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Degradation of Organophosphorus Pesticides in Pear by Ozonation

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The present study investigated the degradation of two organophosphorus pesticides *i.e.*, malathion and dimethoate, in pear by ozonation in order to establish the effect of operational parameters. Four degradation methods were conducted and ozonation was the most effective way with its advantages of cleanness, convenience and facility. The optimized ozonation conditions of degradation of malathion and dimethoate in pear were as following: the degradation mode was bubbling ozone in water and the degradation time was 0.5 h. The two organophosphorus pesticides could be degraded over 60 % in 0.5 h by bubbling ozone. There was no effect on fruit quality after treatment with ozone.

Keywords: Degradation, Malathion, Dimethoate, Ozonation.

INTRODUCTION

Organophosphorus pesticides (OPs) have been widely used as an alternative to organochlorine compounds for the control of insecticide in a wide range of fruit, vegetables and grain all over the world. They are considered as one of the most important classes of chemical pollutants owing to their widespread use and toxicity[1]. The impacts of organophosphorus pesticides on the environment were resulted from several factors *e.g.*, the toxicity, the bioaccumulation, long-term effects and the transport between different organisms. Moreover, it has recently been determined that by-products of transformation in the environment play significant role in defining the impact of pesticides on both human health and the natural ecosystems[2]. In recent years, increasing attention has been paid to organophosphorus pesticides in wastewater and foods for they pose adverse risks to nontarget organisms and humans, inducing effects such as neurotoxicity, immunotoxicity and reproductive toxicity[3]. Residual pesticides can be degraded by different methods, including oxidation[4-6], electrochemical degradation[7,8], chloramination[9], TiO_2 catalytic treatment[10], biotreatment[11] and UV photolysis[12,13]. Ozonation has been developed in recent years and a number of novel advanced ozonation processes have been proposed to improve oxidation efficiency. Acero *et al.*[4] evaluated the influence of the oxidation processes operating conditions on the organophosphorus insecticide chlorfenvinphos removal efficiency and a kinetic model was established for the prediction of the elimination rate of chlorfenvinphos. Kim *et al.*[6] found that ozone was well adsorbed and decomposed simultaneously in microporous silicates, resulting in the production of possible radical species. The results showed that catalytic ozonation was a better toxicity reduction of wastewater. The object of this study was to apply ozonation degradation of malathion and dimethoate in pear and investigate the factors which affected some operating variables, such as ozone time, ozone mode and ozone concentration. The detection method is based on solid phase microextraction (SPME) combined with gas chromatograph-flame photometric detector (GC-FPD). In addition, the pear qualities, such as the content of ascorbic acid, carbohydrate, protein and total acid, were evaluated after treatment with ozone.

EXPERIMENTAL

Standards of malathion and dimethoate (purity: 99 %) were acquired from Sigma (USA). Methanol was of chromatograph grade. Other chemicals were of analytical grade. Water was deionized water. Stock standard solution of 1000 mg/L of each compound were solved in methanol and diluted with deionized water. Working standard solutions of analyzed pesticides was prepared by diluting the stock solutions with deionized water.

Ozone gas produced by Ozonizer (Model WH-H-Y) was bubbled into deionized water in glass cylinder. The dissolved ozone levels were controlled *via* adjusting the duration of bubbling and the flow rates. Dissolved ozone concentration was determined by the iodometry[14]. Two degradation modes

were employed. One way was that ozone gas was bubbled into water continuously and kept the concentration 5 mg/L. Another way was bubbling ozone into water to obtain 5 mg/L ozonated water and then the ozone gas was turned off. The pear with different concentration of organophosphorus pesticides was immersed into the water. Then the pear was taken out and dried at room temperature. The experiment was carried out at 20 ± 2 °C. Removal of pesticides residue in pear was investigated with ozone concentrations (5 mg/L ozonated water with continuously ozone gas bubbling and agitated with magnetic bar) and five different contact times (5, 10, 15, 20, 30 min). Pear was cut into pieces. Different concentration organophosphorus pesticides was dropped on 25 g pear and it was maintained 3 h for the organophosphorus pesticides being absorbed. After treated with different degradation methods, the pear was taken out and air-dried under room condition. The sample and water were homogenated for 2 min. The homogenate was diluted to 250 mL with water and kept in refrigeratory.

