Reaction law of high purity chlorine dioxide and typical substances in raw water

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Abstract. Great concern has been risen due to the harmful by-product formation in chlorine dioxide disinfection. To control the by-product formation, we need to know the factor that make a great contribution to generate by-product in drinking water treatment. The Fe²⁺, Mn²⁺, organic matter and algae are the most presenting matters that could cause the formation of chlorite; thus, they were selected as factors in the study. The results showed that the amount of by-product chlorite produced increased along with the increase of the concentrations of organic matter, algae and Fe²⁺ in water, but the presence of Mn²⁺ didn’t impact on the formation of chlorite. In addition, the interaction between Fe²⁺ and Mn²⁺ was observed, but no obvious interaction between other factors was found. So when the concentration of above factors exceed the standard, the chlorine dioxide is not recommended in any step of the water treatment.

1. Introduction
Chlorine dioxide as a strong oxidant has been widely used in drinking water disinfection in recent years [1, 2]. With the increasing pollution of water quality, chlorine dioxide is gradually being used in the pre-oxidation process [3]. Compared with the liquid chlorine, chlorine dioxide has more advantages, mainly in two aspects. First, it does not produce substances that harmful to human health such as trihalomethane; secondly, it has better inactivation effect on viruses and bacteria [4, 5]. However, there is a potential risk in the use of chlorine dioxide. When reacting with raw materials, chlorine dioxide is easy to produce inorganic disinfection by-products chlorite and chlorate, which is an important reason to limit its application [6, 7]. Therefore, it is rather important to identify what typical reducing substances in water react with chlorine dioxide to produce inorganic disinfection by-products, and how to better control the formation of chlorite and chlorate is a major problem in the application of chlorine dioxide. According to literature, the amount of chlorite production is much larger than the amount of chlorate production in the high-purity chlorine dioxide system [8, 9]. Therefore, this study was aim to find the cause of the by-product chlorite formation in the pre-oxidation of chlorine dioxide, and provided a theoretical basis for the generation of inorganic disinfection by-products, to better control the formation of by-product of chlorite.

2. Materials and methods

2.1. Chemicals and apparatus
The instrument and chemicals utilized in the study as listed:
Hitachi U-5100 UV-Vis spectrophotometer; Dionex ICS-500 ion chromatograph; Dionex Ionpac AS19 chromatographic separation column; ASRS-ULRA type suppressor; conductivity detector; PerkinElmer Optima8000 inductively coupled plasma emission spectrometer.

Sodium chlorite (analytical grade), sodium chlorate (analytical grade), high purity nitrogen (99.99%), ethylenediamine (analytical grade), sulfuric acid (98%), humic acid (analytical grade), ferrous sulfate (analytical grade), manganese sulfate (analytical grade), and the experimental pure water resistivity was 18.0 MΩ cm.

The water used in experiment was synthetic water.

2.2. Experimental method

Chromatographic conditions. A Dionex AS19 column was used with a column temperature of 30 °C and a 4 mm ASRS-ULRA suppressor. A 100 mmol/L KOH eluent was used with a flow rate of 1 mL/min. The gradient concentration was used for elution. The relevant procedure was as follows: The flow rate was set at 8 mmol/L for a duration of 14 minutes and risen to 45 mmol/L for 12 minutes. The injection volume was 500 μL. Samples were quantified with a conductivity detector.

Chlorine dioxide preparation. The chlorine dioxide was generated with a device mainly composed of an air pump, a chlorine dioxide generating device and a collecting device. The procedure is as following: Placing the whole set in the fume hood, adding 300 mL of pure water to the rectifier bottle, connecting one end to the high-purity nitrogen bottle, and the other end to the ClO₂ bottle; filling the bottle with 500 mL of 0.15 mol/L NaClO₂ solution; connecting the upper end with a separator funnel containing 20 mL of 10% H₂SO₄ solution; the gas-washing bottle filling the gas-washing bottle with 300 mL of saturated NaClO₂ solution; connecting the two ends with the generating bottle and the gas collection bottle, respectively; filling the gas cylinder with 1 L of ultrapure water for absorbing the generated ClO₂, and an exhaust pipe for exhausting the remaining gas.

