Reducing of specific carcinogenic disinfection by-products compounds from drinking water using chlorine dioxide as alternative for chlorine

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Abstract---Chlorination has significantly reducing the risk of pathogenic dirt but could pose a chemical hazard to human health due to formation of various disinfection by-products (DBPs). Chlorine dioxide is one of the most intriguing oxidants since it combines a high oxidation capacity with a minimal generation of harmful byproducts like chlorinated organics when used. As a result, it is widely utilized in the disinfection of drinking water and, more recently, in the disinfection of surfaces and structures. Trihalomethanes (THMs) that react with chlorine and organic materials are suspected carcinogens. THMs, haloacetic acids (HAAs), haloacetonitriles (HANs), and halogenated ketones are the most common disinfection by-products (DBPs). Cancer, abortion, poor birth weight, and congenital impairments are all increased by exposure to these by-products. This study aimed to highlight the ability to use chlorine dioxide as alternative for chlorine to reducing carcinogenic hazardous organic material formation. The study resulted that both the concentration of chlorine and chlorine dioxide is one of the major parameters in hazardous organic material formation. Also, the DBPs resulted from using chlorine dioxide is (37.4%, 49.9%, 43.4%, 40.0%, 35.3%, 36.6%) of CHCl₃, BDCM, CDBM, THMs, DCAA, TCAA respectively comparing with the resulted by using chlorine. The study concluded that the
DBPs which produced in case of using Chlorine dioxide is significantly less than which produced by using chlorine. Thus, chlorine dioxide is recommended than chlorine for drinking water disinfection.

Keywords—Disinfection by-products, cancer, chlorine dioxide, surface water, chlorination, dangerous, THMs, DBPs.

Introduction

Chlorination as an acceptable disinfection technique greatly reduced morality rates caused by water-borne infections, making it one of the century’s most significant public health achievements. The National Cancer Institute of the United States released findings in 1976 that showed chloroform, one of the trihalomethanes (THMs) produced as a byproduct of drinking water disinfection, was carcinogenic in rodents (Boorman, 1999). Since then, there has been worry that, while disinfection of water protects against microbiological hazards (Hesham and Moustafa, 2019), it may also expose humans to chemically produced cancer risks (Onstad et al., 2008).

Chlorine dioxide is one of the most intriguing oxidants since it combines a high oxidation capacity with a minimal generation of harmful byproducts like chlorinated organics when used. As a result, it is widely utilized in the disinfection of drinking water and, more recently, in the disinfection of surfaces and structures. Although it is normally created through the chemical reaction of chlorite with hypochlorite/chlorine or hydrochloric acid, the combination of chlorate with hydrogen peroxide in very acidic environments offers an interesting alternative. Both compounds are known to be produced efficiently using electrochemical technology, allowing for the development of a full electrochemical method for the production of this crucial oxidant (Sales Monteiro et al., 2021).

Chlorite and hypochlorite/chlorine or hydrochloric acid are usually combined on site. Chlorine dioxide is usually created by combining chlorite and hypochlorite/chlorine or hydrochloric acid. It can also be made by combining chlorate with methanol, Sulphur dioxide, or hydrogen peroxide in a process (Sales Monteiro et al., 2021). Electrochemical technology appears to have potential since the anodic transition of chloride to chlorate, as well as the cathodic creation of hydrogen peroxide from oxygen, are well-known processes (Bergmann and Koparal, 2005).

The manufacture of this reagent from two species that can be easily produced onsite utilizing electrochemical technology. Strong acidic media are required for the reaction indicated in Eq. (1) to chlorate in the presence of hydrogen peroxide, which produces chlorine dioxide and oxygen as a by-product (Sales Monteiro et al., 2021).

Equation

\[ ClO_3^- + 1/2 H_2O_2 + H^+ \rightarrow ClO_2(aq) + \frac{1}{2}O_2 + H_2O \]
Although chlorine dioxide is stable more than ozone, it does not leave a long-lasting residue. It is effective throughout a wide pH range and does not produce chlorinated compounds in the presence of organics. Chlorite (ClO₂) and chlorate (ClO₃⁻) are two of chlorine dioxide’s byproducts (Stevens, 1982, Sorlini et al., 2014). Although it is normally created through the chemical reaction of chlorite with hypochlorite/chlorine or hydrochloric acid, the combination of chlorate with hydrogen peroxide in very acidic environments offers an interesting alternative.

