Journal of Integrative Agriculture 2017, 16(12): 2914–2923

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REVIEW

pH effect on the formation of THM and HAA disinfection byproducts and potential control strategies for food processing

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Abstract

Chlorine-based sanitizers have seen wide spread use in food sanitation. The reaction of chlorine species with organic matter is a concern for two reasons. Available chlorine can be "used up" by organic compounds resulting in a lower amount of chlorine available for disinfection. Another concern is that some forms of chlorine can react with some organic compounds to form toxic halogenated disinfection byproducts (DBPs). Many studies have been conducted to evaluate the role of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) in the production of DBPs with a particular interest in the production of trihalomethanes (THMs) and haloacetic acids (HAAs). Since most of the chlorine reactions are pH dependent, pH is found to have a significant effect on the formation of chlorine DBPs. In many cases, the concentration of THMs decreases and HAAs increases as pH decreases. pH also plays an important role in the determination of the type and amount of DBPs formed, with lower, more acidic, pHs resulting in the formation of less chloroform. This review summarizes the information from the literature on the role of chlorine-based sanitizers as affected by pH in the formation of different types of DBPs. Alternative novel strategies to minimize the formation of DBPs are also discussed.

Keywords: sanitizer, chlorine, disinfection byproducts, pH, hypochlorite

1. Introduction

Chlorine has long been used for the treatment of drinking water in many countries around the world. Also, chlorine has been used to treat food preparation surfaces as well as the food itself (Wei *et al.* 1985). Chlorine-based sanitizers such as chlorine gas (Cl_2), sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$), and chlorine dioxide (ClO_2) have seen widespread use in food sanitation. For example, fruits, vegetables, and meats can be rinsed with chlorine to help control microbial load (Wei *et al*. 1985).

Chlorine, in its pure form, is a poisonous, yellow-green gas. Chlorine is an excellent sanitizer. However, its efficacy is highly dependent on the water quality, pH, presence of inorganic salts and natural organic matter, etc. Solutions of sodium hypochlorite (bleach) are commonly-used sanitizers in commercial and domestic settings. Typically, bleach solutions of 3–6% NaOCl are used in home applications, and this is often diluted by the user prior to use. As per the United States Department of Agriculture (USDA), Food Safety and Inspection Service (FSIS) guidelines, the poultry

Received 30 March, 2017 Accepted 13 September, 2017
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doi: 10.1016/S2095-3119(17)61798-2

industry is allowed to use up to 50 mg L^{-1} hypochlorite in poultry chiller water. The FSIS also requires that chlorinated water containing a minimum of 20 mg L^{-1} available chlorine be used to sanitize surfaces that carcasses have come in contact with. While produce industry most commonly use hypochlorite solutions with a federally-mandated limit of chlorine in wash water at 200 mg L^{-1}. However, the uses of chlorine as a water disinfectant has come under scrutiny because its potential to react with natural organic matter and form chlorinated disinfectant byproducts (DBPs).

Chloramines (e.g., NH_2Cl, monochloramine) and chlorine dioxide (ClO_2) have shown promise as an alternative disinfectant to free chlorine to avoid the formation of DBPs. However, the biocidal efficacy of chloramines is significantly lower than Cl_2, and the formation of organic chloramines have raised concerns. On the other hand, ClO_2 is an effective antimicrobial agent and less sensitive to water quality and pH changes than Cl_2 (WHO 2000). Although ClO_2 is less stable than Cl_2 and must be generated on-site and used as soon as it is made, some stabilized solution forms of ClO_2 are also available.

Several of the recent reports suggest that the chlorine-based sanitizers have a tendency to form various types of DBPs such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorites, and haloketones, etc., in the presence of food organic matter (Olmez and Kretzschmar 2009; Luo *et al*. 2011; Van Haute *et al*. 2013; Shen *et al*. 2016). Several pH dependent chlorine reactions were believed to be the major factor responsible for the formation of these DBPs. This review presents an overview of various pH dependent chlorine reactions with organic matter, the formation of DBPs and their health concerns as well as novel strategies to minimize the risk.

2. Chlorine chemistry and the effect of pH

Chlorine is a highly reactive gas under normal pressure and temperature. Chlorine is also available in granular or powdered form as calcium hypochlorite ($Ca(OCl)_2$) and in liquid form as sodium hypochlorite (NaOCl). Most elementary reactions involving chlorine compounds are second-order in nature, and the kinetics are pH dependent. Since chlorine has pH-dependent aqueous chemistry, several chlorine species including HOCl, OCl^-, and Cl_2, will be formed in water (Doré 1989). Chlorine gas hydrolyses in water almost completely to form hypochlorous acid (HOCl):

$$Cl_2+H_2O \rightarrow HOCl+H^++Cl^-$$

Where, HOCl is a weak acid with a pKa of about 7.46 at 25°C. The hypochlorous acid readily decomposes upon exposure to light (Molina and Molina 1978). In the process of decomposition, the formation of Cl_2 is possible if the pH is sufficiently low (pH<4). Above pH 7.5, HOCl dissociates into hydrogen ions (H^+) and hypochlorite ions (OCl^-) in the reversible reaction:

$$HOCl \leftrightarrow H^++OCl^-$$

This change of chlorine species with pH is shown in Fig. 1 (Deborde and von Gunten 2008) and HOCl is the predominant species at pH 3–7 (Gordon and Tachiyashiki 1991) and OCl^- dominates above pH 7.5. Hypochlorite ion is most commonly found in the form of sodium hypochlorite or calcium hypochlorite.

HOCl is a strong oxidant, and it freely oxidizes many organic compounds (Folkes *et al*. 1995; Wyman 1996; Winterbourn and Brennan 1997; Hawkins *et al*. 2003). Cell membranes are mostly impermeable to charged substances because ions have a high affinity to water molecules, which develop dipoles by nature. The hydrophobic portion of the cell membrane contains no water, so charged particles cannot pass through it. As a weak acid, HOCl can diffuse through cell membranes and acidify the interior of cells (Gutknecht and Tosteson 1973). Being both uncharged and small, HOCl is free to diffuse across the cell membrane. In addition to hydrolysis of saccharide and peptide bonds, hypochlorite can also interact with disulfide bonds. Disulfide bonds are formed by sulfur-containing amino acids such as cysteine and methionine, and they play an important role in determining a proteins folded structure. Hypochlorite readily oxidizes these bonds, resulting in their cleavage (Wyman 1996). These properties help make HOCl an effective antimicrobial agent.

3. Chlorine and its reactions with organic compounds

Chlorine reactions with organic matter are a cause of concern for two main reasons. First, available chlorine can be "used up" by organic compounds not associated with microorganisms, resulting in a lower amount of chlorine available

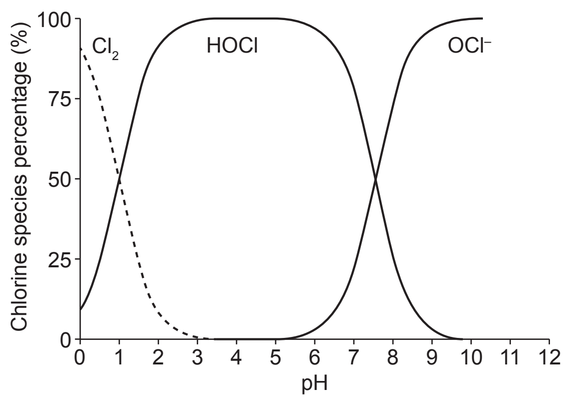

Fig. 1 The relative percentages of three different chlorine species in solution as a function of pH (Deborde and von Gunten 2008).