Article

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Development of sustained release formulations of chlorine dioxide gas for inactivation of foodborne pathogens on produce

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Abstract

Formulations for the sustained release of chlorine dioxide (ClO_2) gas were developed, and their gas-producing profiles and antimicrobial effects against *Escherichia coli* O157:H7 and *Salmonella* Typhimurium were evaluated in spinach leaves and tomatoes under different relative humidity (RH) conditions. Sodium chlorite ($NaClO_2$) and citric acid were used to generate ClO_2 gas, and the generation rate and maximum ClO_2 gas concentration were controlled using diatomaceous earth (DE) and calcium chloride ($CaCl_2$). Under 90% RH conditions, sustained release of ClO_2 gas was achieved in presence of DE. When 12 g of DE was added to the mixture, the ClO_2 gas concentration remained constant at 18 ± 1 ppmv for approximately 28 h. At 50% RH, addition of $CaCl_2$ was effective in maintaining a constant ClO_2 gas concentration. When 0.05 g of $CaCl_2$ was added to mixtures containing 0.5 g of DE, ClO_2 gas concentration remained constant at 11 ± 1 ppmv for approximately 26 h. Treatment with 30 ppmv of ClO_2 gas at 90% RH achieved more than 6.16 and 5.48 log reductions of *E. coli* O157:H7 and *S.* Typhimurium on spinach leaves (in 15 min), and more than 6.78 and 6.34 log reductions of the same in tomatoes (in 10 min). The sustained release formulations for ClO_2 gas, developed in this study, could facilitate the use of ClO_2 gas as an antimicrobial agent in the food industry.

Keywords

Chlorine dioxide, sustained release, *Escherichia coli* O157:H7, *Salmonella* Typhimurium, produce

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INTRODUCTION

Chlorine dioxide (ClO_2) is emerging as a promising chemical for the decontamination of produce and food contact surfaces (Aieta et al., 1984; Trinetta et al., 2012). It is a strong oxidizing agent and has a broad antimicrobial spectrum. Its efficacy is not greatly affected by either organic matter or pH. The use of aqueous ClO_2 in washing fruits and vegetables and disinfecting meat and poultry has already been approved by the U.S. EPA and U.S. FDA. ClO_2 gas has also been approved for sanitizing environmental surfaces, laboratory equipment, and tools, and for cleaning rooms (U.S. EPA, 2015).

Several studies have reported the antimicrobial effect of ClO_2 gas against foodborne pathogens found in spinach (Neal et al., 2012; Park and Kang, 2015), potatoes (Wu and Rioux, 2010), apples (Du et al., 2002), tomatoes (Trinetta et al., 2013), lettuce (Mahmoud and Linton, 2008), cantaloupe (Mahmoud et al., 2008), mung bean sprouts (Prodduk et al., 2014), cabbage (Sy et al., 2005), and strawberries

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(Han et al., 2004). The antimicrobial effect of ClO_2 gas has also been evaluated against foodborne pathogens on food contact surfaces, including wood, plastic (Han et al., 2003), stainless steel (Trinetta et al., 2012; Vaid et al., 2010), polyvinyl chloride, and glass (Li et al., 2012; Morino et al., 2011).

Although ClO_2 gas has a remarkable antimicrobial effect, along with several advantages over aqueous sanitizers, some factors still limit its widespread application in disinfection facilities (Stubblefield and Newsome, 2015). First, ClO_2 gas needs to be generated at the application site owing to its instability during storage. The gas generation typically requires sophisticated equipment and trained personnel (Stubblefield and Newsome, 2015). Although several on-site ClO_2 gas generation methods, without equipment, have been suggested, they have not been applied in the food industry (Engelhard Corporation, 2001; Fred, 2002; Isaac and Tenney, 2014; Yang and Kim, 2005). Sachets that generate ClO_2 gas are often used to inactivate foodborne pathogens on foods; however, they release too much ClO_2 gas in a short time, and there is no control on the generation rate (Mitchell et al., 2019; Popa et al., 2007; Sy et al., 2005; Wu and Rioux, 2010).

