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Effect of gaseous chlorine dioxide treatment on the quality of rice and wheat grain

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ABSTRACT

Gaseous chlorine dioxide (ClO_2), which is a strong disinfecting agent with strong oxidation properties and penetration ability, is used to control insect pests and fungal contamination in stored grains. However, the effect of gaseous ClO_2 on stored grain has yet to be reported. In the present study, we exposed rice and wheat seeds to several concentrations of ClO_2 gas for various durations and found that the viability of rice was affected less than that of wheat. After 100 ppm of gaseous ClO_2 for 12 h, the normal rice seedling rate was not significantly different than that of the control. However, that of wheat was significantly decreased. We also measured the ClO_2 residueon stored rice and wheat after 200 ppm of gas treatment for 24 h. After 10 days of storage following the treatment, ClO_2 and chlorine were not detected on either rice or wheat. Chlorite was detected on rice at 0.22 mg/kg of grain; however, it was not detected on wheat. These results suggest that gaseous ClO_2 treatment affects the viability of rice and wheat seed but leaves minimal chemical residue.

1. Introduction

Stored grains, such as rice and wheat, are threatened by insect pests and contamination by mycotoxin-producing fungi (Baoua et al., 2015; Magan et al., 2003). Methyl bromide and phosphine fumigation can be used to successfully control these organisms (Bell and Glanville, 1973; Hocking and Banks, 1991). Several studies have demonstrated that phosphine does not effectively disinfect fungi on grains (USAID, 2014). However, these chemicals are ozone-depleting substances for which the Montreal Protocol recommended phase-out by 2015 (UNEP, 2006). In addition, methyl bromide is both carcinogenic and neurotoxic (Bulathsinghala and Shaw, 2014), whereas phosphine is toxic to warm-blooded animals (Jittanun and Chongrattanameteekul, 2014) and has experienced diminished efficacy, owing to the widespread development of resistance (Boyer and Zhang, 2012).

Chlorine dioxide (ClO_2) is a potential alternative to these chemicals. It is a strong disinfectant with oxidizing properties and is effective against insects, bacteria, fungi, and viruses (Gordon and Rosenblatt, 2005; Kumar et al., 2015) and is generally used in aqueous or gaseous forms (Choi et al., 2016; Han et al., 2001, 2016; Xinyi et al., 2017). Recently, the application of gaseous ClO_2 has increased, owing to its greater efficacy as an antimicrobial agent, when compared to equal levels of aqueous ClO_2 (Lee et al., 2015). Indeed, gaseous ClO_2 has high penetration and solubility properties (Du et al., 2002) that enable it to reach microorganisms that are protected from the aqueous form by biofilms (Wu and Rioux, 2010). In addition, gaseous ClO_2 treatment effectively controls all stages of *Plodia interpunctella*, which is one of the most important pests of stored food (Han et al., 2016), and may be an effective alternative to methyl bromide during storage (Kumar et al., 2015).

The National Primary Drinking Water Regulations (NPDWR) for disinfectant and disinfection byproducts established a maximum residual disinfectant level for ClO_2 of 0.8 mg/L and a Maximum Contaminant Level (MCL), which is the highest level of a contaminant allowed in drinking water for chlorite ions of 1.0 mg/L, based on the oral reference dose for chlorite. However, the effect of gaseous ClO_2 treatment on the quality and residues on stored

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grain has yet to be reported. Accordingly, the aim of the present study was to determine the effects of ClO_2 concentration and treatment duration on the viability and chemical residues on rice and wheat grains.

2. Material and methods

2.1. Seed preparation

Rice (*Oryza sativa* L. 'Sindongjin') and wheat (*Triticum aestivum* L. 'Baegjoong') grains were cultivated and harvested from the Korea University Farm (Deokso, Korea) in 2010 and were stored at 4 °C until used.

2.2. Chlorine dioxide treatment

Gaseous ClO_2 was generated electrochemically using a chlorine dioxide generator (PurgoFarm Co., Ltd., Hwasung, Korea; Gates, 1998). Briefly, aqueous $NaClO_2$ was electrolyzed, and the cleaved sodium ions migrated to the cathode through a patented multi-porous membrane electrode assembly, leaving highly pure ClO_2 (>99%) in the anode chamber.

Anode (oxidation): $ClO_2^- \rightarrow ClO_2 + e^-$

Cathode (reduction):$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Gaseous ClO_2 was blown through a vent into the test chamber (54 × 44 × 46 cm), and the flow of gas into the chamber was automatically controlled by the preset concentration of ClO_2, which was monitored continuously using a PortaSens II gas leak detector (Analytical Technology, Collegeville, PA, USA). Every 600 g of pre-selected rice seed and wheat seed were single layered on a sieve that was treated with one of the tested concentrations. Grains were exposed 0, 6, 12, 24, and 48 h to 50 ppm, 100 ppm, and 200 ppm of ClO_2 gas.

