



Effects of metal ions on THMs and HAAs formation during tannic acid chlorination

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HIGHLIGHTS

- ▶ Metal ions inhibit THMs formation but enhance HAAs formation during TA chlorination.
- ▶ Metal ions change electron densities of active sites and $\cdot\text{OH}$ formation.
- ▶ Mechanisms were proposed regarding metal ions effects on THMs and HAAs formation.

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ABSTRACT

The present study was implemented to examine THM and HAA formation from the chlorination of tannic acid (TA) in the presence of common metal ions (e.g., Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+}) typically found in water sources. The inhibition efficiency of THM formation followed the order $\text{Mg}^{2+} < \text{Cu}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+} < \text{Al}^{3+}$ and the effect of HAA enhancement followed the order $\text{Mg}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+} < \text{Al}^{3+} < \text{Fe}^{2+}$. Similar to the case of single metal ion, the presence of multiple metal ions exerted analogous influence on the THM and HAA formation but without synergistic enhancement or inhibition. The investigation of nuclear magnetic resonance (NMR) and Electron Paramagnetic Resonance (EPR) spectroscopy indicated that the inhibitory effect of metal ions on THM formation was proportional to the changes in electron densities of active sites of tannic acid while the promoting effect of metal ions on HAA formation was more related to the generation of hydroxyl radical caused by the presence of metal ions. This study suggests that two different mechanisms could be involved in the effects of metal ions on THM and HAA formation from TA chlorination.

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1. Introduction

Genotoxic and carcinogenic halogenated disinfection by-products (DBPs) are usually formed during chlorination of waters containing various organic substances. Among these DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) have been regulated in the countries of European Union (THMs) and the USA (THMs, HAAs) [1]. To meet the regulations, many efforts have been made to minimize the formation. Recent efforts have been directed toward identifying and reducing the precursors for DBPs formation [2]. The identified precursors include humic acid (HA) [2], citric acid [3], algal cells [4], methyl ketones [5], organic nitrogen compounds [6], and hydroxybenzene [7].

Natural organic matters (NOMs), a mixture of organic compounds (e.g., HA, fulvic acid) is a major DBPs contributor with a complex macromolecule containing aromatic rings that are commonly substituted with methoxy, hydroxyl, carboxyl, and other functional groups [8]. Due to the lack of detailed information

regarding the functional groups or substructures that are present within NOM, many studies have focused on the reactions of chlorine with simple alternative model compounds. The model compounds are chosen to represent different functionalistic or substructures which occur within NOM, so as to reasonably represent normal reactions that might undergo in real waters. For example, polyhydroxylated benzenes, which occur commonly in plant material and its degradation products, stand for typical components of organic matter in natural water but are much simpler to investigate [9]. However, it should be noted that both the chemical composition (the amount and variety of functional groups) and steric structure (steric hindrance) are able to influence the pathway of specific reaction, especially for macromolecules [10,11]. Those model compounds with a chemical structure and steric structure similar to NOM, are therefore preferred alternatives. Tannins (commonly referred to as tannic acid) contain several *o*-dihydroxy and trihydroxy aromatic rings (polyhydroxy polyphenols) (Fig. 1), which is more similar to those of NOM in physical and chemical properties, molecular structures, functional groups, chelating properties, etc. [12]. Moreover, the polymeric molecular structure makes tannins superior to other model compounds in

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