Recently, several studies have focused on the stabilization and sustained release of ClO_2 gas. Chen et al. (2020) have reported an encapsulation method for ClO_2 gas by α-cyclodextrin, using which, the release rate could be relatively slowed down compared to that by other systems reported in the literature. A polymeric ClO_2 releasing sheet has also been developed using poly (ether-block-amide) and polyvinyl alcohol, which may be applied to prolong post-harvest life of cherry tomatoes (Sadeghi et al., 2020). Zhang et al. (2019) had evaluated the efficacy of ClO_2 microcapsule antibacterial films for the preservation of mangoes.

This study aimed to develop formulations that could ensure consistent release of low-concentration ClO_2 gas, as appropriate for food application. Subsequently, the antimicrobial effects of ClO_2 gas from the formulations were evaluated against *Escherichia coli* O157:H7 and *Salmonella* Typhimurium on spinach leaves and tomatoes.

MATERIALS AND METHODS

Development of formulations for ClO_2 gas generation

Sodium chlorite ($NaClO_2$), citric acid, diatomaceous earth (DE) (Samchun Chemical Co. Ltd., Pyeongtaek-si, South Korea), and calcium chloride dihydrate ($CaCl_2$) (Junsei chemical Co. Ltd., Tokyo, Japan) were the chemicals used in this study. Table 1 lists the formulations used in this study.

Release profile of ClO_2 gas from mixtures affected by relative humidity (RH) conditions

ClO_2 gas generation mixtures were thoroughly mixed in Petri dishes (90 × 15 mm; SPL Life Sciences, South Korea) and placed in the treatment chamber (length- × width × height, 0.7 m × 0.5 m × 0.6 m). The RH of the treatment chamber was adjusted to 50 ± 2% or 90 ± 2% using 1 L of saturated aqueous salt solutions. Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) (Samchun Chemical Co. Ltd.) and sodium carbonate decahydrate ($Na_2CO_3{\cdot}10H_2O$) (Junsei Chemical Co. Ltd.) were used to create 50% and 90% RH conditions, respectively. ClO_2 gas concentration in the treatment chamber was continuously monitored using a ClO_2 gas transmitter (ATi F12, Analytical Technology, U.K.) for up to 36 h at 22 ± 1 °C. The RH and temperature in the treatment chamber were recorded using a thermohygrometer (SE-342, Center Technology Corp., Taiwan).

Bacterial cultures and cell suspension

E. coli O157:H7 (ATCC 35150, ATCC 43889, and ATCC 43890) and *S.* Typhimurium (ATCC 19585, ATCC 43971, and DT 104) were obtained from the bacterial culture collection of the School of Food Science, Seoul National University (Seoul, South Korea). Each strain was cultured individually in 5 mL of tryptic soy broth (TSB; Difco) for 24 h at 37 °C, harvested by centrifugation at 4000 × g for 20 min at 4 °C, and finally washed thrice with buffered peptone water (BPW; Difco). The final pellets were resuspended in BPW, corresponding to approximately 10^7–10^8 CFU/ml. Mixed culture cocktails containing

Table 1. Mixture composition for generating ClO_2 gas at 50 and 90% RH.

Mixture No.	RH condition	Composition (g)			
		$NaClO_2$	Citric acid	Diatomaceous earth	$CaCl_2$
1	50 %	0.25	0.14	–	–
2		0.25	0.14	0.5	–
3		0.25	0.14	0.35	–
4		0.25	0.14	0.5	0.05
5		0.25	0.14	0.35	0.05
6	90 %	0.25	0.14	–	–
7		0.25	0.14	3	–
8		0.25	0.14	6	–
9		0.25	0.14	7.5	–
10		0.25	0.14	9	–
11		0.25	0.14	12	–

approximately equal number of cells of *E. coli* O157:H7 and *S.* Typhimurium were prepared by combining suspended pellets of the two pathogens.

