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Degradation of pesticide residues by gaseous chlorine dioxide on table grapes

Jia Wei[a,b], Yan Chen[a], Atawula Tiemur[b], Jide Wang[a,*], Bin Wu[b,*]

[a] College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, People's Republic of China
[b] Institute of Commodity Storage and Processing Xinjiang Academy of Agricultural Science, Urumqi, Xinjiang 830091, People's Republic of China

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A B S T R A C T

The use of gaseous chlorine dioxide (ClO_2) as a strong oxidant to degrade the pesticide residues on the table grapes was studied. ClO_2 releasing process in the sealed box was investigated. The grapes were sprayed with three pesticides and fumigated by ClO_2. After 27 d storage in 0 °C, the remaining rates of tebuconazole, azoxystrobin, dimethomorph (E) anddimethomorph (Z) on grapes were 65.33, 50.71, 39.48 and 41.06% by ClO_2-treatment, respectively. The degradation difference showed that the effect of ClO_2 on pesticide residues were dissimilar. The products formed during the ClO_2 treatment of pesticides were analyzed by GC–MS analysis and the possible mechanism of the degradation was proposed. In the meantime, the postharvest quality of table grapes was also evaluated. These results showed that ClO_2 has great potential application in table grapes industry.

1. Introduction

The grape is a non-climacteric fruit which is widely cultivated around the world. The fungal disease is one of the major problems during growth and postharvest storage in vineyard (Grimalt and Dehouck, 2016), such as gray mold, downy mildew and powdery mildew (Noguerol-Pato et al., 2014), which make a great deal of losses in the grape industry every year. So in modern agricultural practices, the application of pesticides is an essential way to keep and increase grape productivity. Tebuconazole, azoxystrobin and dimethomorph (Scheme 1) are three most common used pesticides in grape cultivation, since they are extremely effective for the control of various fungal diseases existed on the grapes.

Despite the benefits for agriculture, the hazardous effects caused by pesticides have received more and more attention in recent years. Although pesticides left on the surface of vegetables and fruits can be partly degraded under sunlight in the field, residues can still be detected (Shabeer et al., 2015), which are harmful for human, animals as well as the environment (Wang et al., 2017). Moreover, it is hard for pesticide degradation in a dark and cold environment when some agricultural products are stored in refrigerators. So many technologies have been applied on pesticide degradation.

Oxidation, one of a chemical process, is the most commonly used method in industry. The oxidants reacts with compound through attacking the oxidative molecule or producing free radicals, such as hydroxyl and superoxide anion. These radicals would react with oxygen forming peroxy radicals which start the beginning of oxidative organic compounds reaction, leading to the pesticide degradation (Agüera and Fernández-Alba, 1998).

As a powerful oxidant, chlorine dioxide (ClO_2) is common in water purification and waste water treatment because it can effectively reduce many organic contaminants. The reaction between ClO_2 and organic compounds has been broadly researched, including antipyrine (Jia et al., 2017), diclofenac (Wang et al., 2014), phenylurea herbicides (chlortoluron, isoproturon and diuron) (Tian et al., 2014), phorate and diazinon (Chen et al., 2014). The oxidation is the major chemical step to degrade organic chemicals instead of chlorine substitution reaction (Jia et al., 2017), so there is no chlorine disinfection by-products which are carcinogenic, teratogenetic and mutagenic. On the other hand, ClO_2 is also used widely for postharvest application in fruits and vegetables. It is proved that ClO_2 is highly effective in product preservation, such as carrots (Gómez-López et al., 2007), tomato (Guo et al., 2014), strawberry (Trinetta et al., 2013) and blueberry (Sun et al., 2014).

Based on these advantages, ClO_2 is used to degrade the pesticide residues on fresh vegetables and fruits. Chen (Chen et al., 2014) reported that ClO_2 could decrease the remaining of phorate and diazinon on fresh lettuce by 40–80% and 10–20% than that in tap water, respectively. However, most studies pay more attention to the reaction between ClO_2 and pesticide in aqueous solution condition, few report has been found to examine the possibility of gaseous ClO_2 on decline of

* Corresponding authors.
E-mail addresses: awangjd@126.com (J. Wang), xjuwubin0320@sina.com (B. Wu).

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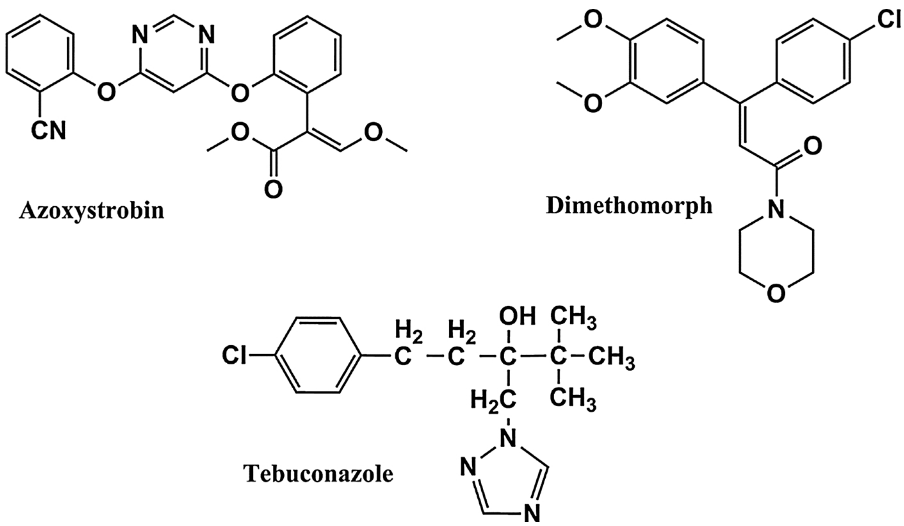

Scheme 1. Chemical structure of tebuconazole, azoxystrobin and dimethomorph.

the pesticide residues.

