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The adsorption of chlorite and chlorate by calcium carbonate in a drinking water pipe network

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ABSTRACT

Chlorite and chlorate are potential health-threatening by-products in drinking water disinfected by chlorine dioxide. Both can be adsorbed and thus removed by calcium carbonate. However, little is known on the adsorption dynamics of calcium carbonate to those by-products. In this study, adsorption efficiency of calcium carbonate to chlorite and chlorate was tested under different factors such as reaction time, chlorate and chlorite concentration, pH, and temperature. The results showed that 16.7–28.7% of chlorate and 23.8–41.3% of chlorite in water was adsorbed within 3 h. In addition, the adsorption of chlorate and chlorite decreased as pH and temperature increasing. In contrast, the adsorption increased as total organic carbon increasing. Furthermore, the effect of residual chlorine dioxide and iron oxide on adsorption was not evident. Taken together, our data provided a detailed characterization of adsorption behavior of calcium carbonate to chlorate and chlorite, which is helpful for making health water by chlorine dioxide.

Keywords: Chlorite; Chlorate; Calcium carbonate; Adsorption; Drinking water

1. Introduction

Chlorine dioxide is increasingly used as an effective disinfectant and deodorant to treat drinking water [1–4]. However, 50–70% of the applied chlorine dioxide is converted to chlorite ion and another 30% to chlorate ion, both of which have negative effects on health [5]. Chlorate is mutagenic for Salmonella, and it can induce chromosome aberrations and micronuclei in mammalian cells [6]. It has also been shown to induce thyroid tumors in animals [7]. Currently, chlorate is on CCL-3 (Contaminant Candidate List 3) list by EPA and monitored under Unregulated Contaminant Monitoring Rule-3 (UCMR-3) [8,9]. The other by-product, chlorite, was found toxic at concentration above 0.2 mg/L in Daphnia magna [10–12], and therefore, WHO recommends that chlorite should not exceed 0.2 mg/L in drinking water [13]. To control the disinfectant residuals, Safe Drinking Water Amendments were also established by EPA in 1996. It sets 1.0 mg/L for chlorite as the maximum contaminant level and 0.8 mg/L for chlorine dioxide as the maximum residual disinfectant level, respectively [14–17].

Chlorite is stable in drinking water and hard to remove. However, chlorite removal strategies adopting now greatly enhance the potential for chlorine dioxide in drinking water treatment [18]. In recent years, extensive efforts have been drafted toward developing

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methods for chlorite removal. Popular strategies includes adding reduced-sulfur compounds, such as sulfur dioxide and sodium sulfite [19]; adding salts such as ferrous chloride and ferrous sulfate [21,22]; applying powdered or granular activated carbon [23,24]. A common shortcoming of these methods is that an additional chemical is added, which may introduce new by-products in the water system.

There are many factors of the attenuation of chlorate and chlorite in drinking water pipe network, the adsorption was one of the factors cannot be ignored, while the calcium carbonate adsorption is the main form of adsorption. This research was set to investigate the adsorption dynamics of calcium carbonate toward chlorate and chlorite in chlorine dioxide–treated water. Results from this study will provide a theoretical basis for the improvement of drinking water disinfection by chlorine dioxide.

2. Materials and methods

2.1. Experimental preparation

A stock solution of chlorate (100 mg/mL) was prepared by dissolving 1.2754 g of sodium chlorate ($NaClO_3$, 99.9%, Tianjin Chemical Importing Corporation) in 10 mL deionized water. A stock solution of chlorite (100 mg/mL) was prepared by dissolving 1.3407 g of sodium chlorite ($NaClO_2$, 99.9%, Tianjin Chemical Importing Corporation) in 10 mL deionized water. The stocks were stored in dark at 4℃. Calcium carbonate ($CaCO_3$, 99.9%, Tianjin Chemical Importing Corporation) and iron oxide (Fe_2O_3, 70% Fe, Beijing Chemical Importing Corporation) were used in the experiment. All working solutions of varying concentrations were obtained by successive dilution. Deionized water was used throughout the experiments. All the chemicals used were analytical grade and were not purified further.

