive inorganics. Reductive inorganics and NOM have higher ClO_2^- generating potential at low concentration. (4) Groundwater had the highest ClO_2^- yields because the content of its reductive inorganics Mn^{2+} was the highest. The final ClO_2^- production of pond water was the highest due to its high Mn^{2+} and the highest concentration of NOM. The ClO_2^- yields of the Yangtze river water were the lowest, but the final ClO_2^- production was close to the groundwater due to higher NOM content. The actual water sample disinfection results show that the generation of ClO_2^- in the process of ClO_2 disinfection should be the result of the joint action of reductive inorganics and NOM.

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.11.033.

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