The extraction of malathion was performed using a 100 μm film thickness polydimethylsiloxane (PDMS) coated fiber mounted in manual syringe holder (Supelco, Bellefonte, USA) and 85 μm thick polyacrylate (PA) for dimethoate. Dilute sample solution with water 10 times before extraction. The sample solution contained 20 % NaCl as the inorganic salt. The volume ratio of methanol and water (extraction solvent) was less than 0.5 %. The fiber was exposed to the headspace above the sample for 45 min. Each sampling was stirred vigorously during the sorption step with magnetic stirring at 900 r/min on the stirrer plate. Thermal desorption of the analytes was achieved by inserting the sorbent fiber into the injection port for 3 min.

Organophosphorus pesticides residue analysis was carried out on a GC-FPD (SHIMADZU, model 14C) equipped with a SE-30 capillary column (30 m length × 0.32 mm I.D. × 0.25 μm thickness). **GC conditions for malathion:** The temperature of oven was 250 °C, the FPD temperature was maintained at 250 °C and the temperature of column was 205 °C. Nitrogen (purity > 99.999 %) was used as the carrier gas with a flow rate of 40 mL/min. Hydrogen was generated with hydrogen generator for FPD at a flow of 55 mL/min. The flow of zero air for FPD was 45 mL/min. The sample (2 μL) was injected in the split mode (seperation ratio: 20:1). **GC conditions for dimethoate:** The temperature of column was programmed as follows: initial 75 °C, from 75 °C (held for 2 min) to 225 °C at the rate of 30 °C/min and held at 225 °C for 8 min. The temperature of oven was 270 °C. The flow of zero air for FPD was 55 mL/min. The sample (1 μL) was injected in the splitless mode (1 min). Other conditions were same as malathion's.

The pear samples were collected after ozonation treatment and air-dried under laboratory conditions. The contents of total ascorbic acid and reduced ascorbic acid were determined by 2,4-dinitrophenylhydrazine spectrophotometric method. Anthrone colourimetry method was adopted to determine the content of carbohydrate components. The total protein content was detected with Coomassie brilliant blue colourimetric method. The total acid content was titrated by aqueous solution of sodium hydroxide.

RESULTS AND DISCUSSION

Effect of different degradation methods on malathion: Different degradation methods were investigated. The result was shown in Fig. 1. For the four methods, ozonation was the best way. Washing rice water degraded malathion better than detergent and untrasonic. The degradation ratios of the washing rice water and detergent were 45.33 %, 40.36 %, respectively. The ultrasonic degradation was also investigated, but the result was not as well as other degradation methods. It was indicated that ultrasonic was not an efficient method of degradation malathion in pear. The comparison of the four methods illustrated their relative advantages and drawbacks. Both washing rice water and detergent were convenient, low-cost and easy to operate. Advancement in technology made it feasible to generate ozone gas easily for domestic application.

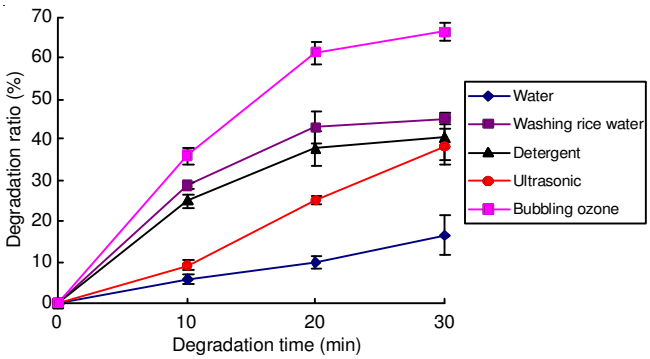

Fig. 1. Effect of different degradation method on malathion

Effect of ozonated water concentration on the degradation: The degradation of removal malathion and dimethoate by ozone was studied in experiments at room temperature for 20 min, by varying the concentration of ozone (Fig. 2). As can be seen there was sharp increase in the degradation ratio with the increasing of ozone initial dose. The degradation ratio of dimethoate in pear was increased from 17.83 to 67.95 % with the increasing of ozone dose in 20 min. The degradation ratios were similar between malathion and dimethoate in pear. The degradation ratios of malathion and dimethoate were 68.65 %, 67.95 %, respectively, when the concentration of ozone was 6.85 mg/L. However, if the concentration of ozone was too