The pH (pH meter 713, Metrohm) of the solution was adjusted to the required value using phosphate buffer and sodium hydroxide. The temperature of the solution was controlled by water bath with shaking at 150 rpm. Total organic carbon (TOC) (TOC-5000, Shimadzu, Japan) was adjusted to the required value using humic acid (Tianjin Chemical Importing Corporation) [25]. Chlorine dioxide (ClO_2, 10^4 mg/L, Tianjin Chemical Importing Corporation) was determined at the beginning of each experiment by Hanna (HI-95711). The chlorine dioxide stock was kept in a refrigerator covered tightly by aluminum foil. Concentrations of chlorite and chlorate were determined by ion chromatograph [26]. The operating conditions of the chromatograph (DX-300, Dionex, USA) were given in Table 1. Because some anions can cause interference with the measurement, a spurge with nitrogen gas was needed [27]. The standard solutions of chlorite and chlorate were prepared by diluting the ultra-pure reagents. Concentration was measured in every 10 injections. The limits of detection were 0.010 mg/L for chlorite and 0.012 mg/L for chlorate.

2.2. Experimental procedure

We set our standard experimental system as a test in 1L deionized water containing 1.50 mg/L initial chlorate/chlorite and 0.4 g/L calcium carbonate at pH 7.0, 20 ± 1℃. To test the effect of individual factor on the adsorption effectiveness, the value of that specific factor was manipulated when other parameters were keeping constant with standard experimental system. Based on the typical drinking water pipe network condition, the range of parameters was set as followings: initial concentration of chlorate/chlorite from 0.50 to 1.50 mg/L, pH from 6.0 to 8.0, temperature from 10 to 30℃, TOC from 1.6 to 3.2 mg/L and the residual concentrations of chlorine dioxide from 0.02 to 0.16 mg/L. For example, to test the effect of initial chlorate/chlorite concentration on the adsorption effectiveness, varying amount of chlorate/chlorite (5, 10, 15 μL) was added to 1 L deionized water containing 0.4 g calcium carbonate, pH 7.0, 20 ± 1℃, respectively, forming the initial concentrations varied from 0.50 to 1.50 mg/L. Blank experiments were conducted at the concentrations varied from 0.50 to 1.50 mg/L (1 L deionized water, pH 7.0, 20 ± 1℃). In addition, blank experiments were also set for each individual test as control. All tests were repeated three times.

Chlorate/chlorite residual concentrations in water were detected at different times after the addition of calcium carbonate (0, 0.5, 1, 1.5, 2, 2.5, and 3 h).

Adsorption effectiveness was represented by the removal percentage, η (%):

$$\eta = (C_o - C_t)/C_o \times 100\% \quad (1)$$

Table 1
Operating conditions of ion chromatograph

Item	Analyzing condition
Separate column	AS9-HC
Guard column IonPac	AG9-HC
Eluent	9.0 mM Na_2CO_3
Eluent flow rate	1.0 mL/min
Suppressor	ASRS-with external water mode
Injection loop	150 μL
Pump	DXP pump
Detector	Suppressed conductivity

where C_o is the concentration of chlorate/chlorite of the blank experiment (mg/L) and C_t is the concentration of chlorate/chlorite at time t or at equilibrium (mg/L).

3. Results and discussion

3.1. Effect of initial concentration of chlorate and chlorite

The adsorption capacity of calcium carbonate was tested with different initial amount of chlorate and chlorite. In Figs. 1 and 2, chlorate and chlorite were adsorbed effectively by calcium carbonate in water within 1 h. However, the adsorption slowed down after 2-h reaction. It is also notable that, after 3-h reaction, there were still 0.40, 0.77, and 1.15 mg/L chlorate left for the initial 0.5, 1, and 1.5 mg/L, respectively. The ratios of adsorbed chlorate to control experiment data were 20.8, 22.8, and 23.3%, respectively. The concentrations of chlorite remaining were 0.33, 0.64, and 0.93 mg/L after 3 h. The ratios of adsorbed chlorite to control experiment data were 28.1, 29.4, and 31.4%, respectively. Taken together, those data suggest a great proportion of chlorate and chlorite can be removed by calcium carbonate in water, and the removal percentage increased as the initial concentration of chlorate/chlorite increase. This in turn supports using calcium carbonate as a chlorate-and-chlorite removing reagent to meet the safety regulations.

