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Effects of organic load, sanitizer pH and initial chlorine concentration of chlorine-based sanitizers on chlorine demand of fresh produce wash waters

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A B S T R A C T

Chlorine-based sanitizers are widely used in fresh produce industry. However, maintaining sufficient free chlorine residual in wash solution in the presence of organic matter is a challenge. The purpose of this study was to evaluate the effects of organic load, sanitizer pH and initial chlorine concentration on chlorine demand of fresh produce wash water. A full factorial design was used to study the chlorine demand of romaine lettuce wash water with different organic load when reacting with NaOCl solution at different pH (2.5, 4.0, 6.0, 8.0 and 9.5) and initial chlorine concentration (50, 75 and 100 mg L^{-1} free chlorine residual). The results showed that the chlorine demand of lettuce wash water significantly increased ($P \leq 0.05$) with increasing organic load. The significant effect ($P \leq 0.05$) of initial chlorine concentration on chlorine demand was only detected at high organic load. Increasing the pH of NaOCl from 2.5 to 9.5 led to decrease in the chlorine demand except slight increase from 6.0 to 8.0. Equations for predicting chlorine demand of various fresh produce wash waters at different organic load for different sanitizer pH and initial chlorine concentration were developed, and verified using four types of produce (romaine lettuce, iceberg lettuce, strawberry and grape) and two types of chlorine-based sanitizers (NaOCl and electrolyzed water). Our study demonstrated that organic load, sanitizer pH and initial chlorine concentration all affected the chlorine demand of produce wash water, and chlorine demand prediction equations developed can be used for different types of fresh produce and chlorine-based sanitizers.

1. Introduction

Fresh fruits and vegetables without sufficient heat treatment may be a vehicle for foodborne illnesses. It was estimated that produce-associated foodborne outbreaks caused approximately $ 1.4 billion economic losses and over 1 million illnesses per year in the US (Batz, Hoffmann, & Morris, 2011). In addition, the Centers for Disease Control and Prevention (CDC, 2014) reported that produce was responsible for 27% of outbreaks and 40% of foodborne illnesses in 2014. Therefore, an effective washing process during produce postharvest handling is a critical step to ensure the safety of fresh produce (Gil, Gomez-Lopez, Hung, & Allende, 2015).

Chlorine-based sanitizers such as sodium hypochlorite (NaOCl) have been widely applied as disinfectants in fresh and fresh-cut produce postharvest washing process in the US (Luo et al., 2011). Previous study showed that the antimicrobial efficacy was largely depended on the free chlorine residual in processing water (Gil, Selma, Lopez-Galvez, & Allende, 2009). On the other hand, excess amount of free chlorine may react with organic compounds in produce wash water to generate carcinogenic halogenated disinfection by-products (DBPs), such as trihalomethanes (THMs) (Fan & Sokorai, 2015). Some countries in the European Union even prohibit the use of chlorine for washing fresh produce partially due to potential health risk associated with DBPs (Van Haute, Sampers, Holvoet, & Uyttendaele, 2013).

Tradeoffs between maintaining the disinfection efficacy and forming hazardous DBPs encourage the development and use of models to predict "chlorine demand", which is the chlorine loss as a consequence of reacting with organic compounds (Pirovani, Guemes, & Piagnetini, 2001; Waters & Hung, 2014; Zhou, Luo, Nou, & Millner, 2014). Our previous study developed equations to

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predict chlorine demand (NaOCl) of various produce wash waters based on the ultraviolet light absorbance of filtered produce wash water at 254 nm (UV254) (Chen & Hung, 2016). We found that UV254 had a higher correlation coefficient with chlorine demand than other water quality parameters such as chemical oxygen demand (COD) or turbidity. However, these equations can only be applied at a specific condition (i.e. non-buffered NaOCl solution at 100 mg L^{-1} free chlorine concentration and pH 6). In practice, buffering agents are commonly added into the processing water (Fan & Sokorai, 2015). In addition, the pH of chlorine-based sanitizers may vary from 2.5 (e.g. acidic electrolyzed (EO) water) to 9.5 (e.g. NaOCl with stabilizer) (Huang, Hung, Hsu, Huang, & Hwang, 2008). Initial free chlorine concentration is usually in the range of 50–100 mg L^{-1} but may vary from one processor to another.

Therefore, the overall objective of this study was to evaluate the effects of sanitizer pH and initial chlorine concentration of NaOCl on chlorine demand of different fresh produce wash waters at different organic load. Specific objectives include the following:

i) to determine the effect of buffering agents on chlorine demand
ii) to determine the effects of organic load, sanitizer pH and initial chlorine concentration on chlorine demand
iii) to develop prediction equations to estimate chlorine demand of various fresh produce wash waters at different processing conditions
iv) to validate developed equations using different types of fresh produce, chlorine-based sanitizers and processing conditions.

