Minimization Of Disinfection By-Products Formation In Water Purification Process Using Chlorine Dioxide – Case Studies

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Abstract

The formation of the by-product chlorite after using chlorine dioxide for the disinfection of drinking water depends on the quantity of the organic matter dissolved in the water. A further decisive factor for the chlorite formation is the level of residual free chlorine dioxide. The chlorine dioxide demand decreases by application of activated carbon filtration, especially after the use of a combination of ozone and activated carbon treatment of the water. Nevertheless, higher chlorine dioxide residuals are a source of chlorite and chlorate formation. The concept of the "Minimum Chlorine Dioxide Dosage (MCDD)" is developed in order to give a clue to the water companies for an optimized chlorine dioxide dose without compromising the disinfection efficiency. By application of the MCDD, the residual level of chlorine dioxide is focused to 0.05 mg/L after 0.5 h contact time. In the range of the MCDD the ratio of the chlorite formation and the chlorine dioxide demand is nearly independent of the level of DOC.

Introduction

Since the mid 1970s there has been concern about possible implications to human health of the occurrence of disinfection by-products (DBP) formed after the chlorination of drinking water at the consumer's tap (1). In Europe, this concern led to regulations and proposals controlling the levels of trihalomethanes (THM) and other chlorinated organic compounds in drinking water (e.g. 2, 3). Therefore, the aim of the water facilities is the minimization of by-products formation during the treatment of
the water as well as during its distribution without compromising the disinfection efficiency.

In Germany, an increasing number of water companies are investigating alternative disinfection agents, e.g. chlorine dioxide. The decisive advantage in this case is the avoidance of THM formation. However, it should be noted that chlorine dioxide reactions in water form the ions chlorite and chlorate as by-products (e.g. 4). In contrast to THM formation, little is known about the toxic implications of these compounds to human health.

The urgent requirement for controlling disinfection by-products formation at low levels, especially at the consumer's tap, is the knowledge about the general correlation between the water quality, the purification regime applied and the by-products formation potential.

In order to obtain information about by-products formation when chlorine dioxide is used for disinfection of drinking water, systematic laboratory experiments were carried out in order to determine the impact of activated carbon filtration including the application of ozone.

**Experimental**

The experiments were carried out with bank filtrated water of the river Elbe, (pH: 7.8-8.3; DOC: 3.7-4.8 mg/L; UV(254 nm): 7.8-9.0 m⁻¹; conductivity: 46.8 μS/cm). In order to remove the absorbable dissolved organic matter different amounts of Granular Activated Carbon (GAC F300 (Chemviron) were added to equivalent volumes the water sample. The GAC-doses were 10; 20; 40; 80 and 500 mg/L. After a shaking period of 24 h the carbon fraction was removed by membrane filtration. The chlorine dioxide was added to the so prepared water sample. The same procedure was also carried out with ozone dosed. The water was ozonated (applied ozone dose: 2.4 mg/L; contact time 1 h) and after quenching the residual ozone, the activated carbon was added.

The chlorine dioxide stock solution was prepared by oxidation of sodium chlorite with sodium peroxodisulphate under laboratory conditions (5). In the case of 0.4 mg/L chlorine dioxide dosage the level of free chlorine was determined to be 0.03 mg/L. For the experiments with chlorine dioxide all samples were stored by exclusion of light at 10°C. In order to minimize the impact of the bottle materials on the chlorine dioxide demand, all materials used were treated with a stock solution of 0.4 mg/l chlorine dioxide for 0.5 h and washed with Milli-Q-water.

The concentration of chlorine dioxide and chlorine were determined by a photometric method with N,N-diethyl-1,4-phenylenediammoniumsulphate (DPD) at 525 nm. Traces of chlorine in the chlorine dioxide stock solutions were masked with "Degussa-Chloreliminierungs-Reagenz" in order to distinguish between chlorine dioxide and the sum of chlorine and chlorine dioxide (6).
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The by-products chlorite and chlorate were determined by ion chromatography with a Dionex DX-300 equipment by using a Dual-1 column (Metrohm) connected with amperometric detection (chlorite) and an AS9-SC column (Dionex) connected with the determination of the suppressed conductivity in the case of chlorate.

Results and Discussion

The most efficient way to achieve a minimization of the level of disinfection by-products is the removal of organic matter dissolved in the water, the so-called precursor compounds.

In general, the application of activated carbon in combination with ozone is of high efficiency in order to minimize the formation of the by-products, e.g. THMs, after the chlorination (7-9).