Opening the nitrogen valve to allow the gas to pass evenly through all the devices; adding 5 mL of 10% H₂SO₄ solution to the bottle every 5 minutes; continuously ventilating the system for 30 minutes when the last solution was added. The prepared ClO₂ was stored in a brown bottle in a refrigerator at 4 °C for further utilization.

Single factor impact test. To investigate the law of the formation chlorite in chlorine dioxide reacting with a single substance, different concentrations of ferrous sulfate, manganese sulfate, humic acid and Anabaena sinensis were transferred in brown bottles, respectively. Chlorine dioxide was added to the bottles at concentrations of 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 3.0 mg /L, 4.0 mg/L, 5.0 mg/L respectively. The reaction time was 1 hour, and reaction temperature was controlled at 20 °C. The reaction was terminated by sparking high-purity nitrogen, and 20 μL of ethylenediamine was added to ensure the stability of the produced inorganic disinfection by-product.

2×2 factor interaction test. To exploring the interaction of different levels of a factor at a specific level of another factor, a combination of ferrous sulfate, manganese sulfate, humic acid and Anabaena sinensis configured to contain a solution of two substances. More than three concentrations of each factor were set to investigate whether there was an interaction for chlorite formation when both of two substances were in present. The reaction time was 1 hour and reaction temperature was controlled at 20 °C. The reaction was terminated with high purity nitrogen, and ethylenediamine was added to ensure the stability of the inorganic disinfection by-product.

2.3. Quality assurance

In order to ensure the quality of the sample, the following measures were taken. Firstly, the water sample was stored in a brown bottle in the dark, ensuring sufficient volume for at least 4 inspections. Secondly, after the sample was collected, it was stored in refrigerator at a temperature lower than 4 °C and sent for inspection in the shortest time. Thirdly, blank, quality control and parallel sample detection were simultaneously carried out in the analysis process. Among them, 1~2 blank samples
and 1~2 quality control samples were set in each batch test. Finally, the blank sample was strictly controlled. The relative standard deviation of the quality control sample and the true value is less than 10%, and the relative standard deviation between the parallel samples is controlled below 10%. If the above requirements were not met, the sample needs to be re-tested to ensure the quality of the test.

3. Results and discussion

3.1. Reaction law of ClO\textsubscript{2} and various substances in raw water

Chlorine dioxide mainly reacts with the reducing substance in the water, and also should be the substances in high concentration [10, 11]. According to this, the following reduced substances were found to have the potential to react with chlorine dioxide to form by-products, as shown in Table 1.

| Substance classification        | Name        | Concentration(mg/L) |
|--------------------------------|-------------|---------------------|
| Inorganic reducing substance   | Sulfide     | 0.2                 |
|                                 | Iron        | 0.3                 |
|                                 | manganese   | 0.1                 |
| Organic reducing substance     | turpentine  | 0.2                 |
|                                 | formaldehyde| 0.9                 |
|                                 | Humic acid  | 4                   |
|                                 | 2.4.6-Trichlorophenol | 0.2 |

As shown in Table 1, the selected materials included inorganic and organic reducing substances in raw water, and the above substances could react with chlorine dioxide at the highest concentration to form chlorite and chlorate as shown in Fig. 1.

![Figure 1. The reaction of reducing substance and chlorine dioxide.](image)

It can be seen that sulfide, formaldehyde, iron, manganese and humic acid were the main contributors in the formation of chlorite when chlorine dioxide was added (Fig. 1). The risk of toxic substances exceeding the standard in water was low. In addition, several researchers have investigated the formation of chlorite and chlorate when combined ClO\textsubscript{2} with the algae [12]. Therefore, this study selected Fe\textsuperscript{2+}, Mn\textsuperscript{2+}, humic acid, and algae as the main reactive substances.

