How can drinking water treatments influence chlorine dioxide consumption and by-product formation in final disinfection?
Sabrina Sorlini, Michela Biasibetti, Francesca Gialdini and Maria Cristina Collivignarelli

ABSTRACT
In this study water samples of different origins (subalpine lake, artificial lake and river) were treated by pre-oxidation, coagulation/flocculation, adsorption on granular activated carbon and disinfection. Different laboratory-scale tests were carried out to evaluate the treatment impact on ClO2 consumption in disinfection and on the formation of disinfection by-products (trihalomethanes, adsorbable organic halogen, chlorite and chlorate). The results showed that coagulation/flocculation and activated carbon adsorption have the most significant impact on reducing disinfectant consumption. Pre-oxidation of artificial lake water with KMnO4 and NaClO determines the highest ClO2 consumption. Regardless of the water source, the amount of chlorite produced after disinfection with ClO2 is 40–60% lower using NaClO as the pre-oxidant rather than KMnO4 or ClO2. Otherwise, NaClO leads to a high formation of adsorbable organic halogens and trihalomethanes in artificial lake water (up to 60 μg/L and 20 μg/L respectively), while in the case of ClO2 oxidation, trihalomethane formation is 98% less compared to NaClO. Further, adding ferrous ion in coagulation/flocculation improves the removal of chlorite produced during pre-oxidation, with a 90% removal, mainly due to the reduction of chlorite to chloride. Finally, activated carbon adsorption after pre-oxidation and coagulation/flocculation removes adsorbable organic halogens and trihalomethanes respectively by 50–60% and 30–98%, and completes the chlorite and chlorate removal.

Key words | activated carbon, chlorine dioxide, coagulation/flocculation, disinfection by-products, drinking water, pre-oxidation

INTRODUCTION
Chlorine is the most common disinfectant used in drinking water treatment. However, during the disinfection treatment, chlorine can react with naturally occurring organic material to produce several by-products, such as total trihalomethanes (TTHMs). Chlorine dioxide (ClO2) is considered one alternative to chlorine for TTHM control since it implies a lower TTHM formation (Sorlini & Collivignarelli 2005a; Zhao et al. 2006; Hua & Reckhow 2007; Badawy et al. 2012; Yang et al. 2013a, 2013b). However, ClO2 can generate, through secondary reactions, both organic and inorganic disinfection by-products (DBPs), in particular chlorite (ClO2) and chlorate (ClO33), which may lead to hemolytic anemia in humans at low levels of exposure, and to oxidative stress resulting in changes in the red blood human cells at higher levels of exposure (Korn et al. 2002; WHO 2011). According to the Italian regulations, the TTHM and the ClO2 maximum allowable concentrations are 30 μg/L and 700 μg/L, respectively (Legislative decree 31/2001), while for ClO3 no limit is fixed; however, the World Health Organization (WHO) suggests a guideline value both for ClO2 and ClO3 of 700 μg/L (WHO 2011).
Several studies investigated different processes for ClO₂ removal, such as the addition of reduced-sulphur compounds like sulphur dioxide and sodium sulphite (Gonce & Voudrias 1994), the addition of ferrous chloride and ferrous sulphate (Henderson et al. 2001; Katz & Narkis 2001; Sorlini & Collivignarelli 2004b; Shao-xiu et al. 2012) or the use of powdered (PAC) or granular (GAC) activated carbon (Gonce & Voudrias 1994; Sorlini & Collivignarelli 2005c).

While the control of ClO₂ and ClO₃⁻ produced in pre-oxidation can be ensured by applying these processes, the control of the DBP formation in the final disinfection stage is more difficult since no additional treatments are generally applied after final disinfection. For this reason, it is necessary to optimize the type and operation of the processes applied in the treatment plant in order to improve the water quality before final disinfection. This allows the amount of disinfectant required to be reduced, and, consequently, to minimize the DBP formation in the final disinfection step and in the distribution system. The disinfectant dose required for final disinfection depends on both the chemical (organic and inorganic compounds) and microbiological pollutants present in the water, and on the disinfectant residual, which should be guaranteed in the distribution system. Increased dissolved organics represent a larger quantity of DBP precursors when disinfectant is applied (USEPA 1999). Therefore, enhancing water treatment performance before final disinfection represents an interesting option for minimizing DBP formation. Coagulation, especially enhanced or optimized coagulation, is considered an interesting treatment option to remove DBP precursors, such as natural organic matter (NOM) (Matilainen et al. 2010); for example, coagulation/flocculation can remove 29–70% of dissolved organic carbon (DOC) (Matilainen et al. 2002; Kaleta & Elektorowicz 2009). Some researchers report that conventional coagulation followed by chemical oxidation-biodegradation processes is a reasonable alternative to enhance coagulation for the removal of total organic carbon (TOC) and dissolved organic halogenide (DOX) precursors (Speitel et al. 2000).