Sample inoculation

Spinach and tomatoes were purchased from a local market (Seoul, South Korea) on the day of the experiments. Both spinach and tomatoes were washed in running water, placed on aluminum foil in a laminar flow biosafety hood ($22 \pm 2\,^{\circ}C$), and dried for 1 h before the experiments. Spinach leaves and outer surface of tomatoes were cut into approximately 5×3 and 5×2 cm pieces, respectively. A culture cocktail (0.1 ml) was inoculated onto one side of the prepared spinach leaves and tomato surfaces by depositing droplets (with a micropipette) at 15–20 locations. After inoculation, samples were dried in a laminar flow biosafety hood for 1 h at $22 \pm 2\,^{\circ}C$ with the fan running.

ClO_2 gas treatment and bacterial enumeration

ClO_2 gas was generated using mixtures No. 4 and 7 (Table 1) in the treatment chamber under conditions of 50% and 90% RH, respectively. When the desired ClO_2 gas concentration (10 or 30 ppmv) was achieved, the inoculated samples were placed in the treatment chamber and treated with ClO_2 gas for up to 20 min at 50 or 90% RH and $22 \pm 1\,^{\circ}C$.

After ClO_2 gas treatment, spinach leaves (10 ± 0.2 g) and one piece of tomato were taken from the treatment chamber and immediately transferred into sterile Stomacher strainer bags (Labplas Inc., Sainte-Julie, Quebec, Canada) containing 90 or 30 ml of neutralizing buffer (Difco), respectively. Stomacher bags were homogenized for 2 min with a Stomacher (easyMIX, AES CHEmunEx, Rennes, France). Aliquots of the homogenized mixture (1 ml) were 10-fold serially diluted with 9 ml of BPW, and 0.1 mL of appropriate diluents were spread-plated onto sorbitol MacConkey agar (Difco) and Xylose Lysine Desoxycholate agar (Difco) for enumeration of *E. coli* O157:H7 and *S.* Typhimurium, respectively. In case of low levels of surviving cells, 1 ml of undiluted Stomacher bag contents was equally divided into 0.25 ml portions and distributed between the four plates of each medium and spread-plated. All plates were incubated at $37\,^{\circ}C$ for 24–48 h, and colonies were counted and calculated as log CFU/g and log CFU/cm^2 for spinach leaves and tomatoes, respectively.

Statistical analysis

All experiments were replicated three times. Data were analyzed by ANOVA suing the Statistical Analysis System (SAS Institute, Cary, NC, USA), and separation of means by Duncan's multiple range test. A value of $p < 0.05$ was used to indicate significant differences.

RESULTS

Release of ClO_2 gas from the mixture affected by RH

The ClO_2 gas concentrations generated from mixtures at 50% RH are shown in Figure 1. A come-up time of approximately 1.5–2 h was observed for all the tested mixtures at 50% RH. ClO_2 gas generated from a mixture containing $NaClO_2$ and citric acid reached 27 ppmv within approximately 6.5 h and then gradually decreased to 16 ppmv after 36 h. Maximum ClO_2 gas concentrations were reduced to 7 and 14 ppmv by the addition of 0.5 and 0.35 g of DE, respectively. ClO_2 gas generated from these mixtures slightly decreased to 4 and 11 ppmv, respectively, after 36 h. A more consistent release of ClO_2 gas was achieved by the addition of $CaCl_2$ to the mixtures. ClO_2 gas generated from a mixture containing 0.5 g of DE and 0.05 g of $CaCl_2$ reached 11 ppmv and maintained consistency from approximately 9.8 to 36 h. When 0.05 g of $CaCl_2$ was used in a mixture containing 0.35 g of DE, ClO_2 gas concentration remained constant at 16 ± 1 ppmv from approximately 12.5 to 36 h. The ClO_2 gas concentrations generated from mixtures at 90% RH are shown in Figure 2. A mixture containing only $NaClO_2$ and citric acid generated 31 ppmv ClO_2 gas within approximately 3.2 h and the ClO_2 gas concentration rapidly decreased to 2 ppmv after 36 h. The rate of ClO_2 gas generation could be delayed by the addition of DE to this mixture. A mixture containing 7.5 g of DE released 30 ppmv ClO_2 gas within approximately 15.2 h and the gas concentration gradually decreased to 22 ppmv after 36 h. ClO_2 gas, generated from a mixture containing 9 g of DE, reached 26 ppmv, and remained relatively constant from 13.2 to 36 h. ClO_2 gas concentration, generated with mixture containing 12 g of DE, reached 18 ± 1 ppmv and remained constant from 7.8 to 36 h, although maximum ClO_2 gas concentration dropped to 19 ppmv.