3.2. Typical substances react with chlorine dioxide to form chlorite
Reaction law of Fe\(^{2+}\) and chlorine dioxide. In the experiment of ferrous ion and chlorine dioxide reaction, the dosage of chlorine dioxide was 0.5~5.0 mg/L, and the concentration of chlorite formed by reaction with different concentrations of Fe\(^{2+}\) was determined. It can be seen that the increase of ferrous ion concentration promotes the formation of chlorite (Fig. 2), the higher the initial concentration of Fe\(^{2+}\) was, the greater the amount of chlorite formed. The more of chlorine dioxide added, the more chlorite was generated. When 0.5 mg/L of chlorine dioxide was added and the ferrous ion concentration was 0.9 mg/L, the produced chlorite remained constant. The possible reason was that the concentration of ferrous ion was excessive and the reaction was completed. Therefore, when the concentration of ferrous ion was 0.1-0.3 mg/L and the chlorine dioxide dosage was less than 5 mg/L, the chlorite production was 100-400 μg/L. When the concentration of Fe\(^{2+}\) in water was higher than 0.6 mg/L, it was not recommended to use chlorine dioxide in the water treatment (pre-treatment or disinfection), and the risk of by-product exceeding the standard increases. Moreover, Sorlini et al [13] had also proposed that chlorite and chloride might have an obvious formation as the increasing of Fe\(^{2+}\) dosage.

![Figure 2](image_url)

**Figure 2.** The generation of chlorite with different initial input of Fe\(^{2+}\).

Reaction law of Mn\(^{2+}\) and chlorine dioxide. In the experiment of the reaction of Mn\(^{2+}\) with chlorine dioxide, the dosage of chlorine dioxide was 0.5~5.0 mg/L, and the concentration of chlorite formed by reacting with different concentrations of Mn\(^{2+}\) was determined. It can be seen that in the low concentration of 0.01~0.1 mg/L manganese ion aqueous solution, the higher the initial concentration of Mn\(^{2+}\) was, the higher the chlorite formed; however, it didn’t go beyond 300 μg/L (Fig. 3). When the concentration of Mn\(^{2+}\) continued to rise, chlorite formation declined. It would be due to that chlorite could react with excess Mn\(^{2+}\) in the water. According to the research of Ji et al [14] on the reaction between chlorine dioxide and Mn\(^{2+}\), when the initial concentration of Mn\(^{2+}\) was 0.282 mg/L and the molar ratio of chlorine dioxide to Mn\(^{2+}\) was 2, the removal efficiency of Mn\(^{2+}\) was 89.6%. In this study, the concentration of Mn\(^{2+}\) was 0.035 mg/L.
Figure 3. The generation of chlorite with different initial input of Mn$^{2+}$.

Reaction law of humic acid and chlorine dioxide. As shown in Fig. 4, after the addition of chlorine dioxide, the concentration of chlorite formed increased as the increase of the concentration of humic acid in the solutions. In Fig. 4, when the dosage of chlorine dioxide was less than 2 mg/L, the concentration of humic acid showed a steady trend. The reason might be that when a low concentration of chlorine dioxide reacted with a high concentration of humic acid, the concentration of humic acid was excessive, which was no longer the decisive factor in the reaction, so the chlorite formed tends to be stable. The higher the humic acid concentration, the greater the chlorite formed. Therefore, when the UV254 in water was higher than 0.143, it was not suitable to use chlorine dioxide as the pre-oxidant. When the concentration of organic matter in the water was too high, the dosage of chlorine dioxide should not be more than 2 mg/L. Barbeau et al [15] also had confirmed that the impact of NOM on chlorine dioxide appeared to be concentration-dependent.

Figure 4. The generation of chlorite with different initial input of humic acid.