Studying the carcinogenicity to human, researchers have paid interest to DBPs (Yang et al., 2018). Furthermore, among all DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) characterized by chlorinated and brominated DBPs are found frequently with high concentrations; therefore, THMs and HAAs have attracted more interest (Liu et al., 2020). Due to the possibility of carcinogenicity of DBPs, various countries have sharp regulations to control DBPs (Aslani et al., 2019).

Due to the possibility of carcinogenicity of DBPs, various countries have sharp regulations to control DBPs. For instance, United States Environmental Protection Agency (US EPA) has established an extreme pollution level for trihalomethanes equal 80, while it has been established a 60 µg/L for five haloacetic acids; European Community legalizes the levels of at 100 µg/L for (Bromoform, Chloroform, Dibromochloromethane and Dichlorobromomethane) (Aslani et al., 2019, Ozdemir et al., 2014).

This paper aimed to investigate the capability to use chlorine dioxide as alternative disinfectant for chlorine to reduce specific carcinogenic disinfection by-products compounds from drinking water. Chlorine dioxide gas generators have a good control of chlorine dioxide gas quantity by electrical solenoid; can be determining digitally of chlorine and oxygen quantities and mixing to pumping the treated water pass way closed system.

Temperature, disinfectant concentration, contact duration between disinfectants and surface water during the disinfection process, and total organic carbon (TOC) for raw water are all factors that determine the amount of hazardous disinfection by-products. When all other variables remain constant,

**Experimental**

**Materials**

All chemical, reagents, reference materials of purgeable volatile organic compounds and inorganic chemicals used were analytical purity grade. Aluminum Sulphate (Al₃(SO₄)₃.18H₂O), was obtained from Alum Misr Company, Abou Zabal, Egypt. As well, Calcium Hypochlorite (Ca (OCl)₂, 30 % chlorine) was obtained from Misr Chemical Company, Alexandria, Egypt. While Reference inorganic chemicals used were of appropriate purity grade. Methanol, Hydrochloric acid, Ascorbic Acid, Sodium thiosulfate, Phosphoric Acid, Sodium Carbonate, Sodium bicarbonate, Sucrose, they were obtained from Acuustanderd Co., Riedel Co, and Sigma Aldrich Co. and Fluka Co. All reagents and media utilized for microbiological tests were prepared according to the standards.

**Sampling**

All Samples were collected from Zeftta drinking plant and at a depth of 35 cm from the water surface to ensure the homogeneity of the sample. Six Samples each of them one liter of water was treated by the same doses of alum. And pumping by varied doses of chlorine or chlorine dioxide gas, have the same total organic carbon and staying the same contact time. At 25°C as temperature, two hours contact time between disinfectant and treated water, whereas total organic carbon between 4.18 mg/l to 4.32 mg/L, six liter of water was treated by the same doses of Alum 20 mg /L at the same Conditions In an attempt to stabilize the surrounding conditions have study to Disinfection process and evaluation of carcinogenic hazardous disinfection by-products in drinking water.

**Statistical analysis**

The results of chlorine dioxide dose, the concentrations of CHCl₃, BDCM, CDBM, THMs, DCAA, TCAA were handled by EXCEL 365. To guarantee the quality of experiment results, distilled water was used as a blank; furthermore, all the samples and blanks were analyzed in duplicate.

**Methodology**

**Determination of DBPs in case of using Chlorine dioxide as a disinfectant**

At 25 °C Six Samples each of them one liter of water was treated by 20 mg /L of alum. And pumping by (0.08, 0.1, 0.3, 0.5, 0.7 and 0.9 mg/l of chlorine dioxide, have the same total organic carbon between 4.18 mg/L to 4.32 mg/L and staying two hours contact time.

**Determination of DBPs in case of using Chlorine as a disinfectant**

At 25 °C Six Samples each of them one liter of water was treated by 20 mg /L of alum. And pumping by (1, 2, 3, 4, 5 and 6 mg/l of chlorine, have the same total organic carbon between 4.18 mg/L to 4.32 mg/L and staying two hours contact time.