Inactivation of E. coli O157:H7 and *S.* Typhimurium on produce by ClO_2 gas

Reduction in the number of *E. coli* O157:H7 and *S.* Typhimurium on spinach leaves and tomatoes, during treatment with ClO_2 gas generated from the mixture, is presented in Tables 2 to 4. Treatment with 10 ppmv of ClO_2 gas for 20 min at 50% RH resulted in 1.02 and 1.16 log reductions, and 1.02 and 1.14 log reductions of *E. coli* O157:H7 and *S.* Typhimurium

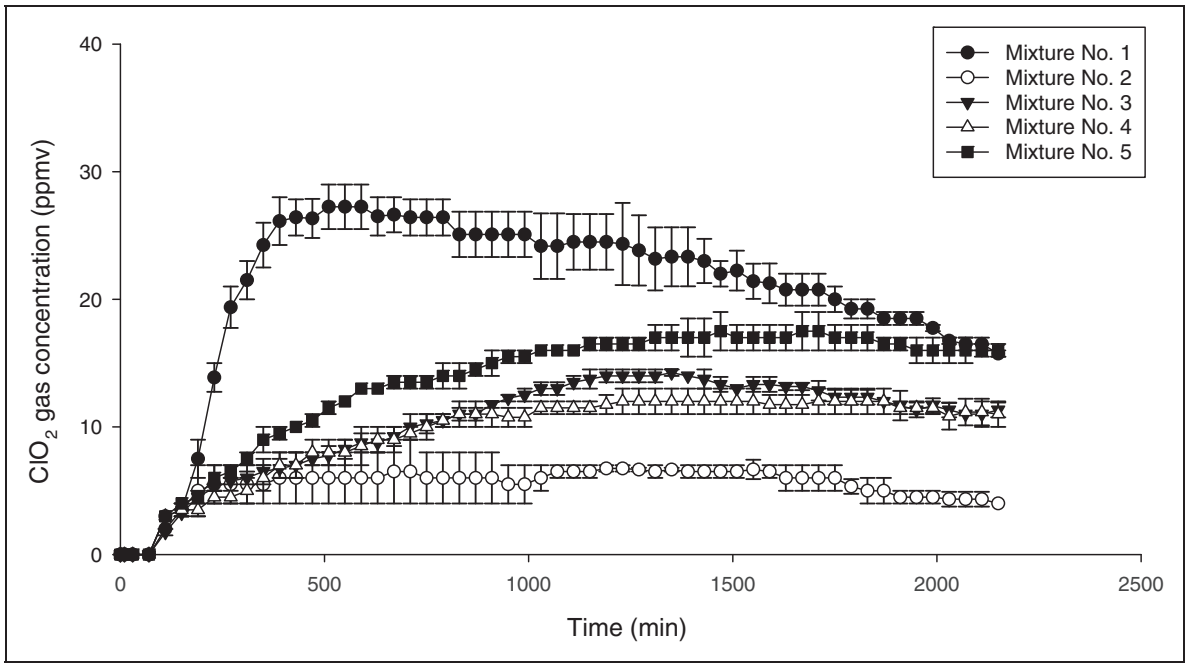

Figure 1. ClO_2 gas concentration released from mixtures into the treatment chamber at 50% RH for up to 36 h. The test was replicated at least three times.

