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Pesticide residue removal from vegetables by ozonation

J.Y. Chen [a], Y.J. Lin [b], W.C. Kuo [b,*]

[a] *Great Eastern Resin Industrial Co., Ltd., Kaohsiung, Taiwan*
[b] *Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan*

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ABSTRACT

A novel machine was developed to remove pesticide residues from vegetables using ozone. This domestic-scale vegetable cleaner consists of a closed cleaning chamber, an ozone generator, a water recirculation pump, and an oxidation–reduction potential (ORP) electrode. Two vegetables, Chinese white cabbage and green-stem bok choy, and three pesticides, permethrin (trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate), chlorfluazuron (1-[3,5-dichloro-4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenyl]-3-(2,6-difluorobenzoyl) urea), and chlorothalonil (tetrachloroisophthalonitrile) were used in tests. Cleaning for 15 min with pump recirculation removed 51% of chlorfluazuron and 53% of chlorothalonil. When the ozone production rate was 250 mg/h, removal efficiencies were 60% for chlorfluazuron and 55% for chlorothalonil, increases of 2–9% over pump recirculation only. When the ozone production rate was 500 mg/h, removal efficiencies were 75% for chlorfluazuron and 77% for chlorothalonil; increases of 24% over pump recirculation only. After the ozone treatment, all the pesticide residuals met the Standards for Pesticide Residue Limits in Foods.

1. Introduction

The world's population is estimated to be 9.22 billion in 2075 (UN, 2004). Along with this rapid population increase, worldwide demand for food will increase, as will pesticide use. China applies an estimated 1.3 Mt of pesticides to agricultural lands annually (Wu et al., 2007). Taiwan's subtropical climate renders many crops susceptible to damage by diseases and insects, resulting in the use of large amounts of pesticides to prevent smiting. According to statistics from Taiwan's Bureau of Animal and Plant Health Inspection and Quarantine, Council of Agriculture, 34,709 tonnes of formulated agro-pesticide were sold in 2010. Notably, Taiwanese farmers are not the only farmers who spray extremely high pesticide concentrations (Zhou and Jin, 2009). Additionally, some harvests are rushed to market, leaving large amounts of pesticide residues on plants, vegetables and fruit. Although humans are exposed to small amounts of pesticide residues after pesticides are metabolized by plants or decomposed by environmental agents, trace amounts of pesticide residing in the human body for long periods can cause chronic diseases and can lead to cancer (Carrozza et al., 2009).

Residual pesticides in water can be destroyed by, say, Fenton oxidation, electrochemical oxidation, TiO_2 catalytic treatment, and UV photolysis (Wu et al., 2009). However, these techniques have some disadvantages; for example, catalytic treatments produce secondary pollutants. Ozone was first used to disinfect water supplies in France in the early 1900s. Well over 1000 ozone disinfection installations now exist worldwide. Ozone, a powerful oxidant ($E_H > 2.0$ volts), has an oxidation capability exceeded by fluorine only ($E_H = 3.06$ V). Ozone's solubility in water at 20 °C is 12.07 mg/L. The stability of ozone in air exceeds that in water; however, both stabilities are within the order of minutes (Metcalf and Eddy, 2003; Eckenfelder, 2000). Ozone is also used to remove pesticide residues from vegetables or aqueous solutions (Benitez et al., 2002; Wu et al., 2007; Chelme-Ayala et al., 2009; Ikeura et al., 2011). Ozone decomposes in water to produce free radicals, and high pH values are favorable for pesticide degradation (Ong et al., 1996; Eckenfelder, 2000; Xiong et al., 2011). Based on ozone's strong oxidation capability and its reaction with other inducer (e.g. OH^- and hydroxyl radicals ($OH\cdot$)), with high oxidation power will be produced; these inducers can decompose most organic compounds. As ozone decomposes into oxygen, it does not produce secondary pollutants. The prevailing ozone treatment method for removing pesticide residues on vegetables is to pump ozone into water in a vessel via an ozone generator. Ozone then oxidizes contaminants via ozone molecules or its derivatives and removes residues. The effectiveness of ozone treatment is limited by ozone's poor solubility and the high cost of ozone generators. Increasing ozone solubility and reducing the cost of ozone production are key problems associated with ozone treatment. The goals of this study are as follows.

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* Corresponding author. Address: Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91207, Taiwan. Tel./fax: +886 8 774 0261.

E-mail address: xwck@mail.npust.edu.tw (W.C. Kuo).

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(1) Develop a novel domestic-scale ozone cleaner for vegetables.
(2) Establish the relative concentration curves for liquid ozone concentrations and ORP.
(3) Conduct experiments to determine the effectiveness of the proposed ozone vegetable cleaner in removing pesticide residues from vegetables.
(4) Evaluate the toxicity of aqueous pesticide solution before and after ozone treatment using the Tox Tracer® biological toxicity test.

