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Experimental Study on the Degradation of Acaricides on the Surface of Kumquat Cuimi by Nonthermal Air Plasma

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Abstract: Nonthermal air plasma, which can be generated by air discharge, contains large amounts of reactive oxygen species (ROS), reactive nitrogen species (RNS) and high-energy particles. The ROS and RNS have strong oxidizing properties, and the high-energy particles can break chemical bonds in organic compounds, a process which can be used to degrade organic matter such as pesticides. In the present study, the effects of nonthermal air plasma on the degradation of several pesticides were investigated. An air plasma processing system was designed and constructed to produce nonthermal air plasma and to degrade five commonly used acaricides, namely, avermectin, bifenazate, spirodiclofen, etoxazole, and lufenuron, during the production of kumquat cuimi. The experimental results showed that nonthermal air plasma could degrade all the acaricides on the surface of the kumquat cuimi effectively. After 20 min of plasma treatment, the residues of avermectin, bifenazate, spirodiclofen, etoxazole and lufenuron on the surface of the kumquat cuimi were reduced by 80.67%, 79.52%, 62.40%, 48.93% and 23.11%, respectively. Further analysis indicated that the primary chemical bonds, hydrophobicity, and the pH value of the plasma-activated water can all affect the efficiency of pesticide degradation.

Keywords: nonthermal air plasma; acaricide; avermectin; bifenazate; spirodiclofen; etoxazole; lufenuron; kumquat cuimi; degradation; food safety

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1. Introduction

Citrus originated in the tropical and subtropical regions of Asia and is now grown as a major fruit crop worldwide [1]. During the past decades, the rising demand for citrus has caused massive land cover changes in the agricultural frontiers of Asia and South America [2]. Mites are considered one of the most important pests in citrus, and controlling them through the use of acaricides has become an essential step in citrus production.

Avermectin, bifenazate, spiromesifen, etoxazole, and lufenuron are common acaricides. Avermectin was put into use as a pesticide in 1985. Avermectin has strong contact and stomach toxicity, and is broad-spectrum. It also has high efficiency and high activity against pests, mites, and parasitic nematodes on a variety of crops [3]. Bifenazate is a new selective foliar spray acaricide, which mainly acts by inhibiting the mitochondrial electron transport chain complex III and the GABA receptor of the central nervous system of mites. Therefore, bifenazate is effective at all stages of mite life, with both ovicidal and adulticidal activities [4]. Spiromesifen is the most recently developed class of acaricides. These acaricides act as an acetyl-coenzyme A carboxylase (ACCase) inhibitor by interfering with lipid biosynthesis [5]. Etoxazole is a 2,4-diphenylthiazole derivative compound that can inhibit the embryonic formation of mite eggs and the molting process from larvae to adults. It has excellent contact killing effects on mites from eggs and larvae to pupae [6].

Lufenuron is a selective benzoylurea insect growth regulator that is safe for the environment and non-target organisms. It has contact and stomach toxicity [7].

The consumption of even trace amounts of pesticide residues in food may lead to accumulation in the body and put the health of consumers at risk with adverse effects including cancer, diabetes, and infertility, etc. [8]. However, currently, the natural decomposition of acaricides cannot meet our requirements for food safety. Therefore, in order to enhance the safety of agricultural products, it is necessary for us to utilize technological means to facilitate the degradation of acaricides and accelerate the degradation process [9]. Common methods for pesticide degradation include washing, ultrasonic degradation, ionizing radiation, encapsulation, hydrolysis, oxidative decomposition, photochemical degradation, microbial degradation, enzyme degradation, and engineered bacterial degradation, among others [9–15].