GAC is effective in adsorbing a wide range of organic compounds, removing taste and odours, controlling the formation of chlorinated pollutants, and reducing bromate; therefore, it has been widely used in drinking water treatment (Zhang et al. 2011). In particular, GAC is effective in NOM removal (Swietlik et al. 2002; Cheng et al. 2005; Velten et al. 2011); some researchers report a NOM adsorption yield on microporous carbons close to 70% (Newcombe et al. 2002), a trihalomethane formation potential (THMFP) removal close to 85% (Iriarte-Velasco et al. 2008) and an AOC (assimilable organic carbon) and TOC removal, respectively, close to 66 and 30% (Matilainen et al. 2010). Other studies show that GAC adsorption can remove 70–90% of organic carbon (Hu et al. 1999; Polanska et al. 2005; Zhao et al. 2009) and NOM (Uyak et al. 2007). BAC (biological activated carbon) filtration can remove biodegradable organic matter, reduce chlorine dosage, remove bad-smelling substances or other pollutants (TOC, DOC, UV₂₅₄ absorbance and AOC) and improve drinking water taste (Huang et al. 2004; Zhang et al. 2011; Lou et al. 2012; Trang et al. 2014); moreover, the combined use of O₂-BAC can remove up to 90% of AOC (Hu et al. 1999; Chen et al. 2007; Lou et al. 2009 2012). Adsorption of dissolved organic matter (DOM) onto activated carbon depends on the pore size and surface chemistry of the adsorbent and on the initial concentration, type and molecular size distribution of the DOM (Newcombe 1999; Swietlik et al. 2002; Cheng et al. 2005; Schreiber et al. 2005).

Other researchers suggest biofiltration following intermediate ozonation as the most effective process for the removal of TTHM and haloacetic acid precursors. In addition, in order to reduce the DBP formation, ozone can be used to remove recalcitrant organic substances, to increase biodegradability and to reduce the taste of natural organic substances (Chaiket et al. 2002; Selcuk et al. 2005, 2007; Chen et al. 2007; Lou et al. 2012).

With regard to the DBP formation, water pre-oxidation can influence the TTHM formation during subsequent final disinfection with chlorine: while UV/Vis pre-oxidation does not have an effect on TTHMs formed by chlorine, pre-oxidation with O₃ often leads to a lower TTHM formation with an unaltered chlorine demand, and pre-oxidation with ClO₂ reduces both the TTHM formation and the chlorine demand (Gallard & von Gunten 2002). Some researchers reported an 85% reduction in TTHMs (i.e., from 30 to 5 µg L⁻¹) treating lake water samples with ClO₂ instead of chlorine (Volk et al. 2002).

Water pre-oxidation can also influence the formation of other DBPs, such as the adsorbable organic halogens
(AOX). For example, some researchers, by means of a pilot plant study, found that the ozonation treatment allows a 35% decrease of the AOX concentration (Vahala et al. 1999).

In this study the aim was to evaluate the impact of different treatments applied in a drinking water treatment plant on the ClO₂ consumption in final disinfection and on the formation of DBPs (TTHMs, AOX, ClO₂ and ClO₃⁻) after each treatment. Laboratory tests in batch conditions were carried out on different water sources (subalpine lake, artificial lake and river), treated by pre-oxidation, coagulation/flocculation, GAC adsorption and final disinfection.

**MATERIALS AND METHODS**

**Types of water tested**

The following types of water were studied:
1. subalpine lake water located in the north of Italy (hereinafter called water 1);
2. river water located in the north of Italy (hereinafter called water 2);
3. artificial lake water located in the south of Italy (hereinafter called water 3 and 4).