The primary aim of our study was to investigate the possible degradation of three pesticides by gaseous ClO_2 on grapes in storage condition. Furthermore, it would provide valuable information for the safe use of ClO_2 and postharvest techniques for the grape industry. In fact, gaseous ClO_2 has showed the effectiveness on delaying the storage of fruits and vegetables.

2. Materials and methods

2.1. Chemicals

Solid ClO_2 powder was supplied by Beijing Startech Science & Technology Co. Ltd. Tebuconazole, azoxystrobin and dimethomorph were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The HPLC-grade methanol was obtained from Sigma-Aldrich Chemie GmbH (Deisenhofen, Germany). Sodium chloride, potassium iodide and starch were of analytical grade and obtained from Guangfu Technology Development Co. Ltd (Tianjing, China). Standard potassium bichromate was purchased from National Standard Material Research Center (Beijing, China).

2.2. Pesticide treatment of grapes

The Red Globe grapes were grown in the vineyards in Changji, Xinjiang Province, China. The grapes were sprayed with pesticide solutions that contained 0.086 g $L^{-1}$of tebuconazole (Gansu Huashi Agrotech Ltd), 1.5 g L^{-1} of azoxystrobin (Jingbo Agrochemicals Technology Co. Ltd) and 0.42 g L^{-1} of dimethomorph (Shanghai Hulian Biological Pharmaceutical Co. Ltd). Pesticide concentration was calculated according to their maximum recommended concentration on the label and water volume of 900 L per hectare. After pesticide treatment, about 20 kg berries were dried in the field for 24 h. Then the grapes were harvested and transported to cold storage at 0 °C (95% RH) for precooling in the Xinjiang Institute of Agro-products Storage and Processing.

2.3. ClO_2 gas release and determination

The release of gas was achieved by reaction between water and ClO_2 powder. A 250 mL beaker with 55.00 g solid ClO_2 powder was put into a sealed box. The box (dimension of 60 (*W*) × 80 (*L*) × 100 (*H*) cm, 480 L) was made of polymethylmethacrylate (PMMA) and was transparent. A fan was settled in the box to make the ClO_2 gas diffuse more quickly and homogeneously. The whole system was put into a dark house to avoid photolysis of ClO_2. After 100 mL deionized water was added, the door of box was closed and the fan was turned on.

ClO_2 concentration was determined by an iodometric method. In order to determine the concentration change of during the gas release, several petri dishes filled with 100 mL 7% (w/v) KI solution were placed into the box. The ClO_2 gas was absorbed by KI solution. The concentration of ClO_2 in solution was titrated with sodium thiosulfate solution to a clear colorless endpoint, using soluble starch as indicator. The concentration of sodium thiosulfate solution was titrated with 0.10 mol L^{-1} potassium bichromate standard solution. The concentration of ClO_2 was calculated by the Eq. (1).

$$C(\mathrm{ClO_2}) = \frac{C_1 \times (V_1 - V_0) \times 13.49}{100} \quad (1)$$

Where C_1 was the concentrations of sodium thiosulfate, V_0, and V_1 were the sodium thiosulfate solution volume for titration of distilled water and ClO_2. 100 was the volume of 7% (w/v) KI solution for absorbing the ClO_2 gas. 13.49 was a constant stood for the mass of ClO_2 which equivalents to 1 mg sodium thiosulfate.

2.4. Fumigation treatment of grapes

Approximately 600 g of pesticide-treated grapes were packed into a polyethylene terephthalate (PET) clam container with 6 holes (each diameter was 5 mm) on it. The open containers were placed in the PMMA box in the dark at 25 °C and fumigated by ClO_2 gas for 2 h. After treatment, containers were closed and put into a polyethylene (PE) bag stored at 0 °C (95% RH) for 27 d.

In order to understand the effect of ClO_2 fumigation treatment on the berries' quality, grapes without pesticide treatment were also fumigated in the same condition but stored for 35 d.

2.5. The grape quality analysis

The grape quality analysis included firmness, total soluble solids (TSS) and titratable acidity (TA). Firmness was measured on the equatorial position of the grapes using a hand-held GY-4 texture analyzer (China) equipped with a 5 mm-diameter probe. Results were given as N. TSS was measured by a digital refractometer (Atago PAL-1, Japan) and expressed as%. TA was determined by titration of the grape juice with 0.05 mol L^{-1} NaOH solution and expressed as equivalent concentration of tartaric acid.