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System feasibility: Designing a chlorine dioxide self-generating package label to improve fresh produce safety part II: Solution casting approach☆

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ABSTRACT

This work evaluated the ability of an innovative and practical package label made from biobased polymers impregnated with sodium chlorite and citric acid to generate and release chlorine dioxide (ClO_2) at levels sufficient to inactivate pathogenic bacteria on packaged fresh produce. The concentrations of generated ClO_2 by these labels were dependent on the number of layers used and the inclusion of barrier layers. Release rates decreased exponentially with number of layers, providing an additional level of control. Storage temperature had no significant effect on the release of ClO_2. All labels released ClO_2 at concentrations capable of complete inactivation of *Salmonella* cells on TSA plates. Under low-humidity conditions, the labels reduced the levels of *Salmonella* on inoculated mung bean seeds by up to 2.0 log CFU/g. These results indicate that these labels can be used in a wide range of storage environments for enhancing safety and shelf-life of packaged fresh produce.

Industrial relevance: The biobased packaging labels present a commercially viable solution to the problem of controlling microbial growth on fresh produce. Due to the ease of manufacture under existing commercial coating technology, they can be produced and activated simultaneously with fresh produce packaging in the plant. These labels can be adapted to different food safety requirements by modulating the number of functional biobased layers, without or with biobased barrier layers, and label surface areas for generating the required concentration of ClO_2 at the optimal rate.

1. Introduction

Foodborne illnesses are associated with the consumption of fresh produce. The food industry uses aqueous chlorine washes as a primary technology for removing dirt and reducing any potential pathogenic and/or spoilage microorganisms on the surfaces of produce. Studies have shown that the use of aqueous wash treatments incorporating sanitizers such as chlorine, peroxyacetic acid, acidified sodium chlorite, hydrogen peroxide, trisodium phosphate, phosphoric acid, or nisin-EDTA were only partially effective in reducing pathogenic and spoilage microbial populations on produce surfaces (Annous, Burke, Sites, & Phillips, 2013). Survival of these microorganisms following aqueous wash treatment was attributed to their attachment to inaccessible sites on the produce such as the netting of a cantaloupe rind and the stem scar and calyx of an apple. It can also be attributed to the formation of microbial biofilms (Annous et al., 2013; Annous, Solomon, Cooke, & Burke, 2005) and surface tension due to hydrophobicity of these regions (Gomez-Lopez, Ragaert, Debevere, & Devlieghere, 2008; Harris et al., 2003).

In contrast, gaseous ClO_2 readily diffuses into inaccessible sites and microbial biofilms to inactivate human pathogens attached to produce surfaces (Annous & Burke, 2015; Han, Sherman, Linton, Nielsen, & Nelson, 2000; Prodduk, Annous, Liu, & Yam, 2014). Chlorine dioxide is a true gas (greenish yellow) at room temperature with effective biocidal activity over a wide range of pH (3–8) (Bernarde, Israel, Olivieri, & Granstrom, 1976; Keskinen & Annous, 2011). It is a selective and strong

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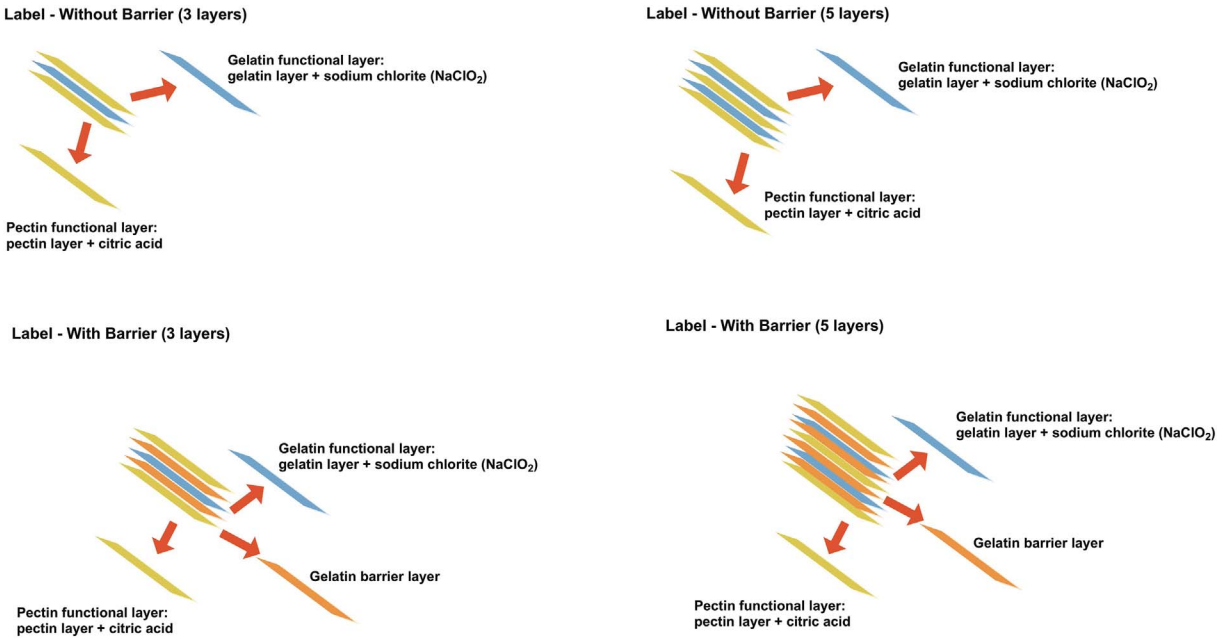