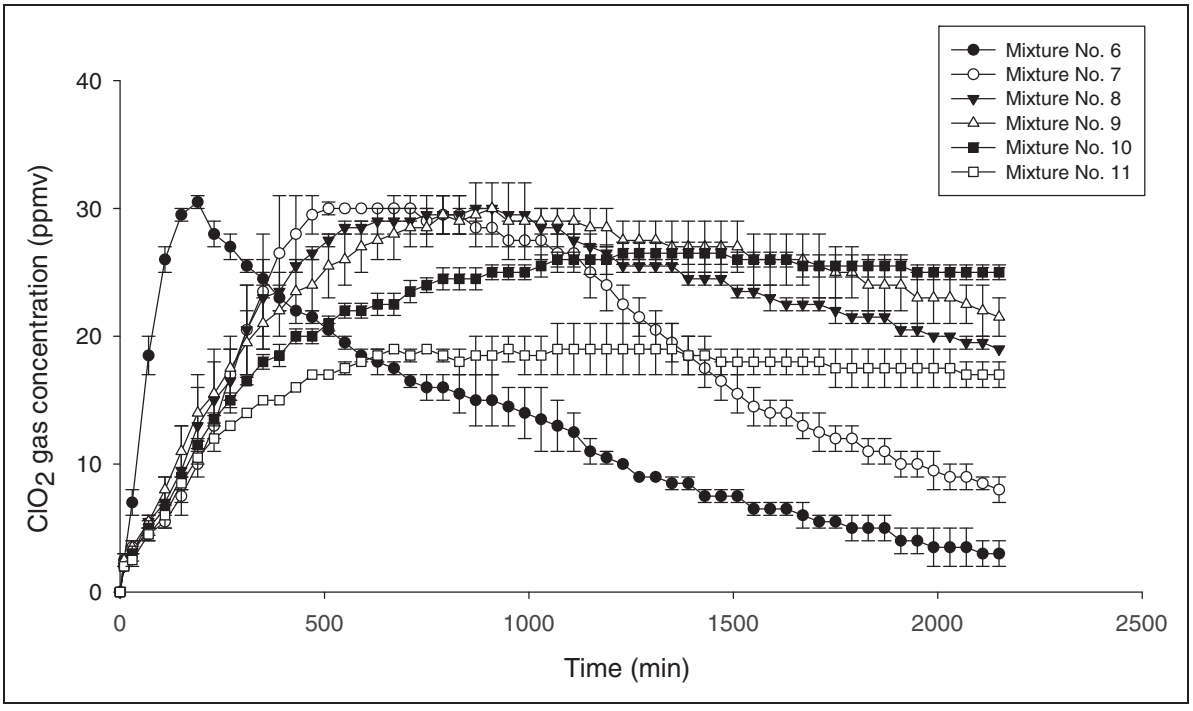

Figure 2. ClO_2 gas concentration released from mixtures into the treatment chamber at 90% RH for up to 36 h. The test was replicated at least three times.

on spinach leaves (Table 2) and tomatoes, respectively. Exposure to 10 ppmv ClO_2 gas for 20 min at 90% RH caused 3.76 and 3.39 log reductions, and 4.38 and 4.39 log reductions of *E. coli* O157:H7 and *S.* Typhimurium on spinach leaves and tomatoes, respectively (Table 3). Treatment with 30 ppmv of ClO_2 gas for 15 min at 90% RH achieved more than 6.16 and 5.48 log reductions of *E. coli* O157:H7 and *S.* Typhimurium on spinach leaves

Table 2. Log reductions[a] of *E. coli* O157:H7 and *S*. Typhimurium on spinach leaves and tomatoes after treatment with 10 ppmv ClO_2 gas generated by mixtures at 50% RH.

	Spinach leaves		Tomatoes	
	Log reduction (log CFU/g)		Log reduction (log CFU/cm^2)	
Treatment time	*E. coli* O157:H7	*S*. Typhimurium	*E. coli* O157:H7	*S*. Typhimurium
5 min	0.79 ± 0.46A[b]	0.87 ± 0.29A	0.74 ± 0.12A	0.95 ± 0.08AB
10 min	0.80 ± 0.58A	0.98 ± 0.20A	0.73 ± 0.11A	0.92 ± 0.10A
15 min	0.96 ± 0.36A	1.00 ± 0.07A	0.92 ± 0.29A	1.01 ± 0.16AB
20 min	1.02 ± 0.45A	1.16 ± 0.05A	1.02 ± 0.17A	1.14 ± 0.06B

[a]Log reduction = population before treatment − population after treatment. Populations of *E. coli* O157:H7 before treatment were 6.15 log CFU/g and 6.97 log CFU/cm^2 on spinach and tomatoes, respectively. Populations of *S.* Typhimurium before treatment were 6.10 log CFU/g and 6.51 log CFU/cm^2 on spinach and tomatoes, respectively.
[b]Means with different uppercase letters within a row are significantly different ($p < 0.05$).

