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Should chlorate residues be of concern in fresh-cut salads?

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ABSTRACT

Chlorine remains the most popular method used by the fresh produce industry for decontamination. However, the occurrence of disinfection by-products (DBP) derived from chlorine-based disinfectants has been highlighted as a problem. After recent reports, chlorate residues in fresh produce are of concern in Europe. This study evaluated the chlorate accumulation in process wash water and the residues in fresh-cut lettuce when sodium hypochlorite was used as a wash aid. At a commercial processing facility, total chlorine was continually added to achieve a free chlorine level of 1–80 mg L^{-1} for water disinfection as the organic load measured as chemical oxygen demand (COD) increased over time (1000–1500 mg O_2 L^{-1}). This resulted in chlorate accumulation (19–45 mg L^{-1}) in the process water. When fresh-cut lettuce was washed in that water, chlorate residues were detected in the lettuce and the concentrations increased linearly with the repeated use of the same process water, reaching concentrations of 4.5–5.0 mg kg^{-1}. To understand the chlorate accumulation in the process wash water, several experiments were performed at a pilot plant scale with different levels of COD and free chlorine. There was a significant ($p < 0.001$) correlation ($R = 0.91$) between the total added chlorine and the chlorate accumulation in the process water. We demonstrated that the added chlorine needed to maintain a free chlorine level in the process water was the contributing factor to chlorate accumulation. Chlorate residues in the washed fresh-cut lettuce after rinsing for 1 min in tap water and in commercial bags were below the limit of quantification. This study contributes to the knowledge of chlorate accumulation in the process water when sodium hypochlorite was used as a sanitizer.

1. Introduction

The role of water during food production and processing has been recognized as an important contributing factor to foodborne disease (EFSA, 2013; FAO/WHO 2008). This is particularly relevant for the fresh-cut produce industry in which the process wash water accumulates debris, dirt, organic matter and microorganisms from the surface of the product as it is washed. If contaminated product is introduced in the washing tank, there is a potential risk for cross-contamination (López-Gálvez et al., 2010; Luo et al., 2011; Van Haute, Sampers, Holvoet, & Uyttendaele, 2013). Water disinfection has been described as an essential activity to reduce cross-contamination during washing and inadequately or improperly disinfected wash water can itself become a major source of contamination (Gil, Selma, López-Gálvez, & Allende, 2009). The risk of cross-contamination is not removed by using large quantities of water; a water disinfection agent is needed (Whitaker & Gorny, 2013).

Chlorine is the most commonly used water disinfectant in the fresh produce industry. This prevalence of commercial chlorine usage is attributable to its established ability to kill pathogens in solution, minimal impact on product quality and low cost (Allende, Selma, López-Gálvez, Villaescusa, & Gil, 2008; Luo, 2007). Chlorine forms several compounds in water such as hypochlorous acid (HOCl), chlorine gas (Cl_2) and hypochlorite ion (OCl^-) in amounts that vary with the water pH. The terms free chlorine or available chlorine are used to describe the amount of chlorine in any form available for oxidative reaction and disinfection (Suslow, 1997). Extensive study has revealed that hypochlorous acid is the most effective antimicrobial form of chlorine (Zhao, Doyle, & Zhao, 2001). The inhibitory or lethal activity depends on the concentration of free chlorine and contact time (Luo et al., 2011; Gómez-López, Lannoo, Gil, & Allende, 2014a). Free chlorine should be remained at a residual dose in the water as a measure of disinfection protection. Consequently, effective chlorination depends upon frequent monitoring of the free chlorine and other water

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parameters such as pH and oxidation-reduction potential (ORP).