2.3. Seed test

Seed tests were performed after applying the gas treatments. Before gas treatments, seeds were pre-selected. For each treatment group, three replications of 100 seeds each were germinated between seed germination paper damped with 100 mL distilled water in a germination test box (20 × 15 × 5 cm). The seeds were germinated at 80% relative humidity and 25 °C in the dark over a period of 7 d, after which the germination rate was recorded. The seedlings were classified as normal seedlings, abnormal seedlings, fresh seed, hard seed, or dead seed, according to standard International Rules for Seed Testing (2010).

2.4. Residue analysis

After treatment with 200 ppm gaseous ClO_2 for 24 h, 100 g rice and wheat samples were rinsed with 900 mL distilled water, to remove any remaining ClO_2 and byproducts, and an AutoCAT 9000 (Hach Co., Loveland, CO, USA) was used to measure the remaining ClO_2 and byproducts in the rinsate, according to manufacturer's instruction. Briefly, a multi-step procedure involving four titrations at different pHs and using C_6H_5AsO (phenyl arsine oxide, PAO) solution at 0.00564 N as the titrator, was conduted to determine the concentration, between 0.10 and 5.00 mg/L, of ClO_2, chlorine and chlorite from two 200 mL samples. These titrations were as follows:

Sample 1

Titraion 1 → $Cl_2 + 1/5\ ClO_2$

Titraion 2 → $4/5\ ClO_2 + ClO_2^-$

Sample 2

Titraion 3 → Cl_2 (not volatized by a nitrogen gas purge)

Titraion 4 → ClO_2^-

2.5. Statistical analysis

All experiments were established as a completely randomized design and conducted with three replicates of 100 seeds each for the seed test and three replicates each for the residue analysis. Data were analyzed using the Statistical Analysis System software 9.4 (SAS Institute, Cary, NC, USA). Percentage data for the seed test were statistically analyzed after arcsine-root transformation, and an analysis of variance (ANOVA) was performed using general linear model procedures, whereas the means were separated using the least significant difference test at $P < .05$.

3. Results

3.1. Effect of 50 ppm gaseous ClO_2 on rice and wheat seed

The seed testing results for seeds treated with 50 ppm gaseous ClO_2 are given in Table 1. For rice, the rates of normal seedlings, abnormal seedling, fresh seed, dead seed, and hard seed were not significantly ($P > .05$) different from that of the untreated seeds. However, for wheat, ClO_2 treatment reduced the normal seedling rate, but it was not significant ($P > .05$). In addition, abnormal seedlings were not significant ($P > .05$) higher. There was a significant ($P < .05$) increase in the fresh seed with increasing treatment time, but this did not significantly ($P > .05$) affect hard seed rate. For wheat, there were no dead seed at 50 ppm gaseous ClO_2 treatment for all treatment times. The test statistics and P values of all germination tests are shown in Table 1.

3.2. Effect of 100 ppm gaseous ClO_2 on rice and wheat seed

The seed testing results for the seeds treated with 100 ppm gaseous ClO_2 are given in Table 2. For rice, the rates of normal seedlings treated for 6 h with 100 ppm gaseous ClO_2 were significantly ($P < .05$) increased compared with treatment for 12 h, 24 h, and 48 h. However, it is not significantly ($P > .05$) different than that of the control. For the control, 12 h, 24 h, and 48 h treatments, normal seedlings were not significantly ($P > .05$) different. The percentage of abnormal seedlings, fresh seed, dead seed, and hard seed were not significantly ($P > .05$) different compared with that of the control. For wheat, normal seedling rates were significantly ($P < .05$) different after 12 h of treatment compare with that of the control. Abnormal seedling rates were significantly ($P < .05$) different compared with that of the control at 12 h and 24 h, but were not significantly ($P > .05$) different at 6 h and 48 h. Fresh seed rates were significantly ($P < .05$) increased. Dead seed and hard seed percentages were not significantly ($P > .05$) different compare with that of the control. There were no dead seed and hard seed for gaseous ClO_2 treated wheat. The test statistics and P values of all of other germination tests are shown in Table 2.

3.3. Effect of 200 ppm gaseous ClO_2 on rice and wheat seed

The seed testing results of the seeds treated with 200 ppm gaseous ClO_2 are given in Table 3. For rice, normal seedling rates were significantly ($P < .05$) decreased. Abnormal seedling and hard