Food Control 40 (2014) 106–112

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Chlorine dioxide treatment for the removal of pesticide residues on fresh lettuce and in aqueous solution

Qinqin Chen [a,b,1], Yun Wang [a,c,1], Fang Chen [a,*], Yuanyuan Zhang [a], Xiaojun Liao [a]

[a] College of Food Science & Nutritional Engineering, National Engineering Research Center for Fruits and Vegetables Processing, China Agricultural University, Beijing 100083, China
[b] Institute of Agro-Products Processing Science and Technology, CAAS, Key Laboratory of Agro-Products Processing, Ministry of Agriculture, Beijing 100193, China
[c] Beijing Yoshinoya Fast Food Co., Ltd, Beijing 100005, China

ARTICLE INFO

Article history:
Received 4 June 2013
Received in revised form
1 November 2013
Accepted 27 November 2013

Keywords:
Chlorine dioxide
Phorate
Diazinon
Degradation
Lettuce

ABSTRACT

The effectiveness of chlorine dioxide (CD) to remove phorate and diazinon residues on fresh lettuce and in aqueous solution was investigated. The results indicated that CD (20 mg/L) added in tap water can significantly improve the removal of phorate and diazinon on lettuce ($p < 0.05$), as compared to tap water wash. The study in aqueous solutions suggested that addition of CD could increase the removal rates of phorate and diazinon by 40–80% and 10–20% more than that in tap water without CD, respectively, indicating CD can result in the degradation of the both pesticides. The removal of the both pesticides in aqueous solutions was influenced by concentration of CD, pH value, treatment time, initial concentration and kind of pesticides. The degradation efficiency increased with the concentration of CD and treatment time, and the least removal rates of the both pesticides were obtained in the aqueous solution at pH 4.6. Furthermore, the lower initial concentration of pesticides, the higher degradation rate would be obtained. The degradation kinetics of both pesticides were fitted to the first-order kinetics model well, and the kinetics parameters indicated that phorate was much easier to be degraded than diazinon. The degradation products of both pesticides were identified by GC–MS, phorate and diazinon were oxidized to phorate sulfoxide and phoratoxon sulfoxide, diazoxon, respectively. The present study validates the application of CD treatment as a safe and promising method for the removal of pesticides on fresh fruits and vegetables.

1. Introduction

Chlorine dioxide (CD) is a powerful oxidizing agent that can be applied in solution (Vandekinderen, Devlieghere, et al., 2009). Several studies have suggested that the use of CD could significantly decrease microbial contaminants on apples, lettuce, strawberries and ground beef (Pohlman, Stivarius, Mcelyea, Johnson, & Johnson, 2002; Rodgers, Cash, Siddiq, & Ryser, 2004; Vandekinderen, Van Camp, et al., 2009). The U.S. Environmental Protection Agency has considered CD as the first choice of the disinfectant in place of liquid chlorine (Huang, Chao, & Wang, 1994). Moreover, CD has proved to be an effective bleaching agent for the treatment of drinking water, cooling water, and wastewater (Hwang, Cash, & Zabik, 2002a; Tzanavaras, Themelis, & Kika, 2007). More importantly, several reports have shown that CD can remove or significantly reduce pesticide residues on fresh fruits and vegetables. Hwang, Cash, and Zabik (2001) reported that only 34% and 32% of mancozeb was left in fresh apples after 5 min wash with CD (5 and 10 mg/L, respectively). CD also could effectively reduce ethylenethiourea, ametryn and isoproturon (Hwang, Cash, & Zabik, 2002b; Lopez, Mascolo, Tiravanti, & Passino, 1997), and mechanisms for methiocarb, mancozeb and ethylenethiourea degradation by chlorine dioxide were revealed (Hwang, Cash, & Zabik, 2003; Tian, Qiang, Liu, Zhang, & Dong, 2010).

In China, organophosphorus pesticides (OPPs) are one of the most important groups of widely used insecticides (Zhang et al., 2010). The application of OPPs can effectively prevent the loss of agricultural production, however, it is well known that OPPs can inhibit the activity of cholinesterases and impair nerve conduction (Pope, Karanth, & Liu, 2005), and have genotoxicity (Cakir & Sarikaya, 2005), reproductive toxicity (Kang et al., 2004) and immune toxicity (Crittenden, Carr, & Pruett, 1998). The OPPs residues in agricultural products have become a public concern. Therefore,

* Corresponding author. Tel./fax: +86 10 62737645x18.
E-mail addresses: chenfangch@sina.com, celerylc@yahoo.cn (F. Chen).
[1] These authors contributed equally to this work.

0956-7135/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodcont.2013.11.035

there is a strong need to develop methods to decrease the OPPs residue levels in agricultural products.

As a representative of fresh-cut vegetable, lettuce (*Lactuca sativa*) is primarily consumed fresh or in salad mixes (Dupont, Mondi, Willamson, & Price, 2000). However, pesticide residues on or in the vegetable are often tested (Latif, Sherazi, & Bhanger, 2011) because OPPs are commonly applied to protect lettuce from the insect attack during growth. The objective of this study was to determine the effectiveness of CD to eliminate the residues of popular OPPs formulations, phorate and diazinon contaminated on fresh lettuce. In addition, the degradation kinetics, as well as factors influencing the removal of pesticides by CD treatment were investigated in aqueous solution.