Cleaning and rinsing designs of a processing facility for fresh-cut produce vary greatly. Different steps include the wash tanks or flume where the product can be exposed to various washes and rinses before de-watering via centrifugation and pack (Pao, Long, Kim, & Kelsey, 2012). The main characteristic of process water is that it contains a large amount of organic matter from the exudates of the cut tissues (Shen et al., 2013). A common practice in fresh produce washing is that large volumes of chlorinated water are continuously replenished into the wash water tanks throughout the processing activity (Barrera, Blenkinsop, & Warriner, 2012). Water replenishing is used to replace water loss during washing, maintain the water temperature at about 4 °C and reduce the accumulation of organic matter. Chlorine is normally applied to process water as chlorine gas, sodium hypochlorite solution or dry calcium hypochlorite to produce free chlorine in water (Suslow, 1997). Sodium hypochlorite is the chlorine source frequently used in small and medium-scale operations because it can be handled without high expertise and with a minimal hazard as compared to chlorine gas. During the last decades, increasing number of large processing facilities has changed to hypochlorite reagents too due to the more stringent norms of security. However, it is difficult to maintain a relatively consistent level of free chlorine during commercial fresh-cut wash operations because chlorine is very reactive and readily combines with almost any substrate capable of being oxidized to form DBP in the water such as trihalometanes (THM) (IFPA, 2001; Luo et al., 2011; Van Haute et al., 2013). In the case of prepared salads, the Committee on Toxicity of Chemicals (COT, 2006) reported that the occurrence of THMs complies with the WHO Guidelines for Drinking Water Quality (López-Gálvez et al., 2010; Van Haute et al., 2013; WHO., 2004). However, a new alarm blew up by a study carried out by the Chemisches und Veterinäruntersuchungsamt (CVUA, Stuttgart) on chlorate residues in plant-based food (Kaufmann-Horlacher, Scherbaum, Stroher-Kolberg, & Wildgrube, 2014a). In this survey, 600 samples of products of plant origin were analyzed. In 19.8% of them, residue levels were found between 0.01 and 0.92 mg kg^{-1}. Chlorate (ClO_3^-) is a substance that is no longer approved as a pesticide according to Commission Decision No 2008/865/EC (EC, 2008). No specific maximum residue levels (MRLs) have been established and therefore, a default MRL of 0.01 mg kg^{-1} was applicable. However, in many fruit and vegetable commodities chlorate levels exceeding the default MRL were found. This limit was temporally increased to 0.25 mg kg^{-1} for all vegetable commodities (EC., 2014). Recently, EFSA was asked by the European Commission to consider the impact on dietary exposure of applying the WHO guidance level for chlorate in drinking water of 0.7 mg per kilogram (mg kg^{-1}) to all foods covered by EU legislation (EFSA, 2015). The EFSA Panel on Contaminants in the Food Chain concluded that based on the current practices in food industry, application of a hypothetical maximum residue limit (MRL) of 0.7 mg/kg for all foodstuffs and drinking water would only minimally reduce acute/chronic exposures and related risks. The Panel reported that the source of the chlorate residues detected in food could arise from the use of chlorinated water for food processing and the disinfection of food-processing equipment. Chlorate levels of up to the level of 0.7 mg/L can be found depending on the extent of chlorination, which varies amongst Member States. Accordingly, in a study carried out in carrots, chlorate residues were traced to chlorinated water used in post-harvest treatment (Kaufmann-Horlacher, Scherbaum, Stroher-Kolberg, & Wildgrube, 2014b). In the case of the water industry, chlorate is considered to come from hypochlorite reagents (García-Villanova, Oliveita Dantas Leite, Hernández Hierra, de Castro Alfageme, & García Hernández, 2010). Chlorine disproportionates slowly but given enough time, it may be almost completely converted to chloride and chlorate. Thus, one potential source of chlorate residues is the use of chlorine-based sanitizers as water disinfectant during washing of fresh produce. The aim of the present study was to gain insight regarding the potential risk of chlorinated water as a source of chlorate residues in the process water and therefore in the washed product.

2. Materials and methods

2.1. Wash process description

Two types of experiments were carried out. First, a sampling was carried out at a commercial processing facility and secondly, a pilot plant was used to understand the different factors responsible for the chlorate accumulation. At the commercial processing plant, lettuce heads were loaded onto a conveyor and passed through a shredder for cutting into 30 × 30 mm slices. Cut lettuce was emptied into a wash tank containing 1000 L of water dosed with sodium hypochlorite (Centauro, Fab. Ind. Gamer, Murcia, Spain) with very little water replenishment during the processing activity (500–700 L h^{-1} approx.). The resident time of the lettuce within the wash tank was approx. 1 min. Then, the washed lettuce was rinse by shower and de-watered via centrifugation prior to being packed. Sodium hypochlorite and cooling water were added into the washing tank as necessary based on the pH and free chlorine.

The experiments performed at a pilot plant were carried out using a 'dynamic system' previously described (Gómez-López, Gil, Pupunat, & Allende, 2014b). A washing tank was filled with a volume of 10 L of tap water before starting the tests. Concentrated process water containing a high concentration of organic load (>2000 mg O_2 L^{-1}, chemical oxygen demand, COD) was generated from the homogenization of Iceberg lettuce. During the experiments, concentrated process water with high organic load was constantly pumped into the washing tank simulating the washing operation in a commercial processing line. The system was assumed to be a perfectly mixed reactor. A concentrated chlorine solution of active chlorine of 40 g L^{-1} was continuously dosed to the washing tank at a flow rate necessary to achieve the desired free chlorine. This chlorine dose represented the total amount of added chlorine and this dose minus the residual is what reacted with the organic matter.

2.2. Water quality parameters

Samples of process water from the washing tank were taken at different time intervals for the evaluation of water characteristics such as pH, oxidation reduction potential (ORP), electrical conductivity (Ec) and chemical oxygen demand (COD). The temperature of process water was also monitored and maintained within 4 ± 1 °C for the product to cool down and the chlorine dissociation at this temperature was considered to be minor. The oxidation reduction potential (ORP) is an indicator of the ability of a solution to oxidize and is related to the concentration of oxidizers and their activity or strength. Temperature, pH and ORP were measured using a multimeter pH & Redox 26 (Crison, Barcelona, Spain). Water pH was adjusted to 6.4 using citric acid to ensure the presence of chlorine in the hypochlorous acid form. Between pH 6.5 and 7.0, hypochlorous acid exists as 95–80% of the free chlorine concentration. Free chlorine was measured by the N,N-diethyl-*p*-phenylendiamine (DPD) colorimetric method (APHA, 1998) using the Spectroquant NOVA 60 photometer (Merck, Darmstadt, Germany). Chemical Oxygen Demand (COD) was measured by the standard photometric method (APHA, 1998) using the Spectroquant NOVA 60 photometer.