For example, in Figure 1 the tendency of the THM-formation in model water after filtration with GAC is compared with the values of water samples which were spiked with ozone prior to the GAC treatment. The THM-values were determined after a short contact time of 0.5 h and after a longer one of 48 h which should simulate the situation during the distribution of the disinfected water.

![Figure 1: Formation of THM in activated carbon filtered and ozonated/activated carbon filtered water. Chlorine dose: 10 mg/L; ozone dose: 2.4 mg/L, contact time of the ozone: 1 h.](image-url)
The total THM concentration formed in the water after chlorination can be reduced significantly by using ozonation as an additional treatment step. The impact of the ozone is clearly seen for the short contact time of 0.5 h and especially for 48 h (Figure 1).

Nevertheless, when using chlorine dioxide for the disinfection of drinking water, the impact of ozone on the formation of its by-product chlorite has to be considered in more detail. In order to show this effect in real water samples, a chlorine dioxide dose of 0.4 mg/L was applied. The chlorite formation is shown in Figure 2. The demand of the chlorine dioxide is shown in Figures 3 - 5.

Figure 2: Formation of chlorite in activated carbon filtered and ozonated/activated carbon filtered water.

Treatment regime:
A and B) filtration with 20; 40; 80; 200 and 500 mg/L carbon F 300; dose of chlorine dioxide: 0.4 mg/L;
C and D) ozone dose: 2.4 mg/L; contact time: 1 h, filtration with 20; 40; 80; 200 and 500 mg/L carbon F 300; dose of chlorine dioxide: 0.4 mg/L.

Figure 2 shows that the formation of chlorite depends on the level of organic matter (DOC) after activated carbon and ozonation/activated carbon filtration of the water. After a short contact time of 0.5 h the chlorite formation decreases with lower levels of DOC, as expected. This tendency was much stronger when ozone was used prior to the activated carbon filtration (Curve C). However, in the period from 0.5 to 48 h the
situation changes completely. In samples with lower DOC the highest chlorite levels were formed, particularly in the case of the ozone application. (Curves B and D)

In order to explain the diagrams presented in Figure 2 the kinetics of the chlorine dioxide reaction to chlorite in drinking water was examined. The results are shown in Figure 3. The model experiment was carried out with an activated carbon filtered bank filtrate. The concentration of chlorine dioxide added was 1 mg/L in order to show clear tendencies of the chlorine dioxide decay and the chlorite formation and to guarantee free chlorine dioxide residuals during the whole contact time.

![Graph showing formation of chlorite and chlorine dioxide decay versus the contact time after the dosage of 1 mg/L chlorine dioxide in bank filtrated water of the river Elbe; DOC: 2.4 mg/L.](image)

In the "first period" (up to 2 h) the transformation rate of chlorine dioxide into chlorite was found to be between 40 and 50 % of the total concentration added to the water. A further amount of the chlorine dioxide (up to 25 % in this case) was transformed into chlorite during the period from 2 up to 72 h, which is a typical time period for water distribution.

The general tendency of chlorite formation after the dosage of chlorine dioxide, as shown in Figure 3, is comparable to that of the THM-formation by use of chlorine for disinfection. However, in contrast to the THM formation which is the result of the reaction of chlorine with organic matter only, two main sources of chlorite formation are known: the reaction of chlorine dioxide with organic matter (equation [1]) and the reaction of free chlorine dioxide with partners of the complex system of OCI/HOCI
which are often components of the chlorine dioxide stock solution (equation [2]), (5,6). The mechanism of these overlapping reactions has discussed by GORDON, (e.g. 10).

\[
\text{ClO}_2 + e^- (\text{DOC}) \rightarrow \text{ClO}_2^-
\]

\[
\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{ClO}_2^-; \text{ClO}_3^-; \text{Cl}^-
\]

Additionally, a decomposition of chlorine dioxide in alkaline solutions according to equation [3] is possible

\[
2 \text{ClO}_2 + 2 \text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}
\]

The reaction path of equations [2] and [3] can be called "auto-decomposition of chlorine dioxide".

In real water samples the chlorine dioxide decay and the formation of chlorite (Figure 2) has to be explained under the consideration of the different reaction paths (see equations [1] to [3]). So, the quality and the quantity of the organic matter dissolved in the water and the concentrations of residual chlorine dioxide as well as of the other reaction components mentioned in equations [2] and [3] are the decisive factors of the chlorite formation.