**Determination of the optimum dose of the disinfectant**

Different doses of the disinfectant (as mentioned in part 2.4.1 and 2.4.2) used to treat water samples which contaminated by one microorganism from (Heterotrophic bacteria (HPC), Total Coliform bacteria (TC), Fecal Coliform (FC) and Streptococcus Faecalis (SF). The results monitored to decide the dose of disinfectant at which the microbiological test results within the limits of guidelines (50 CFU / 1ml for HPC, 1 CFU / 100 ml for TC, FC, and SF.). Incubation temperature for all of the tested serotype was 35 °C except F.C the incubation temperature was 44.5 °C. The isolates tested in this study were
prepared as previously described (Rose et al., 2007, O’Connell et al., 2009, Cabral, 2010).

**Comparison between DBPs concentrations resulted from Chlorine and Chlorine dioxide**

The optimum dose as a result from section 2.4.3 used to treat raw water under the condition mentioned in Section 2.4.1 and 2.4.2. Then the DBPs determined and compared against each other.

**Organic Parameters**

**Determination of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography Mass Spectrometry**

This is a general-purpose method for identifying and measuring purgeable volatile organic chemicals in surface water, ground water, and drinking water at any treatment stage (Dunemann and Hajimiragha, 1993). The approach can be used to analyze a wide variety of chemical substances. Purge and trap processes can be used to remove this substance from water samples because of its high volatility and low water solubility. This approach can be used to identify the following substances. By bubbling an inert gas such as Helium (\(^4\text{He}\)) through the aqueous sample, volatile organic molecules with limited water solubility are removed (purged) from the sample matrix. In a tube containing sufficient sorbent materials, purged sample components are trapped. The sorbent tube is heated, and reverse flushed with helium after purging is complete to desorb (Koester and Clement, 1993, APHA, 2012).

The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database and used to column *Agilent DB-624 Ultra inert 60m /250mm / 0.25µm*. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated using procedural Standard calibration. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard.

- Inlet condition: *split mode, initial temperature 200 C, Column flow 0.8 ml/min, split ratio 40:100.*
- Oven condition: the oven temperature program was adjusted as shown in Table (1).
Table 1
Temperature program for analyzing Purgeable Organic Compounds

<table>
<thead>
<tr>
<th>Level</th>
<th>Ramping (°C/min)</th>
<th>Final Temp. (°C)</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>180</td>
<td>6</td>
</tr>
</tbody>
</table>

The instrument was calibrated by using Purgeable Organic Compounds. Standards corresponding EPA 524.3 have a fixed Concentration of all Compounds (60 Purgeable Organic Compounds) and dilute that fixed slandered under special conditions to more one variable concentration to calibrate the GC MS System by nine Calibration system at 1, 4, 8, 10, 20, 40, 60, 80 and 100 µg/l to construct the calibration curve (Kali et al., 2021).

Chlorine dioxide experiments

Table 2
Effect of Chlorine dioxide doses on Disinfection by Products (DBPs) concentration

<table>
<thead>
<tr>
<th>Chlorine dioxide Dose (mg / L)</th>
<th>CHCl₃ (300 ug/l)</th>
<th>BDCMs (60 ug/l)</th>
<th>CDBMs (100 ug/l)</th>
<th>THMs (100 ug/l)</th>
<th>DCAA (50 ug/l)</th>
<th>TCAA (100 ug/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>19.32</td>
<td>6.87</td>
<td>ND</td>
<td>26.19</td>
<td>6.18</td>
<td>12.01</td>
</tr>
<tr>
<td>0.1</td>
<td>22.21</td>
<td>8.63</td>
<td>1.15</td>
<td>31.99</td>
<td>9.94</td>
<td>14.52</td>
</tr>
<tr>
<td>0.3</td>
<td>28.15</td>
<td>9.19</td>
<td>1.77</td>
<td>39.11</td>
<td>12.97</td>
<td>16.89</td>
</tr>
<tr>
<td>0.5</td>
<td>33.61</td>
<td>12.11</td>
<td>2.07</td>
<td>47.79</td>
<td>18.13</td>
<td>18.39</td>
</tr>
<tr>
<td>0.7</td>
<td>39.64</td>
<td>13.56</td>
<td>3.34</td>
<td>56.54</td>
<td>22.28</td>
<td>23.49</td>
</tr>
<tr>
<td>0.9</td>
<td>48.25</td>
<td>15.32</td>
<td>4.13</td>
<td>67.65</td>
<td>28.19</td>
<td>29.16</td>
</tr>
</tbody>
</table>