Fig. 1. Concept development of the biobased polymer package labels for generating ClO_2. Gelatin and pectin embedded with sodium and citric acid, respectively, are assembled without or with gelatin barrier layers.

oxidizing agent which, unlike chlorine, does not chlorinate organic compounds to produce carcinogenic trihalomethanes (THMs) (Aieta & Berg, 1986; Keskinen & Annous, 2011). Also, it does not react with ammonia to form chloramines (Keskinen & Annous, 2011; Oxenford, 1995), making it very attractive for use as an antimicrobial in foods. Chlorine dioxide acts against vegetative bacterial cells by inhibiting protein synthesis (Bernarde et al., 1976) and by nonspecific oxidation of the cell outer membrane, resulting in the loss of permeability and the inhibition of the respiration process (Berg, Roberts, & Matin, 1986). Chlorine dioxide received FDA approval in 2001 to reduce or eliminate microorganisms in a wide variety of food products such as fruits and vegetables (Rulis, 2001).

Because ClO_2 is explosive at concentrations ≥10% v/v at atmospheric pressure (Keskinen & Annous, 2011), it is usually generated onsite upon demand to eliminate safety hazards associated with its storage and transportation (Keskinen & Annous, 2011). A number of commercial ClO_2 generators have been developed throughout the years to synthesize this compound when needed for diverse applications. Attributes of various generators were reviewed in the first paper of this series (Saade et al., 2017).There we proposed that the reaction of sodium chlorite salt with citric acid incorporated in polymer films could be used to advantage to generate ClO_2 in active packaging systems and release it into individual packages when needed to overcome limitations of large-scale gassing.

1.1. Package label concept

Deshwal and Lee (2005) showed that ClO_2 can be generated by reaction of sodium chlorite (low concentrations) with acid in solution without generating reactive side products that plague other synthesis methods:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$

This reaction occurs slowly in dry systems but is facilitated in or on films by the presence of moisture that dissolves the reactants. Substituting citric acid for HCl provides a food-grade version that can be incorporated safely and conveniently into a packaging system to produce ClO_2 and inactivate bacteria without generating reactive or toxic side products (Ray, Jin, Fan, Liu, & Yam, 2013; Rubino, Netramai, Auras, & Annous, 2014; Rubino, Siddiq, Auras, Annous, & Netramai, 2011; Saade et al., 2017).

As proof of principle we demonstrated the technical feasibility of manufacturing synthetic packaging labels composed of ethylene vinyl acetate (EVA) extruded with citric acid at different loading levels, then sprayed with sodium chlorite and activated by heat pressing to release ClO_2 inside packages (Saade et al., 2017). A burst of ClO_2 was generated from reaction of citric acid molecules on the surface of the label; those molecules located in the bulk of the polymer were inaccessible due to the hydrophobicity of the polymer. That the ClO_2 generated by these labels was 6 to 42% of the theoretical calculated yields supports incomplete utilization of ClO_2 precursors embedded within the EVA film. Even with this limitation, however, EVA labels released ClO_2 in concentrations between 0.5 and 3.8 mg/l air, sufficient for 2.3 log reductions in *Salmonella* Montevideo G4639 population on tryptic soy agar plates (Saade et al., 2017).

The need to achieve better control over the release rate and increase the yields of ClO_2 from package labels led us to investigate other types of packaging labels that may be more interactive with the environment where they are used. Hence, in the current study, ClO_2 was generated in a multilayered biobased package label synthesized by alternating functional layers of pectin embedded with citric acid and gelatin embedded with sodium chlorite. In some labels, optional barrier layers made of gelatin without sodium chlorite were inserted between the functional layers to modify the release rate of ClO_2.

The constituent layers of these labels were first prepared separately using solution casting, then stacked alternately at the point of use. ClO_2 generation and reaction was triggered by the application of pressure. The production of ClO_2 from these labels was facilitated and sustained by a high humidity environment created by moisture from the respiration of fresh produce in the target package. Release of ClO_2 from the package label had two controls: 1) modification of the total quantity of ClO_2 generated by altering the amount of the precursors (for example, increasing the surface area of the label, manipulating the number of the functional layers, or increasing reagent loading); 2) insertion of gelatin barrier layers between functional layers to slow the reaction rate and thus reduce the concentration of ClO_2 released within the package over time.

Layer concept feasibility was tested in four different labels