<table>
<thead>
<tr>
<th>Water</th>
<th>Subalpine lake water (water 1)</th>
<th>River water (water 2)</th>
<th>Artificial lake water (water 3)</th>
<th>Artificial lake water (water 4)</th>
<th>Dir. 98/83/EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7</td>
<td>7.7</td>
<td>8.0</td>
<td>7.3</td>
<td>6.5–9.5</td>
</tr>
<tr>
<td>UV₂₅⁴ absorbance (cm⁻¹)</td>
<td>0.011</td>
<td>0.057</td>
<td>0.099</td>
<td>0.086</td>
<td>–</td>
</tr>
<tr>
<td>TOC (mg L⁻¹)</td>
<td>1.7</td>
<td>2.4</td>
<td>5.9</td>
<td>4.7</td>
<td>Without abnormal variations</td>
</tr>
<tr>
<td>NH₄⁺ (mg L⁻¹)</td>
<td>&lt;D.L.</td>
<td>0.3</td>
<td>0.28</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.5</td>
<td>4.2</td>
<td>7.1</td>
<td>4.9</td>
<td>Without abnormal variations</td>
</tr>
<tr>
<td>Total coliforms (CFU 100 mL⁻¹)</td>
<td>25</td>
<td>11,000</td>
<td>200</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td><em>Escherichia coli</em> (CFU 100 mL⁻¹)</td>
<td>0</td>
<td>390</td>
<td>0</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>Colony count at 22 °C (CFU mL⁻¹)</td>
<td>290</td>
<td>760</td>
<td>1,700</td>
<td>350</td>
<td>Without abnormal variations</td>
</tr>
<tr>
<td>Colony count at 37 °C (CFU mL⁻¹)</td>
<td>30</td>
<td>1,200</td>
<td>300</td>
<td>65</td>
<td>Without abnormal variations</td>
</tr>
</tbody>
</table>

D.L. = detection limit.

The main physico-chemical and organoleptic characteristics of these waters are shown in Table 1. Water sampling and storage were performed following the national standard methods (APAT/IRSA-CNR 2003a). Water sampling was performed by collecting five samples for each type of water (Table 1 shows the average values), during the same season for 2 weeks, in order to have homogeneous samples. Water samples were stored in a fridge at 4 °C in dark conditions. All the analyses were performed in a certified laboratory.

Both artificial lake waters show higher TOC and turbidity values than the other types of water. Moreover, as expected, the river water shows high concentrations of microbiological contaminants.

**Experimental tests**

The experimental tests were performed at laboratory scale in batch conditions (Table 2). All the water samples were treated with chemical pre-oxidation followed by final disinfection. During the first series of tests, a subalpine lake water sample was treated by pre-oxidation alternately with KMnO₄, NaClO and ClO₂, and subsequently disinfected with ClO₂. During the second series of tests, a river water sample and two artificial lake water samples, which showed a poorer
quality than the subalpine lake water, were treated by pre-oxidation alternately with KMnO₄, NaClO and ClO₂ and subsequently treated by coagulation/flocculation with aluminum polychloride (PACl) and FeCl₂ and finally disinfected with ClO₂. During the third series of tests, two artificial lake water samples, that showed a higher TOC content than river water, were treated by pre-oxidation alternately with KMnO₄, NaClO and ClO₂ followed by coagulation/flocculation with PACl and FeCl₂, adsorption on GAC and final disinfection with ClO₂. Water samples were stored in a fridge at 4 °C in dark conditions. All tests were performed in a certified laboratory at a temperature ranging from 20 to 25 °C.

**Chemical pre-oxidation**

Pre-oxidation treatment was performed alternately with KMnO₄ (solution of 1.00 g KMnO₄ L⁻¹), NaClO (solution of 1.00 g NaClO L⁻¹) and ClO₂ (solution of 1.38 g ClO₂ L⁻¹), after determining the oxidant demand for a contact time of 1 hour which is generally applied in the pre-oxidation basin in drinking water treatment plants (DWTPs). It can be noticed that the oxidant with the highest demand is NaClO for each water sample (Table 2). Moreover, the maximum demand with all the tested oxidants is registered for river water, which shows the worst quality characteristics in terms of NH₄⁺, total coliforms, *Escherichia coli* and colony count at 37 °C (Table 1).

The pre-oxidation tests were performed using 2-L water samples in glass jars in dark conditions. Continuous slow mixing at 30 rpm with a magnetic stirring bar ensured a good contact between the reagent and the solution.