Table (2) explains the DBPs Trihalomethanes (Chloroform, Bromodichloromethane, Chlorodibromomethane) and Haloacetic acids as (Dichloroacetic acids, Trichloroacetic acids). The concentrations of CHCl₃, BDCM, CDBM, THMs, DCAA, TCAA were 19.32, 6.87, ND, 26.19, 6.18 and 12.01 µg/L in the treated water with 0.08 ppm chlorine dioxide dose while it is increased with increasing the chlorine dose, reached to 48.25, 15.32, 4.13, 67.65, 28.19 and 29.16 µg/L for CHCl₃, BDCM, CDBM, THMs, DCAA, TCAA, HAAs respectively with 0.9 as ppm chlorine dioxide dose. These results indicating the positive significant relation between disinfectant doses and DBPs species, these finding agreed with the results stated by Bond and co-authors (Bond et al., 2014). The correlation coefficient was equal 0.989 for THMs, the same relation found by Xin Gu and his research team. Figure (1) explain the relation between DBPs and chlorine dioxide dose (Gu et al., 2020).
Figure 1. The relation between chlorine dioxide doses and DBPs concentrations

Figure (1) which shows the Relation between Chlorine dioxide doses and total trihalomethanes as organic disinfection byproduct (DBPs). Also, it shows the effect of chlorine dioxide and relation with organic disinfection by products, Trihalomethanes as total and both of dichloroacetic acids, Trichloroacetic acids as Haloacetic acids. The results confirming that, initial concentration of Trihalomethanes as total 26.19 ppb at first doses of chlorine dioxide 0.08 ppm and reached to 67.65 ppb when the doses of chlorine dioxide 0.9 ppm, which cited availability of chlorine dioxide at surface water and produce low organic disinfection byproducts.

The initial concentration of dichloroacetic acid 6.18 ppb when the of chlorine dioxide dose 0.08 ppm, while the last concentration of dichloroacetic acid 28.19 ppb when the dose of chlorine dioxide 0.9 ppm, the results are passed corresponding (WHO) that cited availability of chlorine dioxide as safe disinfectant with surface water. Initial concentration of trichloroacetic acid 12.01 ppb when the of chlorine dioxide dose 0.08 ppm, while the last concentration of Trichloroacetic acid 29.16 ppb when the dose of chlorine dioxide 0.9 ppm, the results are passed corresponding (WHO) that cited availability of chlorine dioxide as safe disinfectant with surface water. All samples have the same contact time between a variable Chlorine dioxide dose and treated water, that time about two hours and preserved by thiosulphate to analyze corresponding DPBs methods.
Worthy mentioning all samples have the same Total Organic Carbon (TOC) before treated by Chlorine doses, after treated by Chlorine (TOC) differ slightly. Which is worth mentioning the 1st and 2nd of chlorine concentration did not produce any concentrations of Bromate. Bromate in experiment not over range and criteria of water and wastewater Egyptian criteria 2007 low.

**Chlorine experiment**

![Figure 2. The Relation between Chlorine doses and DBPs concentrations](image)

With a 1 ppm chlorine dose, the concentrations of CHCl₃, BDCM, CDBM, THMs, DCAA and TCAA in the treated water were 38.42, 12.78, 3.72, 54.92, 12.31, and 23.19 g/L, respectively, while it increased with increasing the chlorine dose, reaching 135.05, 31.95, 6.53, 173.53, 76.13, and 87.11 for CHCl₃. These findings corroborated Bond and co-authors' findings, suggesting a positive significant relationship between chlorine dosages and DBP species (Bond et al., 2014).

