

Understanding the Role of Chlorine Dioxide as Pre-oxidant and Disinfectant

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Introduction

Disinfection is always the first priority in water treatment works to remove or inactivate pathogenic microorganisms and to protect people from waterborne infectious diseases. Chlorine is the prevalent disinfectant due to its broad-spectrum germicidal potency, low cost and well-established practices [1]. However, the inevitable formation of Disinfection By-Products (DBPs) is considered as one of the primary threats to human well-being. DBPs, such as Trihalomethanes (THMs) and Haloacetic Acids (HAAs), have been regulated by the United States Environment Protection Agency (U.S.EPA) and other national agencies. Alternative disinfectants, such as chlorine dioxide (ClO_2), ozone, UV and chloramines are becoming popular [2,3]. Among these alternative disinfectants, ClO_2 can be also applied for color removal, algal removal, and taste and odor control [4-6]. Its biocidal efficiency is equal or superior to chlorine over a wide pH range [7-10]. Application of ClO_2 does not form appreciable levels of the chlorine-containing by-products such as Trihalomethanes (THMs) and Haloacetic Acids (HAAs) under typical water treatment conditions [11,12]. ClO_2 is often used as preoxidant combined with post-chlorination or -chloramination or used as disinfectant to inactivate microorganism and provide residual in the distribution system.

The major DBPs from application of ClO_2 are chlorite (ClO_2^-) and chlorate (ClO_3^-). Approximately 70% of applied ClO_2 forms chlorite, while about 10% forms chlorate [13]. Due to the health concerns over chlorite and chlorate, the maximum contaminant level (MCL) for chlorite in drinking water is regulated at 1.0 mg/L in the United States [14]. In the new Chinese Sanitary Standards for Drinking Water, it has been regulated at the threshold value of 0.7 mg/L for both chlorite and chlorate (Chinese Sanitary Standards for Drinking Water, 2006). Thus, the doses of ClO_2 should be controlled to prevent the excessive formation of chlorite and chlorate.

Natural organic matter (NOM) is precursor of DBPs. Understanding the reactions between Natural Organic Matter (NOM) and ClO_2 can help clarify the role of ClO_2 during pretreatment. Previous study showed that chlorine dioxide destroys the aromatic and conjugated structures of Natural Organic Matter (NOM) and transforms large aromatic and long aliphatic chain organics to small and hydrophilic organics [15]. Oxidation of NOM with ClO_2 also generates organic by-products such as aldehydes and long chain carboxylic acids, which affected DBP formation during subsequent chlorination/chloramination [16]. It has been shown that ClO_2 oxidation prior to chlorination can reduce the formation of THM and Total Organic Halogen (TOX) [17]. A recent study has reported that ClO_2 preoxidation reduced THM, HAA, HAN and CH formation during subsequent chlorination [15]. ClO_2 pre-oxidation reduces the NDMA Formation Potential (FP) of natural water sources by 32-94% [18]. But enhanced NDMA formation after ClO_2 pre-oxidation has

also been reported in wastewater-impacted waters [19]. Thus, the current understanding of the reactions between NOM and ClO_2 is still quite limited and the role of ClO_2 for subsequent DBP formation still needs further exploration.

Emerging DBPs, such as Iodo-Trihalomethanes (I-THMs), have been reported to form when ClO_2 disinfects waters containing iodide and NOM. In iodide-containing waters, ClO_2 can react with iodide to form Hypoiodous Acid (HOI), which reacts with NOM to form iodinated DBPs, including I-THMs [20,21]. The formation is affected by many factors, including reaction time, pH, temperature, disinfectant doses, concentration, bromide ion concentrations and precursor properties. The generation of byproducts from the application of ClO_2 is still not clear. The reaction mechanisms behind is worth further exploration.

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