3.2. Effect of pH

The fact that pH of a given solution affects the ionization of small molecules and that chlorate and chlorite ionize in water raise the possibility that pH may be involved in adsorption. To address this possibility, we tested the adsorption behavior of calcium carbonate as a function of pH value. The results of effect of pH value were shown in Figs. 3 and 4. After 3-h reaction, the concentrations of chlorate remaining were 1.09, 1.15, and 1.25 mg/L, while 27.3, 23.3, and 16.7% of chlorate was adsorbed with pH 6, 7, and 8, respectively. Similar trend was also observed for chlorite removal at different pH value. It was also interesting that adsorption efficiency of chlorate differed at pH 7 and 8, while it was almost the same for chlorite. The ratios of chlorate adsorbed by calcium carbonate were 38.1, 31.4, and 31.8% at pH 6, 7, and 8, respectively. This possibly results from the oxidation/reduction reaction of chlorate and chlorite ion in the water list below [28].

$$\mathrm{ClO_2^-} \rightarrow \mathrm{ClO_2} + e^- \tag{2}$$

$$\mathrm{HClO_2} + \mathrm{H_2O} \rightarrow \mathrm{ClO_3^-} + 3\mathrm{H^+} + 2e^- \tag{3}$$

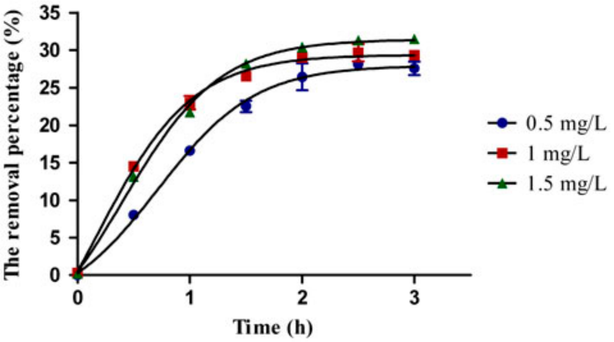

Fig. 2. The removal percentage of chlorite with different initial concentrations of chlorite.

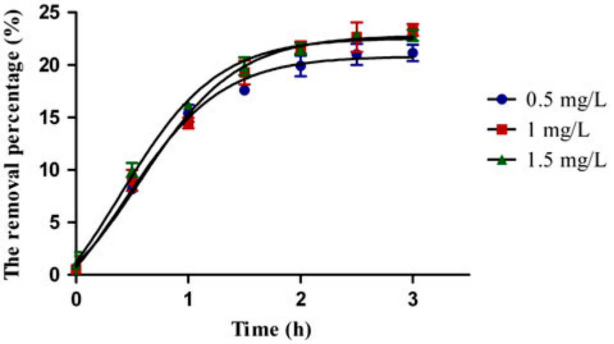

Fig. 1. The removal percentage of chlorate with different initial concentrations of chlorate.

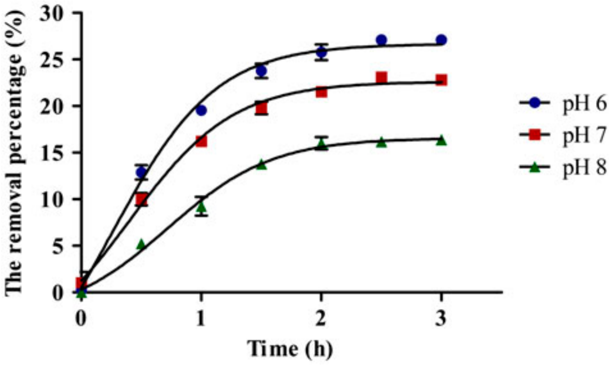

Fig. 3. The removal percentage of chlorate with different pH values.