**Coagulation/flocculation**

The coagulation/flocculation process was performed by adding to the water sample an aqueous solution of PACl containing 18% Al₂O₃. The optimal dosage of PACl (5.7 mg L⁻¹) was determined by means of the Jar Test, performed according to ASTM D2035-08 (2008). The laboratory-scale coagulation/flocculation tests were performed using 2-L samples.
water samples in beakers, following the procedure outlined in Table 3. Other tests were performed on samples pre-oxidized with ClO₂ and treated with PACl, to which ferrous ions were added in order to assess the impact of the Fe²⁺ on the ClO₂ originating from the pre-oxidation. In this case, an aqueous solution of FeCl₂ at 40% w/w (density = 9.27 g L⁻¹) was employed. Ferrous ion dosage was based on the assumption that 3.31 mg of Fe²⁺ is required to deplete 1 mg of ClO₂ (stoichiometric demand), following the reaction: 4Fe²⁺ + ClO₂⁻ + 10H₂O → 4Fe(OH)₃(s) + 1Cl⁻ + 8H⁺. During this process, ferrous ions (Fe²⁺) are oxidized to Fe³⁺ in the form of insoluble Fe(OH)₃, which can easily be removed by means of sedimentation and/or filtration. During a coagulation/flocculation process a lower reagent dose can be applied due to the coagulation/flocculation effect of ferrous ions (Katz & Narkis 2000; Sorlini & Collivignarelli 2005).

**Adsorption with granular activated carbon**

After sedimentation, during the coagulation/flocculation tests, the supernatant of each sample was filtered on GAC. The filtration was performed using an up-flow GAC column (Figure 1): a glass column (height = 50 cm, diameter = 3.5 cm) was filled with mesporous mineral coal-based GAC (NORIT GAC 1240) with a particle size of D₅₀ = 1.12 mm. The flow rate was set to 30 mL min⁻¹ and the EBCT was 10 minutes. The carbon in the GAC column was replaced with virgin carbon after treating each water sample.

**Disinfection**

A dosage of 1 mg ClO₂ L⁻¹ (initial concentration) was added to 1-L dark glass flasks containing the water samples collected at the outlet of the GAC filter. After stirring manually for 1 minute, each 1-L sample was divided into ten 100 mL sealed dark glass jars. The glass jars had different water-disinfectant contact times (0.5, 1, 2, 4, 7, 22, 27, 44, 54 and 72 hours after the addition of ClO₂) and were then opened for the analytical determinations. The different contact times were selected in a different way for each test.

**PARAMETERS AND ANALYTICAL METHODS**

The following parameters were analysed: pH, TOC, DOC, UV₂₅₄ absorbance, deep-ultraviolet absorbance at 254 nm wavelength (DUV₂₅₄ absorbance), turbidity, microbiological contaminants (colony count at 22 °C and 37 °C, total coliforms), residual oxidant, DBPs (ClO₂⁻, ClO₃⁻, TTHMs and AOX).

The following parameters were monitored at the end of the final disinfection, at each contact time: residual ClO₂, ClO₂⁻ and ClO₃⁻.
The instruments and the analytical methods employed are reported in Table 4.

### RESULTS AND DISCUSSION

#### Impact of treatments on quality parameters

With regard to the TOC removal evaluated for artificial lake water (water 4), pre-oxidation is quite ineffective regardless of the type of reagent employed (Figure 2) and also the sequence of treatments composed of pre-oxidation followed by coagulation/flocculation shows low TOC removal yields (25–35%). Moreover, the addition of ferrous ion during coagulation/flocculation after pre-oxidation with ClO₂ does not increase the TOC removal. A significant TOC removal is obtained only by adsorption on activated carbon, which increases the TOC removal yield by up to 70% (40% on average) for the complete treatment sequence. In agreement with this result, other researchers found a 65% TOC removal yield using a bituminous coal-based activated carbon, with a 13 min EBCT in a full-scale water treatment plant (Gibert et al. 2013).

DOC concentrations are not reported because they are very similar to the TOC values in all tests (on average the DOC ranges from 83 to 100% of the TOC). Moreover, the analysis of the effect of the different treatments on UV₂₅₄ and DUV₂₅₄ absorbance shows results comparable with TOC and DOC.