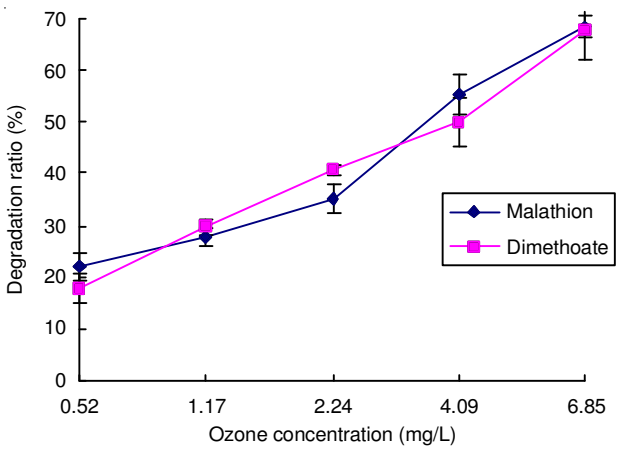

Fig. 2. Effect of ozonated water concentration on the degradation of malathion and dimethoate

high, the ozone would get out of water. It was feasible to produce ozonated water with higher concentration of dissolved ozone by ozonizer.

Effect of ozone modes on the degradation of organophosphorus pesticides: The corresponding degradation plots of different ozone modes were displayed in Figs. 3 and 4. The degradation ratios were 65.18 and 61.43 % in 0.5 h by bubbling ozone for the two insecticides in pear. In general, the organophosphorus pesticides were degraded very fast in the first 15 min and then the degradation rate was slowed down. Malathion degraded faster a little bit than dimethoate for both oxidation modes. The degradation rate of organophosphorus pesticides was fast in the first 15 min because organophosphorus pesticides on the fruit surface were easy degraded by ozone. After that, ozone molecule must penetrate in the tissue of pear. Only about 10 % insecticides residue were degraded in the next 15 min. Compared with the two degraded modes of ozone, bubbling ozone and ozonated water, it was obviously that bubbling ozone in water was more effective than ozonated water. The concentration of ozone was maintained 5 mg/L by bubbling ozone. However, the concentration of ozonated water would be reduced without supplement because ozone decomposed in water within 15 min. Similarly, the bubbling ozone time had a positive effect on the degradation rate, with an increase in removal malathion and dimethoate as expected.

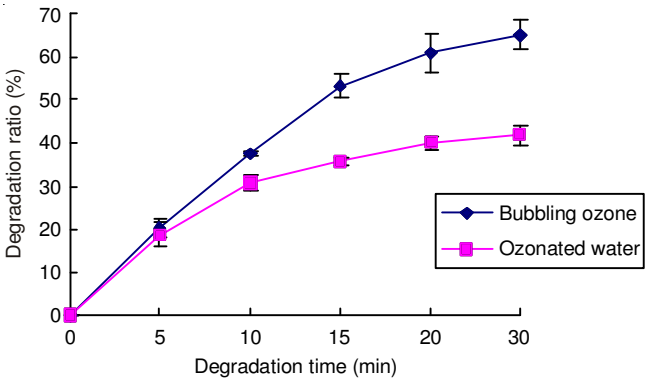

Fig. 3. Effect of ozone mode on the degradation of malathion

Effects of different initial concentration of organophosphorus pesticides: With the concentration of organophosphorus pesticides increased, the degradation ratio was decreased significantly (Fig. 5). Only 51.99 % of 5 mg/L malathion were degraded in 5 mg/L bubbling ozone water in 0.5 h. Dimethoate