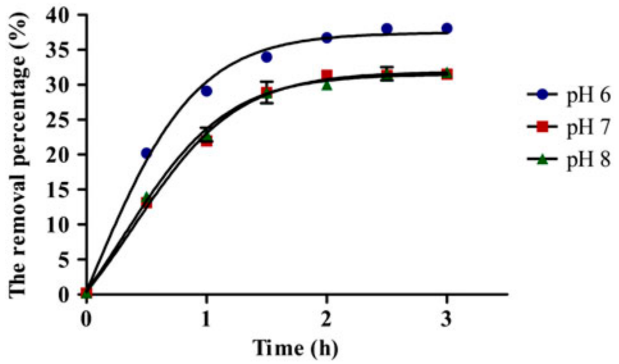

Fig. 4. The removal percentage of chlorite with different pH values.

This means that the adsorption of chlorate and chlorite was promoted with a lower pH value.

3.3. Effect of temperature

As temperature can affect the rate of ion movement, we tested the effect of temperature on the adsorption effectiveness. The results were shown in Figs. 5 and 6, the adsorption of chlorate increased with decreasing of temperature. After 3-h reaction, the concentrations of chlorate remaining were 1.10, 1.15 and 1.18 mg/L, and the ratios of chlorate adsorbed were 26.7, 23.3, and 21.3% at 10, 20, and 30℃, respectively. Similar trend was also observed for chlorite removal at different temperature, but the adsorption efficiency of chlorite was higher than chlorate. The ratios of chlorite adsorbed by calcium carbonate were 23.8 and 31.4% at 30 and 20℃, respectively, and it reached 35.4% at 10℃. Calcium carbonate precipitated when the water temperature in the pipe network was higher than 18℃ [29], so the ratios of chlorate and chlorite adsorbed should not be considered at 10℃.

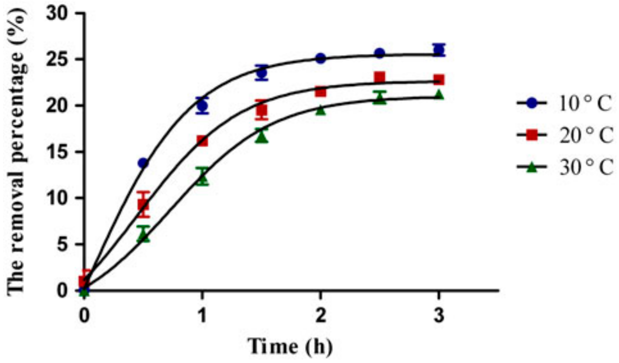

Fig. 5. The removal percentage of chlorate with different temperature.

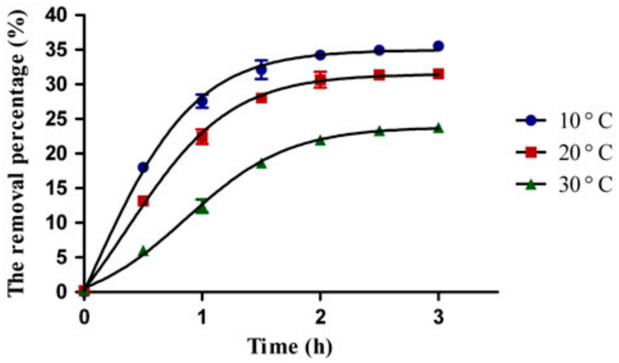

Fig. 6. The removal percentage of chlorite with different temperature.

3.4. Effect of TOC

TOC is often used as a nonspecific indicator of water quality, which is very important in detecting contaminants in drinking water. To test the effect of TOC on the adsorption behavior of calcium carbonate, different TOC value was adjusted to 1.6, 2.4, and 3.2 mg/L using humic acid. The results of effect of TOC were shown in Figs. 7 and 8. After 3-h reaction, the concentrations of chlorate remaining were 1.13, 1.11 and 1.07 mg/L and the consumption ratios were 24.5, 25.8, and 28.7%, respectively, when TOC were 1.6, 2.4, and 3.2 mg/L. The adsorption of chlorate increased with increasing of TOC concentration. Similar trend was also observed for chlorite removal at different TOC. After 3-h reaction, residual chlorite concentrations were 0.97, 0.94 and 0.88 mg/L and the ratios of chlorite adsorbed were 35.3, 37.3, and 41.3%, respectively. Additionally, the effect of TOC on the adsorption behavior of calcium carbonate was similar to the effect of pH. This possibly results from TOC was adjusted with humic acid, which lowered pH value.