In recent years, nonthermal plasma technology is a novel promising strategy that has demonstrated some unique advantages in the field of food sterilization and disinfection due to its outstanding oxidation capability without the need for any chemical additives [16]. Nonthermal plasma technology is a novel advanced oxidation technology that combines multiple oxidation methods such as high-energy electron radiation, wet oxidation, ozone oxidation, and photochemical oxidation [17]. Common plasma discharge methods include dielectric barrier discharge, glow discharge, corona discharge, and radio frequency discharge [18–21]. This synthesis technique is eco-friendly and easy to perform compared with other known techniques. As one of the potential advanced oxidation processes (AOPs), nonthermal plasma production during various discharges has long been exploited for the reduction of metal salts and stabilizers in various emission processes [22]. Its effectiveness is based on the production of in situ oxidative species ($OH\cdot$, $H\cdot$, $O\cdot$, H_2O_2, H_2, O_2, O_3), as well as its ability to initiate a variety of chemical and physical processes (a high electric field, intense ultraviolet radiation, overpressure shock waves) in water for decomposing toxic compounds, while further advantages include its operational simplicity (realized under the conditions of ambient temperature and pressure), its variable reactor configuration, and its good performance degradation of low-concentration organic compounds [23–26]. Among these techniques, dielectric barrier discharge (DBD) has the advantages of simple structure, low cost, and the ability to be operated at room temperature and atmospheric pressure [27], and has been widely used for the treatment of pollutants such as organic pollutants, induced surface modification, and microbial inactivation [28–30].

Ali et al. [31] found that under a transmission voltage of 45 kV, the residual amount of dichlorvos in tomato juice decreased by 47% and 65% after being treated with DBD plasma for 4 and 5 min, respectively; Cong et al. [32] found that under a discharge voltage of 80 kV, the residual levels of malathion and chlorpyrifos on the surface of lettuce were reduced by 59.0% and 57.9%, respectively, after being treated by nonthermal plasma for 180 s; Mahbubeh et al. [33] found that under a discharge voltage of 13 kV, the residual levels of diazinon on the surface of fresh-cut apples and cucumbers were reduced by 87.38% and 82.24%, respectively, after being treated by nonthermal plasma for 10 min, and the residual levels of chlorpyrifos were reduced by 86.96% and 33.74%, respectively. Feng et al. [34] found that under a discharge power of 25 W, the residual levels of chlorpyrifos and imidacloprid on the surface of corn were reduced by 91.5% and 73.1%, respectively, after being treated by nonthermal plasma for 60 s. However, the use of nonthermal plasma for the degradation of acaricides on fruit and vegetable surfaces is still not well established.

Kumquat cuimi, a new cultivar of kumquat developed in China, has gained significant popularity among consumers. This is attributed to its fruit characteristics, including a reduced number of oil cells in the peel, abundant juicy flesh, high content of soluble solids, and absence of a spicy taste. This study utilized kumquat cuimi to investigate five common acaricides: avermectin, bifenazate, spirodiclofen, etoxazole, and lufenuron. A nonthermal air plasma device was designed to treat pesticide residues on the surface of kumquat cuimi and the degradation effects of five commonly used acaricides were investigated. The study explored the degradation efficiency of these five acaricides using the nonthermal plasma

technique and analyzed the impact of various factors on the degradation effectiveness. This research provides insights for the practical application of nonthermal plasma in the degradation of pesticide residues on fruits and vegetables.

2. Materials and Methods

2.1. Main Instruments and Materials

The acaricides used were avermectin (Dongyuan Biotech Co., Ltd., Nanning, China), spirodiclofen (Zouping Pesticide Co., Ltd., Nanning, China), etoxazole (Dongyuan Biotech Co., Ltd., Nanning, China), lufenuron (Taida Feng Biotech Co., Ltd., Nanning, China), and bifenazate (Daxing Biochemical Co., Ltd., Nanning, China).

The experimental plants were purchased from the Red Guard Village Miao Nursery Base, Xiatun, Hongwei Village, Chang'an Town, Rongan County, Liuzhou City, Guangxi Zhuang Autonomous Region, China and were of the cultivar 'Kumquat Cuimi'.