2. Materials and methods

2.1. Materials

Fresh lettuce (*L. sativa*) was purchased from a local market in Beijing, China. Phorate (O,O-Diethyl-S-ethylmercaptomethyl phosophorothioate, >94.5% pure) and diazinon ((O,O-Diethyl-O-(6-methy-2-(1-methylethyl)-4-pyrimidinyl) phosophorothioate, >97.5% pure) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The stock solutions (1000 mg/L) of phorate and diazinon were prepared in acetone and stored in glass-stoppered flasks at −18 °C.

Acetic acid, sodium acetate, disodium hydrogen phosphate, sodium dihydrogen phosphate, sodium bicarbonate, and sodium carbonate were analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd (Beijing, China). HPLC-grade acetonitrile and acetone were purchased from Fisher (Fair Lawn, New Jersey). Nylon syringe filter (13 mm × 0.22 μm) was obtained from Shanghai Anpel Scientific Instrument Co. Ltd (Shanghai, China). CD powder was supplied by Tianjin Zhang Da Technology Co. (Tiangjin, China). The stock solution of CD was prepared by dissolving 13 g of powder into 1000 ml of water and stirred thoroughly for 10 min in a sealed beaker. The concentration of CD in solution was determined using the iodometry method (American Public Health Association, 1987, pp. 298–300).

2.2. Experimental procedure in fresh lettuce system

2.2.1. Treatment of fresh lettuce

The lettuce leaves were immersed for 5 min into water containing the both pesticides with the initial concentration of 2 and 20 mg/L, respectively. Lettuce leaves were taken out and air-dried for 12 h at room temperature (Wu, Luan, Lan, Lo, & Chan, 2007) for further treatment.

The contaminated lettuce samples were divided into three groups: (a) control (no wash); (b) dynamic washing in tap water; (c) dynamic washing in aqueous CD solution at two concentrations (10 mg/L and 20 mg/L). Then lettuce samples were taken out and spin-dried at room temperature after washing for 5, 10, 15 and 20 min, respectively.

2.2.2. Pesticides extraction

The extraction of pesticides from fresh lettuce was carried out according to the standard NY/T 761-2004 established by the Ministry of Agriculture of China (2004) with some modifications. Briefly, the lettuce samples were homogenized. An aliquot (20.00 g) of lettuce homogenate was transferred into a 200 ml conical flask, and 50.00 ml of acetonitrile was added. Activated carbon (0.50 g) was added and the solution was stirred for 30 min using a magnetic stirrer. The mixture was filtered through filter paper (Whatman No.1) into a 100 ml cylinder containing 7.00 g of NaCl. The mixture was shaken vigorously for 1 min and kept for 10 min. A portion of the upper acetonitrile layer (10.00 ml) was carefully transferred to a round-bottom flask and evaporated to dryness at 40 °C in a rotary evaporator. The residues on the wall of glass tube were dissolved in 2.00 ml of acetone and were transferred to vials. The solution was filtered through a 0.22 μm organic membrane before GC analysis.

2.3. Experimental procedure in aqueous solution system

The 0.2 mol/L acetic acid/sodium acetate (pH 4.6), 0.2 mol/L disodium hydrogen phosphate/sodium dihydrogen phosphate (pH 7.0), and 0.2 mol/L sodium bicarbonate/sodium carbonate (pH 10.7) were prepared. CD stock solution was added to each pH solution to bring the final concentration to 10 or 20 mg/L. Each pH solution was spiked with the phorate and diazinon stock solution to give a final concentration of 2 and 20 mg/L. CD and pesticides solutions were mixed thoroughly using a magnetic stirrer. After reacting for 0, 5, 15 and 20 min, an aliquot (10.00 ml) of solution was transferred into a 50 ml beaker, and 10.00 ml of a 0.1 mol/L sodium thiosulfate solution was added to quench the reaction. This mixture was extracted 3 times with 10.00 ml dichloromethane. The dichloromethane layer was collected in a round-bottom flask and evaporated to dryness at 40 °C in a rotary evaporator. The residue was dissolved in 5.00 ml acetone, and filtered through a 0.22 μm organic membrane before GC analysis. The solution without the addition of CD was used as a control.

2.4. Determination of pesticides by GC analysis

Phorate and diazinon were detected with GC-14A (Shimadzu Corporation, Kyoto, Japan) equipped with an HP-5 fused silica capillary column (30 m × 0.53 mm × 1.5 μm, Hewlett Packard, Avondale, USA) and flame photometric detector (FPD). The injector and detector temperatures were 250 °C and 260 °C, respectively. The temperature program was as follows: 120 °C (1 min), 10 °C/min to 240 °C (10 min). Nitrogen carrier gas, hydrogen gas and air were used at the flow rate of 59.0 ml/min, 85.0 ml/min and 120 ml/min, respectively. Sample solution (1.0 μl) was injected in splitless mode, and the quantification of pesticide was performed using an external standard method.

2.5. Degradation kinetics

The degradation kinetics of both pesticides were investigated by the first order kinetic model. A general reaction rate expression can be written as follows (Ambrus & Lantos, 2002; Chen et al., 2009):

$$C_t = C_0 e^{-kt} \quad (1)$$

Where C_0 and C_t were the concentrations of pesticides before and after CD treatment, k was the rate constant and t was the treatment time. Defining $y = \ln(C_0/C_t)$ and combing into Eq. (1) got the function of y versus t as:

$$y = kt \quad (2)$$

The higher k value, the better degradation effect would be obtained.

2.6. Identification of degradation products by GC/MS analysis

The qualification analysis of potential degradation products of phorate and diazinon in aqueous solution was performed by GC/MS-QP2010 Plus (Shimadzu Corp., Kyoto, Japan) configured with a