The use of redox potential to estimate free chlorine in fresh produce washing operations: Possibilities and limitations

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Abstract

Maintaining free chlorine (FC) residual at appropriate pH values is a control approach used to prevent pathogen cross-contamination during tomato dump tank handling and fresh-cut produce washing operations. Oxidation reduction potential (ORP) is a rapid measurement of oxidant-based sanitizer strength, and has been used to estimate FC residual. However, factors, in addition to FC and pH, which influence ORP are not fully understood. This study examined the relationship between ORP and FC under chlorine demand (CLD) free conditions and during fresh produce washing. An equation predictive of FC was developed in the form logFC = f(ORP, ORP^2, ORP.pH). A good correlation between ORP and logFC was maintained when other variables changed, but the resulting ORP-logFC curve changed (slope, intercept). A decrease in pH or temperature led to an increase in ORP. Using tap water to wash the produce instead of distilled water significantly changed the ORP. For different types of tested produce, i.e., fresh-cut carrot, onion, romaine and iceberg lettuce, and for whole tomatoes, increasing the product-to-water ratio (i.e., increasing the organics transferred into the water) led to a decrease in ORP for a specific FC residual. The choice of acidulant during washing also influenced ORP. Overall, the correlation of ORP with logFC is more reliable at the lower end (5 mg/L FC) than at the higher end (100 mg/L FC) of the FC range used in fresh produce washing. However, since the ORP in fresh produce wash water is affected significantly in multiple ways by the wash water and process conditions, the predicted FC values with ORP under certain fresh-cut produce washing conditions cannot be generalized for other conditions.

Introduction

In fresh produce processing or packaging, washing is used for removal of dirt from, transport of, and disinfection of the produce. Disinfection is mostly done by adding chlorine (mostly dosed in the form of sodium hypochlorite) to the water that contacts the produce. This disinfection process can remove microorganisms from the produce surface to some degree, but disinfection is limited to about 1–2 log. In the water on the other hand, the microorganisms do not receive protection from the produce (although microbial clumping and particle association can provide some protection), which makes killing microorganisms in the water much more efficient. Even though elimination of pathogens from produce surfaces cannot be fully achieved with water disinfection, maintaining a sufficiently high water disinfectant concentration in the wash water is needed to limit or eliminate cross-contamination of pathogens among produce, and as such avoid spreading of the pathogen to more crops and potentially more consumers (Suslow, 2004; Gil et al., 2009; Van Haute et al., 2015; Gombas et al., 2017).

Chlorine over-dosing (in combination with a pH below 4.5) will lead to chlorine off-gassing in the work space as well as increased production of carcinogenic by-products in the presence of organics in the wash water (Van Haute et al., 2013). In addition, as chlorate is formed during storage of sodium hypochlorite, increased chlorine dosing during the washing process leads to accumulation of chlorate in the wash water (Stanford et al., 2011). As chlorate is no longer allowed as pesticide in the European Union, introduction of chlorate in the food chain due to excessive chlorination is considered a potential issue (Gil et al., 2016; Nestlé, 2017). Chlorine under-dosing on the other hand can increase food safety risks due to insufficient protection from pathogen cross-contamination via the wash water. Chlorine is consumed by organics introduced into the water during produce washing (Nou and Luo, 2010; Luo et al., 2011; Van Haute et al., 2013). Ammonia reacts very rapidly with chlorine, but there is very little ammonia present in fresh produce wash water as degradation of N-containing organics has not yet set in during washing (Van Haute et al., 2013). Therefore, an easy-to-use technology for continuously measuring the FC residual is of great interest for the fresh produce processing industry.

The ORP is a measurement of the tendency of a chemical species to acquire electrons. The potential, measured using an ORP electrode, is influenced by all the redox reactions that occur at the electrode surface. As such, the ORP in a produce wash operation is a mixed potential that is usually impossible to relate to one particular redox reaction (White, 2010). However, in some systems the ORP is dominated by one reaction of interest, thereby providing useful information about that redox reaction, even though the signal is fundamentally semi-quantitative. Information about the presence of strong oxidants/reductants can be acquired in this way, because of the strong oxidizing/reducing properties of these chemicals. Thus, ORP has been used to estimate the presence of free chlorine in water (White, 2010). Limitations to the usage of ORP for chlorine measurement is the slow response time and the non-linear response of ORP to free chlorine (Hoorfar, 2014). The use of ORP for measuring free chlorine during the washing of fresh produce has been described in some tomato packing houses (Tomas-Callejas et al., 2012; Zhou et al., 2014b), and fresh-cut lettuce operations (Fu et al., 2018; López-Gálvez et al., 2019).

There are some clear practical benefits to using ORP. The probe can be put straight into the wash water. There is no need for tapping from the flow of water and passing it through a tubing system, adding reagents and doing a titrimetric or spectrophotometric analysis on the water sample, which is the case in automated *N,N*-diethyl-p-phenylenediamine (DPD) method devices. In addition, ORP is a voltage measurement and as such easy to be used as a signal for communicating with the pump of a dosing system in a feed-back loop.

In the early editions of the industry food safety guidelines in the US, 150 mg/L free chlorine at pH 6.5, or an ORP of 650 mV in wash tanks were used as control measures to prevent pathogen cross-contamination (FTEC, 2006; UFPA, 2008) based on scientific findings available then. With the advancement in science, the industry has recently updated their food safety standard, changing ORP requirement from previously 650 mV to 850 mV (UFPA, 2018). However, most of the scientific studies evaluating pathogen cross-contamination use only free chlorine and pH (Luo et al., 2011; Gereffi et al., 2015; Sreedharan et al., 2017), while many tomato packers and fresh-cut processors use ORP to gauge their sanitizer strength. Thus, a formula that allows the conversion between ORP, FC, and pH is highly desirable. Thus, this study was designed to address these critical data gaps. Specifically, the main objectives of this study are to i) evaluate the relationship between ORP and FC under ideal conditions, i.e., in chlorine demand (CLD) free water, ii) observe the changes that occur to the ORP-FC relationship under the conditions of tomato and fresh-cut leafy vegetable water (water source, organic matter, acidulant).

Section snippets

Production of fresh produce wash water

Carrots (*Daucus carota* L. subsp. *sativus*), onions (*Allium cepa* L.), romaine and iceberg lettuce (*Lactuca sativa* L.) were purchased from a local wholesale market in Jessup, MD, USA, and stored at 4 °C for 24 h before processing. Root hairs of carrots were manually removed. Onions were peeled and de-cored in the packing house and were shredded without additional preparation. Lettuce was prepared by trimming the leaf edges and removing the stems (Luo, 2007). The vegetables were shredded into

Log-linear relationship between FC and ORP with accounting for pH

A relationship between ORP and the logarithm of FC in CLD free water was observed (Fig. 1). This relationship was significantly affected by water temperature (ANCOVA: $p < 0.001$). At 4 °C, the ORP was higher than that at 25 °C (Fig. 1). The difference in ORP at 4 and 25 °C decreased with increasing FC, and at about 100 mg/L FC ($\log FC = 2$), the ORP was virtually equal at both temperatures (Fig. 1). A quadratic equation was significantly better (R-square change F-test from linear to quadratic

Conclusion

During a produce washing process with FC as the water sanitizer, the ORP is at least dependent on four major variables: FC, T, pH and water matrix constituents. The water matrix constituents include the mineral and organic chemical composition of the tap water or ground water (water source), along with the constitution and amount of substances introduced with the produce. The ORP increases with the logarithm of the FC residual. This implies high changes at very low FC and low changes at higher

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