The reagents and chemicals used were avermectin standard solution, spirodiclofen standard solution, etoxazole standard solution, lufenuron standard solution, and bifenazate standard solution (all with a purity of ≥98.0%, 1.2 mL, 100 μg/mL, Wuhan Rhodes Biotechnology Co., Ltd., Wuhan, China), and acetonitrile (chromatographic grade, Sigma-Aldrich Corporation, St. Louis, MO, USA).

The instruments used were a plasma generator (self-made by Guangxi University), a liquid chromatography-mass spectrometry system (LC-MS) (EXPEC 5210 triple quadrupole LC-MS from Spectrum Labs, Hangzhou, China), an ultrasonic cleaner (YL-080S from Yulu Technology, Shenzhen, China), and a high-purity water system (WP-UP-WF-30 from Waters Corporation, Chengdu, China).

2.2. Experimental Setup

The nonthermal air plasma generation device (as shown in Figure 1) comprised a DC power supply (DP605B from Maistech Electronics Co., Ltd., Shenzhen, China), a high-frequency inverter, a brushless diaphragm pump (D50H-42H from Chengdu Hailin Technology Co., Ltd., Chengdu, China), a flow meter oscilloscope (TDS2024C from Tektronix, Inc., Cincinnati, OH, USA), a voltage probe (P6015A from Tektronix, Inc., Tianjin, China), and a current probe (H-FCT-200 from Shanghai Pinyan Measuring and Controlling Technology Co., Ltd., Shanghai, China). The plasma treatment process involved dielectric barrier discharge (DBD), where the high-voltage electrode is a tungsten needle with a diameter of 2 mm, and the dielectric tube is a quartz tube with an inner diameter of 6 mm, an outer diameter of 8 mm, and a length of 135 mm. The tube is wrapped with copper foil and grounded, and the plasma excitation region is located in the annular gap between the tungsten needle and the copper foil. The high-frequency sinusoidal output voltage ranged from 0 to 20 kV, and the flow rate of the excitation gas ranged from 1 to 5 L/min.

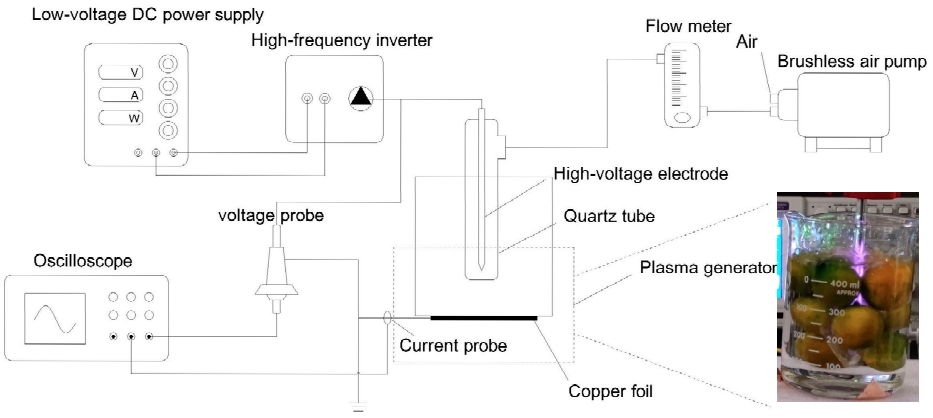


Figure 1. Plasma generation device diagram.

2.3. Experimental Methods

2.3.1. Preparation of Contaminated Fruits and Treatment

Commercially available kumquat cuimi were cleaned using an ultrasonic cleaner and tested to confirm the absence of the five acaricides to be tested on their surface. The fruit were then refrigerated for later use. Separate stock solutions of each acaricide at a concentration of 1000 ppb were prepared using Milli-Q (MQ) ultrapure water. About 100 g of the kumquats were immersed in a 1 L solution of the acaricide for 30 s, then removed and air-dried in preparation for plasma treatment.