With regard to turbidity, which was measured 1 hour after the oxidation, for artificial lake water (water 4) (Figure 3) pre-oxidation is quite effective with removal.
yields ranging from 30% for NaClO to 50% for ClO2; this may be due to the precipitation of some compounds 1 hour after the oxidation, by means of incorporation of suspended colloids in the precipitates. Coagulation/flocculation increases the turbidity removal with an additional removal yield of 30% and 50–60% respectively after pre-oxidation with KMnO4 and ClO2/NaClO. A very low removal yield is obtained when ferrous ion is added during coagulation/flocculation with PACl after pre-oxidation with ClO2. GAC adsorption contributes to turbidity removal by about 50–70% and final disinfection by about 10–40%. The highest turbidity removal yields are obtained with a treatment sequence consisting of pre-oxidation with NaClO, coagulation/flocculation and adsorption on GAC, with a total removal yield of about 90%.

Figure 4 shows the effect of the pre-oxidation treatment of different water sources on the results for colony count at 37 °C, colony count at 22 °C and total coliforms. The highest concentrations of colony count at 37 °C and total coliforms in the raw water are registered for the river water (water 2), while the highest concentration of colony count at 22 °C is registered for the artificial lake water (water 3). Predictably, regardless of the water source, (Kim et al. 2002), the removal of microbiological contaminants during pre-oxidation is higher using ClO2 and NaClO than using KMnO4. In particular, the best results are obtained with ClO2 applied to river water, which enables a reduction of the colony count at 37 °C by 98–100%, the colony count at 22 °C by 92–100% and the total coliforms by 100%. Moreover, chemical pre-oxidation tests performed on river water (water 2) (Figure 5) confirm the effectiveness of chlorine, both as NaClO and as ClO2, in reducing colony counts at 37 °C (by 94% and 96% respectively) compared to the low reduction rates reached with KMnO4 (27%). Reduction of colony counts at 37 °C is significantly improved by coagulation/flocculation after pre-oxidation with KMnO4, with an additional reduction of about 70% due to coagulation (Figure 5). Conversely, the coagulation/flocculation process contributes to the reduction of colony counts by 4% and 6% using respectively NaClO and ClO2 in pre-oxidation, compared to the pre-oxidation process alone. This is due to the fact that KMnO4 has a low oxidation potential implying a negligible microbial inactivation, which is almost completely achieved by the subsequent coagulation/flocculation; in contrast, NaClO and ClO2 are efficient oxidants that completely ensure microbial removal, thus the subsequent coagulation/flocculation does not further improve the result.

In agreement with these results, Table 5 shows that for artificial lake water (water 3) ClO2 allows the best removal yield (94%) to be obtained, and the coagulation/flocculation contributes to a further removal of 5% when ClO2 is used in pre-oxidation; moreover, the ferrous ion addition slightly decreases the removal efficiency compared to the coagulation with PACl alone. As expected, activated carbon adsorption, applied to artificial lake water (water 3), slightly reduces the concentration of microbiological parameters in treated water (Table 5).

Impact of treatments on disinfection by-products

The results represented in Figures 6 and 7 show that the highest concentrations of AOX and TTHMs are observed when artificial lake water (water 4) is pre-oxidized with NaClO, due to the high reactivity of this oxidant with DOM (Vahala et al. 1999; Sorlini & Collivignarelli 2005a; Zhao et al. 2006; Hua & Reckhow 2007; Badawy et al. 2012) to form these compounds. In particular, the results show that for the case of ClO2 oxidation, TTHMs are reduced by 98% compared to NaClO, as agreed by other researchers who have reported an 85% reduction in TTHM formation (i.e., from 30 to 5 μg L⁻¹) when treating lake water samples with ClO2 instead of NaClO (Volk et al. 2002). The application of KMnO4 resulted in low TTHM formation compared to the other oxidants. Coagulation/flocculation has a negligible influence on the removal of AOX and TTHMs, except in the case when NaClO is used.
Figure 4  | Effect of the pre-oxidation of different water sources on the microbiological contaminant concentration: (a) colony count at 37°C; (b) colony count at 22°C; (c) total coliforms.
in pre-oxidation, as about 20% less AOX can be found in the water after coagulation. The adsorption with activated carbon contributes to the removal by 50–60% (depending on the pre-oxidant used) for AOX, and by 30–98% (depending on the pre-oxidant used) for TTHMs. Moreover, after the GAC treatment, as expected, disinfection does not affect the AOX and TTHM concentrations. Furthermore, the results show that AOX and TTHM concentrations slightly increase after pre-oxidation with KMnO4 or ClO2 followed by coagulation/flocculation and disinfection compared to pre-oxidation alone (Figures 6 and 7).

