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Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation

Sabrina Sorlini*, Francesca Gialdini, Michela Biasibetti, Carlo Collivignarelli

University of Brescia, Department of Civil Engineering, Architecture, Land, Environment and Mathematics, via Branze 43, 25123 Brescia, Italy

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ABSTRACT

Disinfection is the last treatment stage of a Drinking Water Treatment Plant (DWTP) and is carried out to maintain a residual concentration of disinfectant in the water distribution system. Chlorine dioxide (ClO_2) is a widely used chemical employed for this purpose. The aim of this work was to evaluate the influence of several treatments on chlorine dioxide consumption and on chlorite and chlorate formation in the final oxidation/disinfection stage. A number of tests was performed at laboratory scale employing water samples collected from the DWTP of Cremona (Italy). The following processes were studied: oxidation with potassium permanganate, chlorine dioxide and sodium hypochlorite, coagulation/flocculation with ferric chloride and aluminum sulfate, filtration and adsorption onto activated carbon. The results showed that the chlorine dioxide demand is high if sodium hypochlorite or potassium permanganate are employed in pre-oxidation. On the other hand, chlorine dioxide leads to the highest production of chlorite and chlorate. The coagulation/flocculation process after pre-oxidation shows that chlorine dioxide demand decreases if potassium permanganate is employed as an oxidant, both with ferric chloride and aluminum sulfate. Therefore, the combination of these processes leads to a lower production of chlorite and chlorate. Aluminum sulfate is preferable in terms of the chlorine dioxide demand reduction and minimization of the chlorite and chlorate formation. Activated carbon is the most effective solution as it reduced the chlorine dioxide consumption by about 50% and the DBP formation by about 20–40%.

1. Introduction

Drinking Water Treatment Plants (DWTPs) are generally composed of different processes to remove specific pollutants. The oxidation/disinfection process requires the use of chemicals that allow the removal of various contaminants but, at the same time, can determine the formation of unwanted Disinfection by-Products (DBPs), such as trihalomethanes (THMs), chlorite (ClO_2^-) and chlorate (ClO_3^-). Chlorine dioxide (ClO_2) is a widely employed oxidant in DWTPs (Richardson et al., 2000; Korn et al., 2002; Schmidt, 2004). When chlorine dioxide is employed, it can react with both organic and inorganic compounds to form chlorite

* *Corresponding author*. Tel.: +39 (0)30 371 1299; fax: +39 (0)30 371 1312.
E-mail address: sabrina.sorlini@unibs.it (S. Sorlini).

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Nomenclature

Abbreviations

BAC	Biological Activated Carbon
BET	Brunauer–Emmett–Teller
ClO_2-D	Chlorine dioxide-Demand
COD	Chemical Oxygen Demand
DBPs	Disinfection by-Products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DWTP	Drinking Water Treatment Plant
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
VSS	Volatile Suspended Solids
SUVA	Specific Ultraviolet Absorbance
THMs	Trihalomethanes
TOC	Total Organic Carbon

and chlorate, which can have negative effects on human health. The primary and most consistent finding arising from exposure to chlorite and chlorate is oxidative stress resulting in changes in the red blood cells (WHO, 2011). The Italian regulation includes a maximum allowable concentration of 700 μg/L for chlorite (Legislative Decree 31/2001) but does not fix any limit for chlorate, while the World Health Organization (WHO) suggests a guideline value for chlorite and chlorate of 700 μg/L separately (WHO, 2011). The chlorite and chlorate formation is strongly dependent on the chlorine dioxide consumption: about 68% and 9% of the chlorine dioxide consumed becomes respectively chlorite and chlorate (Korn et al., 2002; Collivignarelli and Sorlini, 2004). In order to control the production of these compounds it is possible to adopt specific removal techniques (Katz and Narkis, 2001; Sorlini and Collivignarelli, 2005a, 2005b), or to apply solutions aimed at minimizing the reagent doses required during oxidation/disinfection. When chlorine dioxide is applied in final disinfection, before water distribution, the required dose can be minimized by enhancing the contaminants removal in each single step of the DWTP. Few specific data are available in the literature concerning the influence of drinking water treatments on the chlorine dioxide demand (ClO_2-D), so the influence on the THM precursor removal and the chlorine demand is addressed below. An effective method for reducing organic THM precursors is represented by pre-ozonation/enhanced coagulation/activated carbon adsorption (Teksoy et al., 2008). Water pre-oxidation can influence the chlorine demand and the THM formation during subsequent final disinfection with chlorine: while UV/Vis' pre-oxidation does not have an effect on THMs formed by chlorine dioxide, pre-oxidation with ozone leads to a lower THM formation with an unaltered chlorine demand and pre-oxidation with chlorine dioxide reduces both the THM formation and the chlorine demand (Gallard and von Gunten, 2002). A study found that the percentages of removal for DBP organic precursors are 7% for pre-oxidation with potassium permanganate, 25% for coagulation with $FeCl_3$/air floatation, 6% for granular filtration, 45% for adsorption onto activated carbon and 7% for free chlorination (Chen et al., 2007). Ozone combined with Biological Activated Carbon (BAC) could decrease the Total Organic Carbon (TOC) by about 32%. Pre-oxidation with ozone or with potassium permanganate followed by coagulation/air floatation/filtration/free chlorination has a mean Chemical Oxygen Demand (COD) removal of 36% or 39% respectively (Chen et al., 2007). Other researchers found a removal both for TOC and Dissolved Organic Carbon (DOC) of about 20% with coagulation/sedimentation or, alternatively, with a rapid filtration process (Lou et al., 2012). Moreover, a study demonstrates that a 25–67% DOC removal is obtained with alum coagulation and a 29–70% natural organic matter (NOM) removal is obtained with ferric-based coagulation. When oxidation is performed after coagulation, about 5–32% enhancement on the removal of DOC occurs (Matilainen et al., 2010).

This study deals with a DWTP located in the City of Cremona (Italy), treating a groundwater contaminated by hydrogen sulfide, ammonia, iron, manganese and arsenic. The plant is composed of the following treatment stages: aeration, biofiltration, chemical oxidation with potassium permanganate, sand filtration and disinfection with chlorine dioxide. Treated water presents a high ClO_2-D (1,18 mgClO_2/L with a 4 min contact time) during final disinfection with a consequent high formation of chlorite (400–800 μg/L). Several experimental tests were performed at laboratory scale in order to evaluate the influence of different treatments (pre-oxidation, coagulation/flocculation, filtration and adsorption onto activated carbon) on the ClO_2-D and the chlorite/chlorate formation.

2. Material and methods

2.1. *Drinking water treatment plant (DWTP) of Cremona*

Two DWTPs, treating a maximum water flow of 38,9 ML/d (for 76,000 inhabitants) each one, were started up in 2006 (from January to June) to produce drinking water for the city of Cremona (North of Italy). Each plant treats groundwater containing the following main contaminants: methane, hydrogen sulfide, ammonia, iron, manganese and arsenic; their variation in the plant is shown in Table 1.

Each plant is composed of the following processes (Fig. 1): aeration for methane and hydrogen sulphide stripping and iron oxidation; aerated biofiltration for manganese, iron and arsenic oxidation and for ammonia nitrification; chemical oxidation with potassium permanganate ($KMnO_4$) for the oxidation of manganese and arsenic and the precipitation of arsenate with ferric chloride ($FeCl_3$), sand filtration for the removal of iron/manganese hydroxides/oxides and the insoluble arsenic-containing compounds and final disinfection with ClO_2.