Different voltages (10 kV/15 kV/20 kV) were used to excite air, and the generated plasma was injected into a 300 mL beaker containing 3 L/min of deionized water. The prepared contaminated fruits were treated with plasma for different treatment times (10 min/15 min/20 min). The active substances and high-energy particles in the non-thermal air plasma react with the acaricide on the surface of the kumquat cuimi to achieve the effect of degrading the acaricide.

Due to the capability of liquid chromatography-tandem mass spectrometry (LC–MS) to determine extremely low levels of pesticide residues, as low as 1 part per million (1 ppm) or even lower [35], this method was selected to measure the residue of acaricides using the liquid chromatography coupled with mass spectrometry instrument.

2.3.2. Preparation of Contaminated Fruits and Treatment

A 10 g sample of the fruit was accurately weighed (to 0.01 g) and placed in a 50 mL centrifuge tube, followed by the addition of 10 mL of acetonitrile. The mixture was vortexed for 15 min, followed by the addition of 2 g of sodium chloride, and vortexed again. The mixture was centrifuged at 4000 rpm for 5 min, and the supernatant was quantitatively transferred to a centrifuge tube containing a water removal agent and a purification material (25 mg of PSA per milliliter of extract). The mixture was vortexed for 1 min, and the supernatant was filtered through a 0.22 μm filter membrane and diluted, if necessary, for further analysis.

(1) Standard curve preparation process:

The standard stock solution (100 μg/mL) was diluted with acetonitrile to prepare a series of standard solutions with concentrations of 1.0, 2.0, 5.0, 10, 20, 50, 100, 200, and 500 ng/mL, which were used to construct the standard curve.

A mixed standard working solution of avermectin, bifenazate, spirodiclofen, etoxazole and lufenuron was injected and detected under the above instrument conditions. The concentrations of the mixed solution were 1.0, 2.0, 5.0, 10, 20, 50, 100, 200, and 500 ng/mL. The obtained MS response values (peak area, Y) were used to construct a linear regression equation with the injection concentration (X). The results showed that there was a good linear relationship between 1.0 and 500 ng/mL. The obtained standard curves for bifenazate and spirodiclofen were $Y = 992.8659X + 532.6314$, $Y = 3931.2446X + 30{,}000.7846$, $Y = 27{,}198.9796X + 99{,}277.9849$, $Y = 138{,}192.2898X - 133{,}027.2403$ and $Y = 17{,}879.8776X - 3481.7118$, respectively. The determination coefficients (R^2) were 0.9985, 0.9951, 0.9974, 0.9992 and 0.9990, respectively. Under these detection conditions, the limit of quantitation (LOO) was calculated to be 0.0005 mg/kg using a signal-to-noise ratio (S/N) of 10, indicating the high sensitivity of the method.

(2) Chromatographic conditions:

Column: Waters ACQUITY UPLC BEH C18 1.7 μm 2.1 × 100 mm; flow rate: 0.3 mL/min; column temperature: 40 °C; injection volume: 5.0 μL; mobile phase: A: 0.1% formic acid water, B: acetonitrile. The chromatographic separation gradient elution program is shown in Table 1.

Table 1. Gradient elution program for chromatographic separation.

Time (min)	Flow Rate (mL/min)	Mobile Phase A (%)	Mobile Phase B (%)
0	0.3	80	20
2	0.3	20	80
6	0.3	5	95
7.5	0.3	5	95
7.6	0.3	80	20
10	0.3	80	20

(3) Mass Spectrometry Conditions:

Scan mode: MRM positive ion; ion source: ESI; nebulizer: nitrogen (N2, PEAK NM32LA nitrogen generator); collision gas: nitrogen (purity 99.999%); capillary voltage: 5.0 kV; cone voltage: 700 V; ion source temperature: 105 °C; desolvation gas temperature: 495 °C; cone gas flow rate: 72 L/h; desolvation gas flow rate: 300 L/h. Other conditions are shown in the Table 2 below.