![Figure 4: Kinetics of chlorine dioxide decay. Pseudo-first order, chlorine dioxide: 0.4 mg/L.](image-url)
The kinetics of the chlorine dioxide decay in DOC-containing (equation [1]) and DOC-free waters (equations [2] and [3]) are quite different, as shown in Figure 4. In order to illustrate the rate of the decay in both cases, the reaction constants were calculated by assuming a pseudo first order reaction. It is well seen in Figure 4 that in the DOC-containing water the chlorine dioxide decay takes place faster in comparison to the "auto-decomposition" of the chlorine dioxide in DOC-free water.

Considering these rate constants, the impact of the activated carbon filtration including the ozonation step on the chlorine dioxide decay and the formation of chlorite can be explained (Figure 5).

![Graph showing chlorine dioxide decay in activated carbon filtered and ozonated/activated carbon filtered water.](image)

**Figure 5:** Chlorine dioxide decay in activated carbon filtered and ozonated/activated carbon filtered water.

**Treatment regime:**

a) filtration with 20; 40; 80; 200 and 500 mg/L carbon F 300; dose of chlorine dioxide: 0.4 mg/L;
b) ozone dose: 2.4 mg/L; contact time: 1 h, filtration with 20; 40; 80; 200 and 500 mg/L carbon F 300; dose of chlorine dioxide: 0.4 mg/L.

The residual chlorine dioxide concentrations in activated carbon filtered and ozonated/activated carbon filtered water samples after a dosage of 0.4 mg/L ClO₂ and 0.5 h contact times are shown versus the level of DOC. The chlorine dioxide decay is less with lower DOC levels as expected, plus the application of ozone causes an
additional reduction of the chlorine dioxide decay. Therefore, the residual chlorine dioxide concentration in the water increases with lower DOC and by the application of ozone in the case of a constant dosage of the oxidant. This effect of ozone on the chlorine decay in the case of drinking water disinfection is similar(7).

Nevertheless, in contrast to chlorine residuals, which do not form a significantly higher THM-level with an increasing contact time, if the precursor concentration could be minimized (low DOC-levels), the free chlorine dioxide residuals are recognized to be a source of additional by-products formation (compare equations [2] and [3]).

This function is described by the result of a model experiment shown in Figure 6, where the kinetics of the reaction of chlorine dioxide in water with low DOC-level is illustrated.

The removal of the adsorbable DOC fraction with the help of an overdose of GAC (1000 mg/L) was necessary in order to avoid the reaction of the disinfectant with the organic matter. Water prepared in this way was spiked with 0.4 mg/L chlorine dioxide.

![Figure 6: Chlorine dioxide demand and by-products-formation in water low level of reactive organic matter (DOC). Dose of chlorine dioxide: 0.4 mg/L; DOC < 0.3 mg/L; pH-value: 8.1.](image)

The level of chlorite increases nearly linearly with the contact time as shown in Figure 6. In parallel, the concentration of chlorine dioxide is reduced and a second by-product, chlorate, is formed during the time up to 48 h. Nevertheless, the example of Figure 6 shows that in this water with low content of reactive DOC, the chlorine dioxide concentration decreased to nearly 50 % during the test.

In order to minimize the concentration of free residual chlorine dioxide without compromising the disinfection efficiency, the dosage has to be optimized. In Germany,
the regulation of disinfection with chlorine dioxide requires a minimum level of free chlorine dioxide of 0.05 mg/L at the end of the treatment process, i.e. at the outlet of the waterworks.

Following this strategy, the concept of the "Minimum Chlorine Dioxide Dosage, (MCDD)" was developed (7, 11). The objective of this concept is to identify target values of optimal disinfection doses to the water works. The MCDD is defined as the chlorine dioxide dose which yields to a residual chlorine dioxide level of 0.05 mg/L after a contact time of 0.5 h. The advantage of this concept is the constant ratio between the dose of chlorine dioxide and its demand components. Therefore, this concept considers the characteristics of the water, especially the level and the character of the DOC which is the main cause of the chlorine dioxide decay. On the other hand, the concentration of residual chlorine dioxide in the water is minimized to 0.05 mg/L and below.

In Figure 7 the MCDD is given for water samples with different DOC-values. According to the concept of the MCDD the linear decrease of the dose of chlorine dioxide required for lower DOC levels was expected. It is notable that the level of chlorite formed after 0.5 as well as 48 h contact time decreases and correlates well with the DOC. A significant difference between the two curves could not be observed because the concentration of free chlorine dioxide in the water was minimized (compare with Figure 2).