Table 3. Log reductions[a] of *E. coli* O157:H7 and *S*. Typhimurium on spinach leaves and tomato after treatment with 10 ppmv ClO_2 gas generated by mixtures at 90% RH.

	Spinach leaves		Tomatoes	
	Log reduction (log CFU/g)		Log reduction (log CFU/cm^2)	
Treatment time	*E. coli* O157:H7	*S*. Typhimurium	*E. coli* O157:H7	*S*. Typhimurium
5 min	1.74 ± 0.18A[b]	1.89 ± 0.33A	1.25 ± 0.03A	1.37 ± 0.18A
10 min	2.30 ± 0.24AB	2.48 ± 0.35B	1.75 ± 0.09B	1.78 ± 0.06A
15 min	2.72 ± 0.22B	2.93 ± 0.32BC	3.28 ± 0.28C	3.05 ± 0.25B
20 min	3.76 ± 0.49C	3.39 ± 0.10C	4.38 ± 0.21D	4.39 ± 0.36C

[a]Log reduction = population before treatment − population after treatment. Populations of *E. coli* O157:H7 before treatment were 6.37 log CFU/g and 7.01 log CFU/cm^2 on spinach and tomatoes, respectively. Populations of *S.* Typhimurium before treatment were 6.23 log CFU/g and 6.66 log CFU/cm^2 on spinach and tomatoes, respectively.
[b]Means with different uppercase letters within a row are significantly different ($p < 0.05$).

Table 4. Log reductions[a] of *E. coli* O157:H7 and *S*. Typhimurium on spinach leaves and tomatoes after treatment with 30 ppmv ClO_2 gas generated by mixtures at 90% RH.

	Spinach leaves		Tomatoes	
	E. coli O157:H7		*S*. Typhimurium	
Treatment time	*E. coli* O157:H7	*S*. Typhimurium	*E. coli* O157:H7	*S*. Typhimurium
1 min	1.35 ± 0.17A[b]	1.56 ± 0.17A	1.26 ± 0.23A	1.15 ± 0.33A
5 min	2.06 ± 0.06B	1.96 ± 0.11A	2.52 ± 0.36B	2.68 ± 0.12B
10 min	4.39 ± 0.11C	3.54 ± 0.59B	>6.78 C	>6.34 C
15 min	>6.16 D	>5.48 C	>6.78 C	>6.34 C

[a]Log reduction = population before treatment − population after treatment. Populations of *E. coli* O157:H7 before treatment were 6.08 log CFU/g and 6.68 log CFU/cm^2 on spinach and tomatoes, respectively. Populations of *S.* Typhimurium before treatment were 6.45 log CFU/g and 7.15 log CFU/cm^2 on spinach and tomatoes, respectively.
[b]Means with different uppercase letters within a row are significantly different ($p < 0.05$).

(Table 4). On the other hand, exposure of tomatoes to 30 ppmv of ClO_2 gas for 10 min at 90% RH caused more than 6.78 and 6.34 log reductions of *E. coli* O157:H7 and *S*. Typhimurium, respectively.