Table 2. Mass spectrometry conditions.

Acaricide	Parent Ion (*m*/*z*)	Product Ion (*m*/*z*)	Residence Time (S)	Cone Voltage (V)	Collision Energy (eV)	Quantitative Ion Pair *
Avermectin	895.5	751.5	0.05	50	53	*
Avermectin	895.5	449	0.05	50	59	
Bifenazate	301.1	198.05	0.05	50	9	*
Bifenazate	301.1	170.1	0.05	50	21	
Spiromesifen	411.2	71.1	0.05	50	30	*
Spiromesifen	411.2	313.1	0.05	50	15	
Etoxazole	360.2	141	0.05	50	42	*
Etoxazole	360.2	304	0.05	50	25	
Lufenuron	511	158	0.05	50	24	*
Lufenuron	511	141	0.05	50	67	

(4) Pesticide degradation rate:

The pesticide degradation rate is calculated using Formula (1):

$$\text{Pesticide degradation rate (\%)} = (C0 - Ct)/C0 \times 100 \quad (1)$$

where C0 is the pesticide residue before sample treatment and Ct is the pesticide residue after sample treatment.

2.3.3. Data Processing

The chart data are presented as mean ± standard deviation. Each experiment was repeated 5 times, and Excel 2021 was used for data processing. Duncan's multiple range analysis, which is a non-parametric test that has the advantages of flexibility, wide applicability, and strong interpretability of results, was conducted using SPPS 26.0, with a significance level of $p < 0.05$. The graphs were drawn using Origin 2021.

3. Results and Analysis

3.1. Mass Spectrum of Acaricide Solution before and after Plasma Treatment

The liquid chromatography-mass spectrometry (LC-MS) chromatograms of five acaricide residues on the surface of kumquats before and after plasma treatment are shown in Figure 2. Panel a represents the LC-MS chromatogram of acaricide residues on the surface of kumquats before plasma treatment, and panel b represents the LC-MS chromatogram of acaricide residues on the surface of kumquats after plasma treatment. It can be seen from

the chromatograms that there are significant differences in the LC-MS chromatograms of the five acaricide residues before and after treatment, with a stable baseline. Moreover, the peak heights of the acaricide residues after treatment are significantly lower than those before treatment. Therefore, it can be concluded from the chromatograms that the plasma treatment had strong effects on the acaricide residues on the surface of kumquats.