Figure 7: Minimum Chlorine Dioxide Dose (MCDD) and chlorite formation after different contact times versus the DOC after activated carbon filtration.
Following the concept of the MCDD, it could be proved that the ratio of chlorite formation and chlorine dioxide demand is nearly independent of the level of the DOC in water (equation [4]), (11).

\[
\frac{[\text{ClO}_2^-]}{\Delta[\text{ClO}_2]} \equiv \text{constant} = K; \ (0.5 \leq \text{DOC} \leq 5 \text{ mg/L})
\]

\[
[\text{ClO}_2^-] = K \Delta[\text{ClO}_2] \tag{4}
\]

Moreover, in the case of total chlorine dioxide decay which is often characteristic for water distribution the chlorite level can be calculated from the dose of chlorine dioxide added to the water (equation [5]).

\[
\Delta[\text{ClO}_2] = [\text{ClO}_2], \\
[\text{ClO}_2^-] = K \{[\text{ClO}_2]_0\} \tag{5}
\]

\([\text{ClO}_2^-] \): concentration of chlorite formed

\(\Delta[\text{ClO}_2] \): chlorine dioxide decay

\([\text{ClO}_2]_0 \): dose of chlorine dioxide

For example the K-values were calculated by equation 5 for some waters of different origin (see Table 1). The DOC level of these waters was reduced by the application of different amounts of activated carbon and by use of ozone prior to the activated carbon filtration. The MCDD was added into these water samples. It is noted that

1. the K-values differ in the range from 0.4 to 0.8 in different waters and
2. those of the ozonated/activated carbon filtered water samples are greater than for the activated carbon treated water samples.

Further examinations are necessary in order to explain this effect.

Table I: K-values of waters of different origin, calculated by equation [5].

<table>
<thead>
<tr>
<th>Type of the water</th>
<th>Treatment regime</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>bank filtrate I</td>
<td>activated carbon*</td>
<td>0.52</td>
</tr>
<tr>
<td>bank filtrate I</td>
<td>ozone/activated carbon</td>
<td>0.67**</td>
</tr>
<tr>
<td>bank filtrate II</td>
<td>activated carbon</td>
<td>0.59</td>
</tr>
<tr>
<td>bank filtrate II</td>
<td>ozone/activated carbon</td>
<td>0.71</td>
</tr>
<tr>
<td>bank filtrate III</td>
<td>activated carbon</td>
<td>0.44</td>
</tr>
<tr>
<td>bank filtrate III</td>
<td>ozone/activated carbon</td>
<td>0.71</td>
</tr>
<tr>
<td>ground water I</td>
<td>activated carbon</td>
<td>0.58</td>
</tr>
<tr>
<td>ground water I</td>
<td>ozone/activated carbon</td>
<td>0.82</td>
</tr>
</tbody>
</table>

* see Experimental   ** calculated in the case of two DOC-levels only
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Nevertheless, the ratio of chlorite concentration and chlorine dioxide demand (K) was calculated to be constant in the whole range of the DOC level for each type of water as per the example in Figure 4. Due to the fact that the residual chlorine dioxide level was not greater than 0.05 mg/L, its reaction with the other components of the stock solution (see equation [2] and [3]) could be minimized. Therefore, the chlorine dioxide decay should be caused by the organic matter dissolved in the water only. It is remarkable that under these conditions the K-values are in the range from 0.4 to 0.8.

Conclusions

The results of systematic examinations concerning the chlorite formation using chlorine dioxide for disinfection of drinking water show the significant impact of the remaining chlorine dioxide level in the water. Chlorite formation is caused not only by the oxidation of organic matter, but also by a complex mechanism of the decomposition of chlorine dioxide in water and its reaction with other components of the stock solution like chlorine and chlorite, and especially a measurable chlorate concentration. If the precursor role of the organic matter can be reduced by activated carbon- or ozonation/activated carbon filtration, a significantly lower chlorine dioxide demand of the water has to be considered to minimize by-products formation.

Therefore, the minimization (= optimization) of the chlorine dioxide dose without compromising the disinfection efficiency should be the best way to minimize the disinfection by-products formation when chlorine dioxide is used.

References


**Key Words**

Ozone; Disinfection; Chlorine Dioxide; Chlorite; Chlorate; Minimum Chlorine Dioxide Dosage (MCDD); Trihalomethane Formation; Germany Drinking Water Treatment;