Reaction law of algae and chlorine dioxide. As shown in Fig. 5, the greater the concentration of chlorophyll A (Chla) which could be indicated the concentration of the algae in the water, the more chlorite was formed. When the concentration of chlorine dioxide in the water was increased, the higher the concentration of chlorite formed, indicating that the presence of algae in the pre-oxidation stage could promote the production of chlorite, but there was no significant relationship with the dosage of chlorine dioxide. When the algae content was greater than 150 μg/L, and chlorine dioxide was used in pre-oxidation, there was a great risk of chlorite concentration exceeding the standard.
However, several researchers focused on the forming of organic disinfection by-productions and studied the production of chlorite. For example, Zhou et al [16] had indicated that ClO$_2$ could inhibit the photosynthetic capacity of M. aeruginosa cells and almost no integral cells were left after oxidation at a ClO$_2$ dose of 1.0 mg/L. The total toxin was degraded more rapidly with the ClO$_2$ dosage increasing from 0.1 mg/L to 1.0 mg/L.

![Figure 5](image.png)

**Figure 5.** The generation of chlorite with different initial input of the algae.

### 3.3. Two-factor influence law

Reaction law when algae in water coexist with other substances. In this experiment, the effect of algae presence along with Mn$^{2+}$, Fe$^{2+}$, or humic acids on the formation of chlorite was evaluated. It could be seen that when the concentration of Chla was 27.90 μg/L and the concentration of Mn$^{2+}$ was increased from 0 mg/L to 0.3 mg/L, the chlorite concentration response increased by 439.13 μg/L (Fig. 6a). At Chla concentration of 78.12 μg/L, the chlorite concentration response increased by 455.2 μg/L, and the amount of change was on the same order of magnitude. At a Mn$^{2+}$ concentration of 0.05 mg/L, the concentration of Chla increased from 0 μg/L to 78.12 μg/L, resulting in a chlorite concentration response increase of 265.8 μg/L. When the concentration of Mn$^{2+}$ was 0.05 mg/L, resulting in a chlorite concentration response increased by 251.2 μg/L. The amount of change was on the same order of magnitude. It suggests that the chlorite concentration response was parallel, indicating no significant interaction between the concentration of Mn$^{2+}$ and algae.

From Fig. 6b, it was found that when the concentration of Chla was 27.90 μg/L and the concentration of Fe$^{2+}$ was increased from 0 mg/L to 0.3 mg/L, the concentration response of chlorite increased by 333.3 μg/L. At a Chla concentration of 78.12 μg/L, the response to chlorite concentration increased by 318.2 μg/L. The amount of change was on the same order of magnitude. At a ferrous ion concentration of 0.1 mg/L, the concentration of Chla increased from 0 μg/L to 78.12 μg/L, which resulted in a chlorite concentration response increase of 234.5 μg/L, a ferrous ion concentration of 0.3 mg/L, and the response to chlorite concentration increased by 171.2 μg/L. The amount of change was on the same order of magnitude. It indicates that the change in chlorite concentration response was parallel, indicating no significant interaction between the concentration of Fe$^{2+}$ and algae.

The concentration of Chla was 27.90 μg/L, and the change of UV254 was increased from 0 to 0.120, resulting in an increase in chlorite concentration response of 359.6 μg/L (Fig. 6c). When the concentration of Chla was 78.12 μg/L, the chlorite concentration response increased by 329.8 μg/L, and the amount of change was on the same order of magnitude. At UV254 value of 0.059, the Chla concentration increased from 0 μg/L to 78.12 μg/L, resulting in a chlorite concentration increase of 84.74 μg/L, at UV254 value of 0.12, resulting in a chlorite concentration response increased by 125.44 μg/L. The amount of change was on the same order of magnitude. The change in chlorite concentration response was parallel, indicating no significant interaction between the concentration of
humic acids and algae. In summary, the study of coexistence of algae and Mn$^{2+}$, Fe$^{2+}$ and humic acids, respectively, showed that there is no interaction with the reaction of chlorine dioxide.

Figure 6. The regularity of the existence of algae and other substances. a. Mn$^{2+}$ and algae b. Fe$^{2+}$ and algae c. Organic matter and algae

Reaction law when organic matter in water coexists with other substances. In this experiment, the organic matter was reacted with Mn$^{2+}$ and Fe$^{2+}$, respectively, to explore the effect of three levels of organic matter at a certain level of another specific factor, in order to characterize whether there was interaction between the two factors.