**Determination of the optimum dose of Chlorine dioxide**

As discussed in part 2.4.4, the optimum dose of the disinfectant was determined, the results showed at Table (3).
Table 3
Chlorine and Chlorine dioxide efficiency for pathogens inactivation

<table>
<thead>
<tr>
<th></th>
<th>Chlorine Dose</th>
<th>1 mg/L</th>
<th>2 mg/L</th>
<th>3 mg/L</th>
<th>4 mg/L</th>
<th>5 mg/L</th>
<th>6 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine used as a disinfectant</td>
<td>Heterotrophic bacteria (HPC), Total Coliform bacteria (TC), Fecal Coliform (FC), Streptococcus Faecalis (SF)</td>
<td>750</td>
<td>160</td>
<td>20</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chlorine Dioxide Dose</td>
<td>0.08 mg/L</td>
<td>30</td>
<td>10</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.1 mg/L</td>
<td>1&gt;</td>
<td>1&gt;</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.3 mg/L</td>
<td>1&gt;</td>
<td>1&gt;</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.5 mg/L</td>
<td>1&gt;</td>
<td>1&gt;</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.7 mg/L</td>
<td>1&gt;</td>
<td>1&gt;</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.9 mg/L</td>
<td>1&gt;</td>
<td>1&gt;</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

The accepted limits of bacterial indicators as surface water pathogens is:
- Heterotrophic bacteria (HPC) general bacteria are (50 CFU/ml).
- Total Coliform bacteria (-ve) gram (TC) is (1 CFU/100ml).
- Fecal Coliform (FC) (-ve) gram is (1 CFU/100ml).
- Streptococcus Faecalis (SF) (+ve) gram is (1 CFU/100ml).

From Table (3) it is clear that, the optimum dose of chlorine dioxide is 0.3 mg/L. While, for chlorine the optimum dose is 4 mg/ L for pathogens inactivation.

Table 4
DBPs with different doses from chlorine and chlorine dioxide

<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>CHCl₃ (300 ug/l)</th>
<th>BDCM (60 ug/l)</th>
<th>CDBM (100 ug/l)</th>
<th>THMs (100 ug/l)</th>
<th>DCAA (50 ug/l)</th>
<th>TCAA (100ug /l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine Dioxide 0.3 mg/L</td>
<td>28.15</td>
<td>9.19</td>
<td>1.77</td>
<td>39.11</td>
<td>12.97</td>
<td>16.89</td>
</tr>
<tr>
<td>Chlorine 4 mg/L</td>
<td>75.33</td>
<td>18.42</td>
<td>4.08</td>
<td>97.83</td>
<td>36.71</td>
<td>46.11</td>
</tr>
<tr>
<td>ClO₂ DBPs / Chlorine</td>
<td>37.368</td>
<td>49.891</td>
<td>43.382</td>
<td>39.977</td>
<td>35.330</td>
<td>36.629</td>
</tr>
<tr>
<td>DBPs %</td>
<td>91</td>
<td>42</td>
<td>35</td>
<td>51</td>
<td>97</td>
<td>8</td>
</tr>
</tbody>
</table>
From table (4) and figure (3) it is confirmed that, the concentration of chlorine and chlorine dioxide is one of the major parameters in hazardous organic material formation. Also, the DBPs resulted from using chlorine dioxide is (37.4%, 49.9%, 43.4%, 40.0%, 35.3%, 36.6%) of CHCl3, BDCM, CDBM, THMs, DCAA, TCAA respectively comparing with the resulted by using chlorine.

**Conclusion and Recommendation**

In this study, levels of THMs and HAAs has been analyzed after simulated coagulation and disinfection process with dissimilar the disinfectant dosage (0.08, 0.1, 0.3, 0.5, 0.7 and 0.9 mg/L of chlorine dioxide) or (1, 2, 3, 4, 5 and 6 ppm from chlorine). According to our study, we can conclude that, The THMs and HAAs levels increased with the increasing the disinfectant dosage. Chloroform was the main component of four kinds of THMs, while Bromoform not detected in all samples. By comparing the produced DBPs levels in both cases at the optimum dose of the disinfectant, the chlorine dioxide found to produce minimum DBPs levels. Due to the carcinogenicity of DBPs to human, the dosage of chlorine must be controlled strictly in drinking water treatment plants. Thus, this study recommended chlorine dioxide as alternative disinfectant for drinking water to control the THMs and HAAs formation.
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