DISCUSSION

ClO_2 gas is commonly generated by the reaction of $NaClO_2$ with acids or $FeCl_3$ (both aqueous and dry precursors can be used). Chai et al. (2020) have

evaluated the feasibility and efficacy of using ClO_2 gas, generated by dry precursors ($NaClO_2$ and $FeCl_3$) and dry $NaClO_2$ and aqueous HCl dosage methods, for the inactivation of pathogens on produce. The results have shown ClO_2 gas generation rate to be more easily controllable when dry precursors are used to produce the gas. Buckley et al. (2020) have produced ClO_2 gas by combining powdered $NaClO_2$ and citric acid, and quantitatively evaluated ClO_2 production under different temperature conditions. Powdered $NaClO_2$ and citric acid released significantly less ClO_2 gas at low temperatures, and required water to produce the gas. This implied that humidity could affect the quantification of ClO_2 gas production. Similar to the findings from a previous study, RH conditions significantly affected the release of ClO_2 gas from the mixture, in our study. ClO_2 gas was more rapidly generated at 90% RH than that at 50% RH, from mixtures containing only $NaClO_2$ and citric acid. $NaClO_2$ and citric acid seemed to easily dissolve and react more rapidly at 90% RH, owing to the greater moisture content in the treatment chamber, and the rapid release of ClO_2 gas. For practical applications, it would be necessary to control the ClO_2 gas generation rate under different RH conditions.

In this study, DE, which is a soft, friable, very fine-grained, siliceous sedimentary rock, created by the deposition of fossilized single-cell algae on the ocean and fresh water beds, was used to induce the sustained release of ClO_2 gas (Janićijević et al., 2014). DE presents a highly porous, yet rigid, amorphous silica skeletal framework, whose frustules vary in size, shape, and architecture, depending on a diverse array and species of diatoms (Akhtar et al., 2009; Janićijević et al., 2014). DE has a wide spectrum of applications, such as filters, drug delivery, and removal of heavy metals or pollutants, owing to its low cost, well-defined porosity, and low density (Arik, 2003; Caliskan et al., 2011; Janićijević et al., 2014; Martinovic et al., 2006; Zhang et al., 2011). DE can absorb and gradually release water due to its porous structure, thereby delaying the rapid reaction between $NaClO_2$ and citric acid. DE can also absorb ClO_2 gas and release it slowly thereafter. The use of DE in the generation mixture could hence control the generation rate and the maximum concentration of ClO_2 gas at 90% RH.

In the present study, $CaCl_2$, a salt adsorbent, had greater hygroscopic capacity than organic adsorbents, and was used to achieve a more consistent release of ClO_2 gas at low RH conditions (Zhang and Qiu, 2007). At 50% RH, a more consistent ClO_2 gas concentration was maintained due to the addition of both DE and $CaCl_2$ in the mixture. $CaCl_2$ seemed to facilitate a more regulated reaction of $NaClO_2$ with citric acid by absorbing water, under conditions of lower RH.

ClO_2 gas, generated from mixtures, had a significant effect on the inactivation of *E. coli* O157:H7 and *S.* Typhimurium on spinach leaves and tomatoes. The levels of reduction of *E. coli* O157:H7 and *S.* Typhimurium, due to the treatment with ClO_2 gas (generated by mixtures) were not significantly ($p > 0.05$) different from those achieved by a lab-scale ClO_2 gas generation system (Park and Kang, 2015). This implied that mixture-generated ClO_2 gas exerts the same effect in inactivating foodborne pathogens as ClO_2 gas generated by a lab-scale system.

CONCLUSIONS

Gaseous antimicrobial agents are ideal for commercial antimicrobial applications owing to their rapid spread from the releasing system onto food or food contact surfaces. However, the generation rate of gaseous antimicrobial agents needs to be controlled, in order to represent optimal antimicrobial effects, without adverse impact on food quality. In this study, we developed formulations for the generation and sustained release of ClO_2 gas using $NaClO_2$, citric acid, DE, and $CaCl_2$. RH conditions affected the ClO_2 gas release profile, and the generation rate and maximum ClO_2 gas concentration could be controlled using DE and $CaCl_2$. In addition, ClO_2 gas produced by mixtures showed a significant effect in inactivating *E. coli* O157:H7 and *S.* Typhimurium on food or produce surfaces. Although the developed ClO_2 gas-generating mixture could be used for food storage and food transportation, further studies would be required to optimize the packaging conditions of the mixture for practical application.

Declaration of conflicting interests

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