Figure 8 shows the ClO2 formation over time for different water sources pre-oxidized alternately with KMnO4, NaClO and ClO2, and subsequently treated with ClO2 in order to simulate the influence of final disinfection. The results show that for water 1 the highest ClO2 formation rate is in the first 200–800 minutes after the ClO2 addition, while for water 2, 3 and 4 the ClO2 formation rate is high in the first 60 minutes after the ClO2 addition; during this time, the highest ClO2 formation in disinfection is obtained in the case of pre-oxidation with ClO2, which is to be expected as additional ClO2 is generated during the pre-oxidation process (Sorlini et al. 2014). At 60 minutes after the ClO2 addition, pre-oxidation using both KMnO4 and NaClO followed by disinfection with ClO2 determines a slower but still significant ClO2 formation in each water sample; this is due to the reactions of ClO2 with organic and inorganic pollutants which lead to the conversion of about 50–70% of the chlorine consumed to ClO2 (Korn et al. 2002). Overall, the ClO2 formation is 40–60% lower after the addition of ClO2 in the water samples oxidized with NaClO instead of KMnO4 or ClO2. Comparing the different water sources, the ClO2 formation in subalpine lake water (water 1) and in artificial lake water (water 4) is always below the current regulatory limit of 0.7 mg L−1.

### Table 5

<table>
<thead>
<tr>
<th>Treatment</th>
<th>KMnO4</th>
<th>NaClO</th>
<th>ClO2</th>
<th>ClO2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-oxidation</td>
<td>114</td>
<td>92</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Pre-oxidation + coagulation/flocculation</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Pre-oxidation + coagulation/flocculation + GAC adsorption</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pre-oxidation + coagulation/flocculation + GAC adsorption + disinfection</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

ClO2* = addition of ferrous ion in coagulation/flocculation after pre-oxidation with ClO2.
while in river water (water 2) and in artificial lake water (water 3) it exceeds the limit after 60 minute contact time. Moreover, more ClO₂ is formed when KMnO₄ is applied as pre-oxidant in the case of subalpine lake water (water 1) and artificial lake water (water 3); this result may be due to the fact that KMnO₄ is more reactive with ClO₂ precursors, such as NOM, compared to the other oxidants.

Figure 9 shows the effect of different treatments on ClO₂ and ClO₃⁻ concentration in artificial lake water (water 3). The results show that coagulation/flocculation with PACl does not influence ClO₂ formation, whereas the addition of ferrous ion after PACl during coagulation/flocculation has a markedly visible influence on the ClO₂ depletion, with a removal yield close to 90%. In fact, ferrous ions efficiently decrease chlorite ions concentration by reducing them to chlorides. In agreement with this result, several researchers showed that ferrous ion addition to raw waters pre-disinfected with ClO₂ completely removes chlorite ions by reducing them to chloride ions (Griese et al. 1991, 1992; Iatrou & Knocke 1992; Katz & Narkis 2001; Matilainen et al. 2006). The addition of GAC filtration after pre-oxidation, coagulation/flocculation and ferrous ion addition leads to a complete removal of the residual ClO₂. However, final disinfection with 1 mg ClO₂ L⁻¹ leads to the reformation of ClO₂ up to a concentration of 0.03 mg L⁻¹ after one hour contact time.