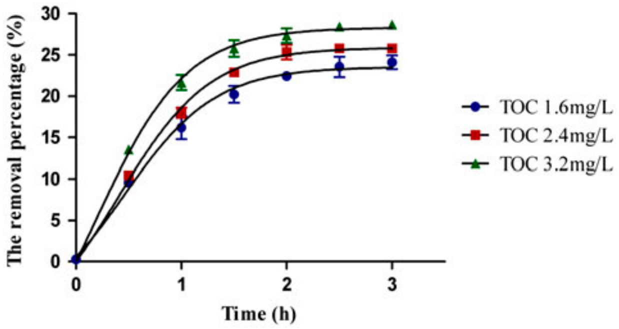

Fig. 7. The removal percentage of chlorate with different TOC.

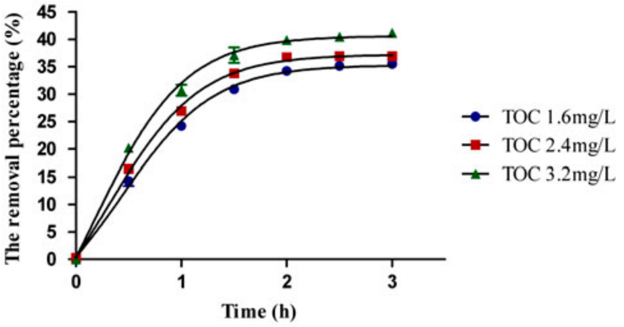

Fig. 8. The removal percentage of chlorite with different TOC.

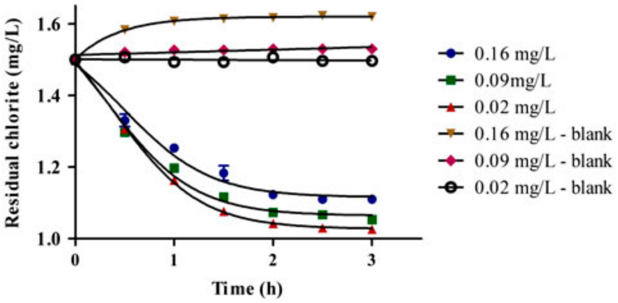

Fig. 10. Variation of residual chlorite with different concentrations of chlorine dioxide.

3.5. Effect of concentration of chlorine dioxide

Chlorite and chlorate existing in drinking water are by-products during the disinfection process by chlorine dioxide. Therefore, the effect of residue chlorine dioxide on the adsorption of chlorite and chlorate was also examined here. Figs. 9 and 10 illustrated the effect of different concentrations of chlorine dioxide on the adsorption of chlorate and chlorite by calcium carbonate. When the initial concentrations of residual chlorine dioxide existed in water were 0.16, 0.09, and 0.02 mg/L, the chlorate concentrations remained in blank experiment were 1.50, 1.50, and 1.50 mg/L; while the chlorite concentrations remained in blank experiment were 1.62, 1.53 and 1.5 mg/L after 3-h, respectively. This indicated that the residual chlorine dioxide in water generated chlorite at higher concentration. Additionally, the stabilized concentration of residual chlorine dioxide in water was almost 0.03 mg/L. After 3 h reaction, the concentrations of chlorate remaining were 1.13, 1.16, 1.15 mg/L, and the consumption ratios were 23.6, 22.7, and 22.8%, respectively. The concentrations of chlorate remaining were 1.11, 1.05, 1.03 mg/L, and the consumption ratios were 31.5, 31.2, and 31.4%, respectively. It was evident that the adsorption of calcium carbonate to chlorate and chlorite affected by residual chlorine dioxide illegibility.