2. Materials and methods

2.1. Field tests for pesticide residues on vegetables

This experiment had three stages. The first field experiment was conducted during June–August 2004. The planted vegetables were Chinese white cabbage and green-stem bok choy (foliole vegetables with short growing periods). Pesticides applied were 10% permethrin emulsion and 5% chlorfluazuron emulsion. Pesticide doses were classified into the following three groups: none (no spraying); standard doses (spraying following plant protection criteria of 50 ppm permethrin and 25 ppm chlorfluazuron); and, twice the standard dose (over-spraying). The second field experiment was conducted during February-April 2005. The planted vegetable was Chinese white cabbage, and pesticides applied were 10% permethrin emulsion and 5% chlorfluazuron emulsion. Pesticide doses were classified into the following two groups: standard doses of 50 ppm permethrin and 25 ppm chlorfluazuron; and 1.5 times the standard doses (over-spraying). The third field experiment was conducted in November and December 2005. The planted vegetable was Chinese white cabbage, and pesticides were permethrin, chlorfluazuron, and 75% chlorothalonil powder (*i.e.*, 50 ppm permethrin, 25 ppm chlorfluazuron and 100 ppm chlorothalonil). Pesticide doses were 1.5 times the standard dose, simulating general farmer practices.

2.2. Experimental setup

The proposed domestic-scale ozone vegetable cleaner consists of an airtight cleaning tank, a vegetable basket, an ozone generator, an ozone concentration controller, a recirculation pump, and a timer. The cleaner generates and controls the liquid ozone concentration during the cleaning process for removing pesticide residues. Fig. 1 shows a schematic diagram of the proposed pesticide cleaner.

2.3. Analytical instruments

Analytical instruments used in this study were as follows.

(1) The ozone generator, a Fischer ozone generator (Model 500), was used in liquid ozone determinations.
(2) The ozone gas analyzer was a Seki electronic ozone UV photometric analyzer (SOZ-6000, Japan).
(3) The ORP electrode was a pH/ORP controller (Model PC-310, Suntex, Taiwan).
(4) A UV–visible spectrophotometer (Model UV-160A, Shimadzu, Japan) was used to determine liquid ozone concentrations.
(5) The following devices were used in pesticide residue analyses.
    (i) Blender: Osterizer (10 speeds).
    (ii) Rotary evaporator: Eyela Model N-1000 (Eyela, Japan).
(6) The GC Electron Capture Detector (ECD) used for sample analysis of pesticide residues and aqueous pesticide solutions was an HP-6890 equipped with an ECD. The carrier gas was N_2 and the analytical column was an HP-5 packed with Crosslinked 5% PH ME Siloxane.
(7) The Tox Tracer® Toxicity test used the following devices.
    (i) Tox Tracer Luminometer photodetectors (Skalar, Netherlands) used a photomultiplier tube, isothermal reaction tank (15 ± 0.1 °C), and a digital screen that displayed% inhibition.
    (ii) The Tox Tracer cooling block constant temperature incubator held 30 tubes and 2 microbe index tubes for microbes cultivation, with automatic temperature control (15 ± 0.1 °C).

2.4. Analytical reagents

(1) Indigo reagent
The Indigo Colorimetric Method was used to determine liquid ozone concentrations (Hoigne and Bader, 1982).
(2) Pesticides
Three pesticides, permethrin, chlorfluazuron, and chlorothalonil, were chosen based on farmer use and seasonal variations.
    (i) Standard pesticide solutions, 1000 ppm permethrin, 1000 ppm chlorfluazuron, and 867 ppm chlorothalonil, were prepared for calibration curves. These standards were obtained from the Agricultural Chemicals and Toxic Substances Research Institute, Council of Agriculture, Taiwan. Suppliers and purities of permethrin, chlorfluazuron, and chlorothalonil were Dr. Ehrenstorfer GmbH, 94%; R.D.H., 99.4%; and R.D.H., 98.5%, respectively.
    (ii) Commercial pesticide products: 10% permethrin emulsion, 5% chlorfluazuron emulsion, and 75% chlorothalonil powder were used as aqueous pesticide solutions for field tests and pesticide removal experiments.
(3) Reagents for pesticide residue determination: acetone, NaCl (30%), dichloromethane, petroleum ether, n-hexane, carbonic acid sodium hydride (12%), and anhydrous sodium sulfate (all were analytical grade).
(4) Reagent for the Tox Tracer Toxicity Test.
    (i) Fluorescence biological reagent: a patented Vibrio fisheri was adopted (luminous bacteria were used in this study). These bacteria were made into biological agent after being dried and frozen. Each bottle contained about 1 billion bacteria stored at −20 °C. Notably, analysis was completed within 4 h after a bottle was opened.
    (ii) Bacteria activator: a kind of distilled water which can be added to the biological agent and activate the bacteria.
    (iii) Diluent: 2% NaCl solution.
    (iv) Osmotic pressure modulation liquid: 22% NaCl solution for adjusting the NaCl concentration of sample to 2% to balance the osmotic pressure among biological agents and samples.

2.5. Analytical methods

(1) Preparation of aqueous pesticide solutions.
Human tolerances of pesticide residues are 2 mg/L for permethrin, 2 mg/L for chlorfluazuron, and 1 mg/L for chlorothalonil. Initial concentrations were twice the strength of pesticide residue concentrations, *i.e.*, 4 ppm permethrin, 4 ppm chlorfluazuron, and 2 ppm chlorothalonil.
(2) Analysis of aqueous pesticide solutions.
The initial pesticide concentration was based on Taiwan's Safety Tolerance Criteria of Pesticide Residues on Farm Products, Department of Health, Republic of China (2012). To simulate farmer practices in controlling pests within short periods, doses 1.5–2.0 times the standard dose were adopted. Therefore, twice the safety tolerance was used as the initial pesticide concentration. The safe tolerance for permethrin, chlorfluazuron, and chlorothalonil is 2.0 mg/L, 2.0 mg/L, and 1.0 mg/L, respectively. Analytical methods