The Fig. 7a showed that at the ferrous ion concentration of 0.1 mg/L, the value of UV254 increased from 0.029 to 0.143, resulting in a chlorite concentration response increased by 303.8 μg/L. When the concentration of ferrous iron was 0.5 mg/L, resulting in an increase in chlorite concentration response of 291.1 μg/L, and the amount of change was on the same order of magnitude. At a UV254 value of 0.029, the concentration of ferrous ion increased from 0.1 mg/L to 0.5 mg/L, resulting in a concentration of chlorite response increase of 338.6 μg/L, a UV254 value of 0.143, resulting in a chlorate concentration response increased by 325.9 μg/L. The change in chlorite concentration response was parallel, indicating no significant interaction between the concentration of Fe$^{2+}$ and organic matter.

It can be seen from Fig. 7b, that the concentration of UV254 is increased from 0.000 to 0.075 at a concentration of Mn$^{2+}$ is 0.02 mg/L, resulting in an increase in chlorite concentration response of 279.02 μg/L. The Mn$^{2+}$ concentration was 0.1 mg/L, resulting in a concentration of chlorite response increase of 224.4 μg/L. The amount of change is on the same order of magnitude. The value of UV254 was 0.000 when the concentration of Mn$^{2+}$ was increased from 0.02 mg/L to 0.1 mg/L, resulting in an increase in the response of chlorite concentration by 212.9 μg/L. At UV254 of 0.075, the response to chlorite concentration increased by 166.4 μg/L. The change in chlorite concentration response was parallel, indicating no significant interaction between the concentration of Mn$^{2+}$ and organic matter.
summary, when humic acid and Fe\(^{2+}\) and Mn\(^{2+}\) were separately present, there was no interaction with chlorine dioxide.

![Graph](image)

**Figure 7.** The regularity of the existence of Organic and other substances. a. Fe\(^{2+}\) and organic matter b. Mn\(^{2+}\) and organic matter

Reaction law in the presence of inorganic reducing substances in water. In this study, Cl\(_2\)O was added to the solution containing Mn\(^{2+}\) and Fe\(^{2+}\) to investigate if there was any effect on the formation of chlorite due to the simultaneous presence of Mn\(^{2+}\) and Fe\(^{2+}\).
Figure 8. The regularity of the existence of Inorganic and other substances.

As shown in Fig. 8, that when the concentration of Mn$^{2+}$ was 0.00 mg/L, the change of Fe$^{2+}$ concentration is increased from 0.01 mg/L to 0.03 mg/L, which caused the response value of chlorite concentration to increase by 205.04 μg/L. The concentration of Mn$^{2+}$ was 0.05 mg/L, which caused the response of chlorite concentration to increase by -231.33 μg/L, and the amount of change was not on the same order of magnitude. At a Fe$^{2+}$ concentration of 0.01 mg/L, the change in Mn$^{2+}$ concentration increased from 0.00 mg/L to 0.05 mg/L, resulting in a chlorite response increase of 247.92 μg/L; at Fe$^{2+}$ concentration of 0.03 mg/L, resulting in an increase in the response of chlorite concentration - 188.13 μg/L. The change in chlorite concentration response was a cross-change, indicating a significant interaction between the concentration of Mn$^{2+}$ and Fe$^{2+}$.

4. Conclusion

Humic acid, algae and Fe$^{2+}$ in water were positively correlated with the formation of chlorite. The formations of chlorite was not impact on the presence of Mn$^{2+}$. When the concentration of organic matter in the water is too high, or the water is eutrophic, and the concentration of sulfide and formaldehyde in the water exceeds the standard, the chlorine dioxide is not recommended in any step of the water treatment due to the great risk of the chlorite exceeding the regulated limit.

When organic matter and algae are present in the water, and there is a single kind of inorganic reducing substance, there is no interaction with the chlorine dioxide reaction. When the inorganic reducing substance Fe$^{2+}$ and Mn$^{2+}$ exists at the same time, there is a relatively obvious interaction.

5. References

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