2. Materials and methods

2.1. Preparation of NaOCl solutions

NaOCl solutions at different free chlorine concentration were prepared by diluting 6% bleach (RICCA Company, Arlington, TX, USA) in deionized water (dH_2O). Free chlorine concentration was measured by a DPD-FEAS titrimetric method (Hach Company, Loveland, CO, USA). A dual channel ACCUMET pH meter (Model # AR50, Fisher Scientific, Pittsburgh, PA, USA) with appropriate electrode was used to measure the pH of samples. The pH of NaOCl solution with or without 10 mmol L^{-1} phosphate buffers was adjusted using 1 mol L^{-1} phosphoric acid/NaOH or 1 mol L^{-1} HCl/NaOH, respectively.

2.2. Preparation of romaine lettuce wash water

Romaine lettuce (*Lactuca sative*) was purchased from a local grocery store in Griffin, GA, stored at 4 °C, and used within 48 h. Lettuce was cut into small pieces (3 × 3 cm^2) and homogenized with dH_2O in a stomacher (Seward Stomacher®, 80 biomaster, Worthing, UK) at 265 rpm for 120 s. Lettuce extract was then filtered through filter papers (No. 4, Whatman™, Boca Raton, FL, USA) and diluted to targeted organic load with dH_2O. For this study, standard chlorine demand (D_{ST}) expressed as the chlorine loss when 1 ml of produce wash water reacts with 9 ml of NaOCl solution containing 110 mg L^{-1} free chlorine at pH 6.0 for 5 min was used as the organic load indicator. The reaction time was set at 5 min, since practical produce washing time is usually several minutes, and more than 60% of chlorine demand of romaine lettuce wash water occurred within first 5 min over a 90 min observation period (Weng et al., 2016).

2.3. Effect of buffering agent on chlorine demand

NaOCl solutions at 110 mg L^{-1} initial chlorine concentration were adjusted to pH 2.5, 6.0 and 9.5 with or without buffering agent, and stored at 4 °C for 2 h before use. A 1 ml of dH_2O (control) or romaine lettuce wash water at organic load of D_{ST} 35 mg L^{-1} was mixed with 9 ml of NaOCl solution with or without buffering capacity for 5 min. The pH and residual free chlorine of NaOCl solution before and after reacting with romaine lettuce wash water were measured. Chlorine demand of produce wash water was calculated as the difference of residual free chlorine between control and lettuce wash water after the treatment.

2.4. Determination of chlorine demand of romaine lettuce wash water at different organic load, sanitizer pH and initial chlorine concentration

A three-factor design (organic load, sanitizer pH and initial chlorine concentration) was used. Romaine lettuce wash waters at organic load of D_{ST} 20, 40 and 60 mg L^{-1} were prepared. Initial chlorine concentration of NaOCl solution was adjusted to 50, 75 and 100 mg L^{-1}. The pH of NaOCl solution was adjusted to 2.5, 4.0, 6.0, 8.0 and 9.5 using 1 mol L^{-1} HCl/NaOH. The pH and oxidation-reduction potential (ORP) of NaOCl solution were measured with a dual channel ACCUMET meter (Fisher Scientific) with appropriate probes. After 1 ml of lettuce wash water was added to 9 ml of chilled (4 °C) NaOCl solution for 5 min, chlorine demand of the respective solution was determined as described before.

A multiple regression model was used to identify the relation between response variable (D, chlorine demand of lettuce wash water) with three independent variables.

$$D = f(\mathrm{OL}, \mathrm{pH}, \mathrm{C}) \tag{1}$$

where OL is the organic load as the standard chlorine demand, pH is the sanitizer pH and C is the initial chlorine concentration.

2.5. Procedure for model validation

In order to validate developed equations, two validation experiments using various produce wash waters at low and high organic load were conducted. For each experiment, four types of fresh produce including iceberg lettuce (*Lactuca sativa*), grape (*Vitis labrusca*), romaine lettuce (*Lactuca sative*) and strawberry (*Fragaria × ananassa*) were used. Iceberg lettuce and romaine lettuce were cut into 3 × 3 cm^2 pieces before use. Whole, undamaged strawberries and grapes were selected. Produce was then homogenized with dH_2O and filtered through filter papers (No. 4, Whatman™). Produce wash waters were adjusted to D_{ST} 30 and 50 mg L^{-1} for low and high organic load validation experiments, respectively.

Both NaOCl and EO water were used for validation experiments. NaOCl solution at 110 mg L^{-1} initial chlorine concentration was prepared by diluting 6% bleach. EO water was prepared by electrolyzing 0.03% NaCl solution using an EO water generator (Model #P30HST44T, EAU, GA, USA) and diluted to 110 mg L^{-1} initial chlorine concentration. The pH of NaOCl solution and EO water were adjusted to 2.5, 6.0 and 8.0 using 1 mol L^{-1} HCl/NaOH. Chlorine demand of different produce wash waters when reacting with NaOCl solution and EO water was determined after 5 min of contact time.

2.6. Wash water properties determination

Produce wash water at organic load of D_{ST} 30 and 50 mg L^{-1} was