Regarding ClO₃⁻, Figure 9 shows that coagulation/flocculation, both with and without addition of ferrous salts, does not influence ClO₃⁻ formation. This is confirmed by other researchers who reported an efficient reduction of residual ClO₂ and ClO₂ to chloride ions by ferrous ions, while the concentration of ClO₃⁻ was almost unaffected (Griese et al. 1991, 1992; Iatrou & Knocke 1992; Katz & Narkis 2001; Matilainen et al. 2006). Conversely, the results of this study show that GAC filtration can completely remove ClO₃⁻. After final disinfection, further ClO₃⁻ is generated (0.02 mg L⁻¹), as a consequence of the ClO₂ addition.
Impact of treatments on chlorine dioxide consumption in final disinfection

The ClO₂ consumption was calculated as the difference between the ClO₂ dosed initial concentration and the residual ClO₂ concentration after a certain contact time. The analysis of the ClO₂ consumption in final disinfection in artificial lake water (water 4) samples shows that pre-oxidation with KMnO₄ and NaClO determines the highest ClO₂ consumption rates (Figure 10). Moreover, in the case of pre-oxidation with KMnO₄, with respect to NaClO, consumption occurs more rapidly during the first 60 minutes.

The analysis of the ClO₂ demand after 60 minutes, evaluated for artificial lake water (water 4) (Figure 11), shows that after pre-oxidation with KMnO₄ water consumes the maximum ClO₂ dosage, whereas for pre-oxidation with NaClO and ClO₂ about 60% and 50% of the disinfectant dose, respectively, is consumed.

The addition of the coagulation/flocculation process significantly reduces the ClO₂ consumption, by 75% to 95%, respectively, after pre-oxidation with KMnO₄ and ClO₂. This result agrees with other studies that proved an effective reduction of water permanganate oxidability (70–80%), DOC (25–67%), UV₂₅₄ absorbance (44–77%), THMFP (25–66%) and turbidity (97%) by means of coagulation (Kaleta & Elektorowicz 2009; Matilainen et al. 2010).

Adsorption on GAC further reduces the ClO₂ consumption by about 80–85% compared to the consumption observed for water treated only with pre-oxidation (Figure 11). This is due to the effective adsorption on GAC of NOM (Matilainen et al. 2006) and other THM precursors (Iriarte-Velasco et al. 2008). In particular, after treatment with GAC the highest ClO₂ demand reduction is observed in the case of pre-oxidation with KMnO₄, compared to the ClO₂ demand for water treated with pre-oxidation followed by coagulation/flocculation. GAC is successfully employed in reducing the oxidant consumption after pre-oxidation with KMnO₄, since this oxidant is less effective in the removal of organic substances compared to other oxidants tested (Chen & Yeh 2005).

CONCLUSIONS

The aim of this study was to evaluate the impact of different treatments on the ClO₂ consumption and on the formation of DBPs (THMs, AOX, ClO₂/C₀ and ClO₃/C₀) in the final disinfection. Moreover, water quality parameters were evaluated, such as pH, ultraviolet absorbance at 254 nm wavelength, turbidity, colour, total organic carbon and microbiological parameters. The experimental tests were performed at laboratory-scale on four different water sources applying chemical pre-oxidation, coagulation/flocculation, adsorption on granular activated carbon and final disinfection.

The results show that the stability of ClO₂ added in final disinfection depends on the type of oxidant used during pre-oxidation and on the type of treatments applied before the final disinfection. The effectiveness of coagulation/flocculation and GAC adsorption in reducing the ClO₂ consumption in final disinfection is confirmed due to the removal and adsorption of the organic matter. Further, the addition of ferrous ion in coagulation/flocculation leads to the reduction of ClO₂ concentration, due to the reduction of chlorite to chloride.

Finally, the results confirm that GAC treatment is also effective in adsorbing other disinfection by-products, such
as AOX and THMs. Comparing the different water sources, the ClO₂ formation in subalpine lake waters is always below the current regulatory limit of 0.7 mg L⁻¹, while in river water and in artificial lake water (water 3) it exceeds the limit after 60 minute contact time.

Therefore, enhancing the treatment processes prior to final disinfection increases the efficiency in contaminant and DBP precursor removal and, consequently, decreases the disinfectant consumption.

ACKNOWLEDGEMENTS

The authors wish to thank the technicians at Caffaro S.p.A., especially Dr Mario Belluati for research collaboration and the water treatment plant operators who provided water samples. We also wish to thank the engineer Andrea Cotelli for performing the tests as part of his 3-year thesis. Sabrina Sorlini coordinated the experimental work, the discussion of results and the drafting of the paper, Francesca Gialdini carried out the experimental test, the data processing and the drafting of the paper; Michela Biasibetti and Maria Cristina Collivignarelli contributed to the drafting of the paper.

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First received 22 June 2015; accepted in revised form 7 September 2015. Available online 21 September 2015.