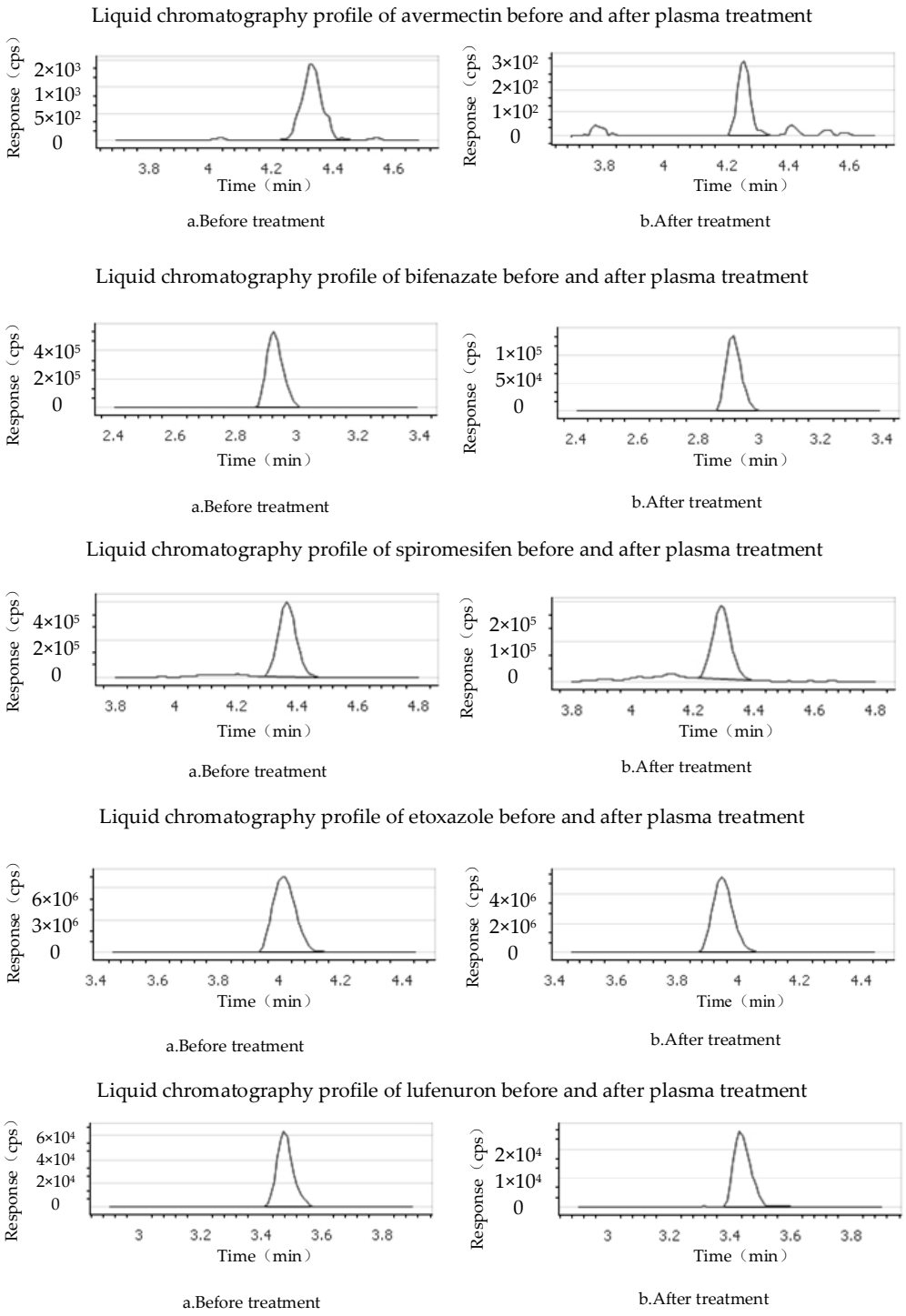
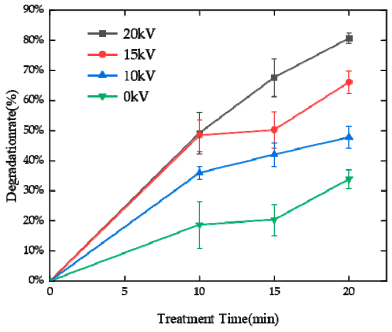


Figure 2. Liquid chromatography-mass spectrometry (LC-MS) chromatograms of acaricide residues on the surface of kumquats before and after plasma treatment.

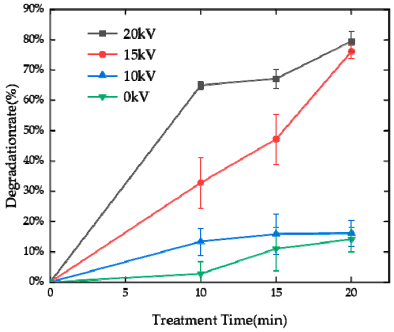
3.2. Plasma Degradation Effect of Five Acaricides on the Surface of Kumquats

The influence of discharge voltage and treatment time on the degradation of avermectin is shown in Figure 3A. The results of the variance analysis indicate that both the