3.6. Effect of iron oxide

Oxides of Fe may affect the attenuating of chlorite and chlorate in iron pipe network. We have, therefore, completed experiments regarding the effect of the absorption of calcium carbonate by iron oxide (Fig. 11). When the initial concentration of iron oxide was 0.4 g/L, after 3-h reaction, the concentration of chlorate remained in blank experiment was 1.39 mg/L, the concentration of chlorite remained in blank experiment were 1.36 mg/L. The ratios of adsorbed chlorate and chlorite by iron oxide were 7.4 and 9.3%. Those data suggest a proportion of chlorate and chlorite can be removed by iron oxide; however, the adsorption efficiency was less than one-third of the adsorption efficiency of calcium carbonate in same mass concentration. After 3-h reaction, the concentrations of chlorate and chlorite remained were 1.07 mg/L and 0.93 mg/L, and the ratios of adsorbed chlorate and chlorite by calcium carbonate and iron oxide to control

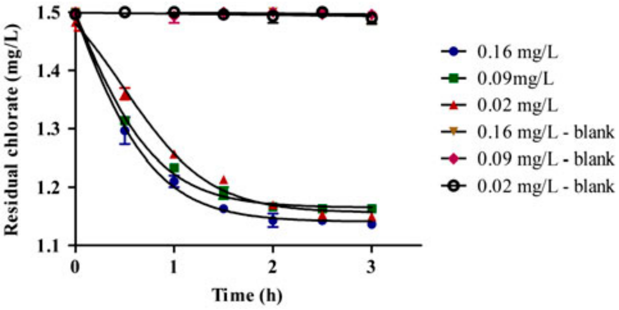

Fig. 9. Variation of residual chlorate with different concentrations of chlorine dioxide.

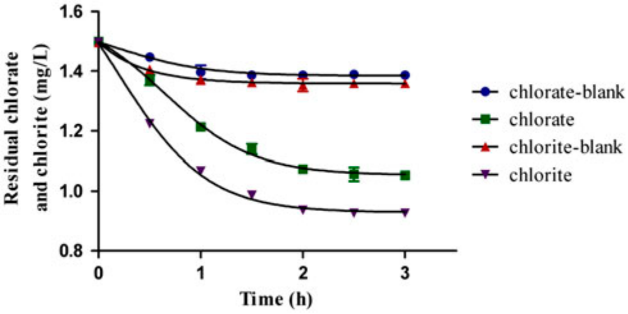

Fig. 11. Variation of residual chlorate and chlorite with iron oxide.

experiment data were 23.0 and 31.6%, respectively. In other words, there was no obvious effect of iron oxide on the adsorption process of chlorate or chlorite by calcium carbonate.

4. Conclusions

Absorption of calcium carbonate toward chlorite and chlorate, by-products of chlorine dioxide in drinking water pipe network were investigated in this study. Significant amount of both chlorate and chlorite were adsorbed rapidly within the first hour of reaction and last for three hours with a nonlinear manner. Interestingly, the adsorption amount of chlorite was 1.5 times higher compared with that of chlorate. Moreover, the adsorption increased with higher initial chlorite and chlorate concentrations. Our data also showed that low pH, low temperature, and high TOC favor the absorption reaction. Yet, residual chlorine dioxide and iron oxide had little effect on absorption.

The quality of drinking water is directly related to health. All the substances within the water supply network, especially by-product of disinfectant, are likely to affect water safety, which makes study of potential health-threatening molecular in the water supply network become important. This study suggests that a great proportion of chlorate and chlorite can be adsorbed by calcium carbonate. Therefore, calcium carbonate could be applied to remove by-products of chlorine dioxide in the drinking water system. However, more attention should be paid in regard of the scale of the absorption reaction. In conclusion, this paper provides the basis for study on disinfection by-products treatment and adds new ideas to water quality improvement. The environment of pipeline network is complex and changing. Therefore, experiments on dynamics and modeling are also needed.

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