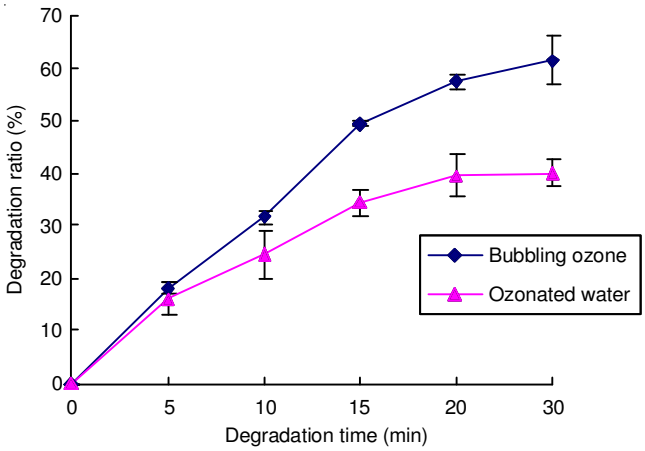

Fig. 4. Effect of ozone mode on the degradation of dimethoate

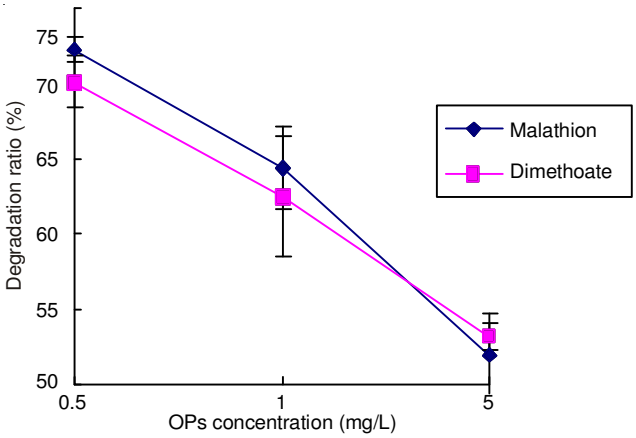

Fig. 5. Effects of different initial concentration of malathion and dimethoate

was degraded 53.12 % at the same condition. However, when the concentration of organophosphorus pesticides was low, the degradation ratio could be over 70 %. The result showed that ozonation was an effective way to degrade low concentration of organophosphorus pesticides, while it was not very effective to high concentration of organophosphorus pesticides in fruits.

Effect of ozone treatment on the quality of pear: The qualities of pear treated with ozone were summarized in Table-1. The ozone treatment had no significant effect on the contents of the total acid and total ascorbic acid in pears. However, the content of reduced ascorbic acid was decreased significantly ($p < 0.01$). A part of reduced ascorbic acids were

TABLE-1
EFFECT OF OZONE TREATMENT ON THE QUALITY OF PEAR

Ozone Time (min)	Total ascorbic acid (mg/100 g)	Reduced ascorbic acid (mg/100 g)	Total carbohydrate (%)	Total protein (g/100 g)	Total acid (%)
0	7.29Aa	4.49Aa	10.7413Aa	0.45Aa	0.1307Aa
5	7.10Aabc	4.33Bb	10.6947Aa	0.45Aa	0.1309Aa
10	7.20Aab	4.23Bb	10.2347Bb	0.42Bb	0.1306Aab
15	7.05Abc	4.06Cc	10.2013Bb	0.40Cc	0.1306Aab
20	7.01Abc	3.76Dd	9.8480Cc	0.40Cc	0.1303Aab
30	6.96Ac	3.55Ee	9.7347Cd	0.37Dd	0.1301Ab
p	0.0485	0.0001	0.0001	0.0001	0.1033

Same capital letter on the same tier indicated no significant difference ($p < 0.05$) and same small letter indicated no significant difference on the level $p < 0.01$

oxidated into oxidized form by ozone water. Therefore, there were no changes of total ascorbic acid content.

The results showed that the content of total carbohydrate components was decreased after treatment with ozone. The aldehyde group of reducing carbohydrates might be oxidated into carboxyl group. The carboxyl group could not condense with anthrone. Thus, the content of total carbohydrate components would be less.

The content of protein in pear was decreased significantly ($p < 0.01$). In the first 10 min, the content of protein was invariant. With prolonging the bubbling ozone time, the content of protein decreased fast. The amino acid residue of protein might also be oxidated. The methionine, cysteine and cystine could be oxidated. Some oxidation products could be absorbed by human.

In summary, the total contents of carbohydrates and protein in pear were decreased. In the first 15 min, total carbohydrates and protein contents were decreased slowly, while it decreased dramatically after 20 min. Therefore, we should control the time of bubbling ozone to reduce the negative effects on the quality of fruits.

Conclusion

In conclusion, four degradation methods of malathion and dimethoate in pear have been studied by using ozone, washing rice water, detergent and ultrasonic. Ozonation was proved to be the most efficient way. The optimized ozonation conditions of degradation of two organophosphorus pesticides in pear were as following: the degradation mode was bubbling ozone in water, the degradation time was 0.5 h and the concentration of the organophosphorus pesticides should be low 1 mg/L. Under these conditions, the degradation ratios of the malathion and dimethoate were 66.25 and 61.43 %, respectively. There were no obvious effects on fruit qualities after treatment with ozone. Furthermore, SPME-GC-FPD was also a simple, rapid and convenient procedure to extract and detect the residue of organophosphorus pesticides .

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