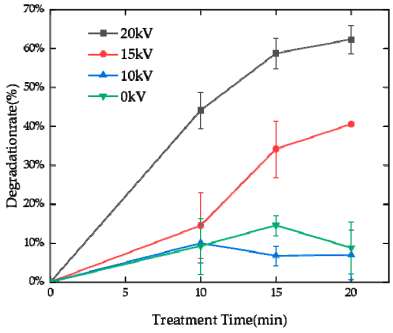
discharge voltage and treatment time have a significant effect on the degradation rate of avermectin ($p < 0.05$), and the degradation rate of avermectin increases with increasing discharge voltage. As shown in the figure, when the discharge voltage is 10 kV and the treatment time is 20 min, the discharge phenomenon is relatively obvious, and the degradation rate is 47.83%. When the voltage is increased to 20 kV and the treatment time is 20 min, the discharge phenomenon is more intense, and the degradation rate is 80.67%. The main reason for the increase in avermectin degradation rate with increasing discharge voltage may be that, within a certain voltage range, as the discharge voltage increases, the electric field energy increases, and therefore, the quantity of reactive species, such as ozone, and high-energy electrons in low plasma increases within a unit of time. These active substances react with more pesticide molecules to decompose them, thus increasing their degradation rate.



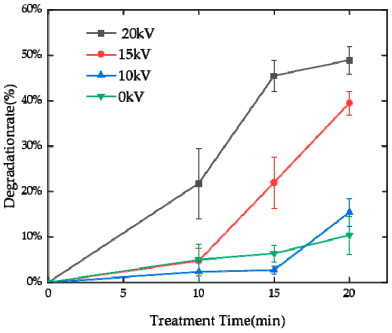
（A） The influence of discharge voltage and treatment time on the degradation rate of avermectin.



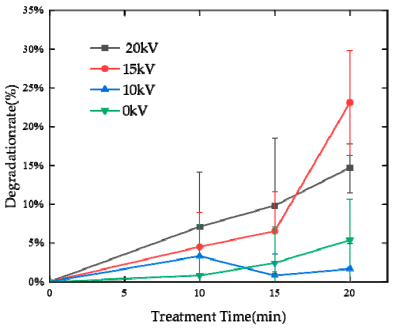
（B） The influence of discharge voltage and treatment time on the degradation rate of bifenazate.



（C） The influence of discharge voltage and treatment time on the degradation rate of spiromesifen.



（D） The influence of discharge voltage and treatment time on the degradation rate of etoxazole.



（E） The influence of discharge voltage and treatment time on the degradation rate of lufenuron.

Figure 3. The influence of discharge voltage and treatment time on the degradation rate of avermectin (**A**), bifenazate (**B**), spiromesifen (**C**), etoxazole (**D**) and lufenuron (**E**).

The degradation rate of avermectin increases with the increase in treatment time. When the discharge voltage is 20 kV, the degradation rate of avermectin is 49.24% after 10 min of treatment, and it increases to 80.67% after 20 min of treatment. The main reason for the increase in avermectin degradation rate with increasing treatment time is the presence of more active substances in the plasma, resulting in a higher degradation rate.

The influence of discharge voltage and treatment time on the degradation of bifenazate is shown in Figure 3B. The results of the variance analysis indicate that both discharge voltage and treatment time have significant effects on the degradation rate of benzene sulfonyl hydrazide ($p < 0.05$), and the degradation rate of bifenazate increases with increasing discharge voltage. As shown in the figure, when the discharge voltage is 10 kV and the treatment time is 20 min, the degradation rate of bifenazate is 16.18%, and obvious discharge phenomena are observed. When the discharge voltage is increased to 20 kV and the treatment time is also 20 min, the degradation rate increases significantly to 79.52%. The main reason for the increase in the degradation rate of bifenazate with increasing discharge voltage is the same as that of avermectin, which will not be further elaborated here.

The degradation rate of benzene sulfonyl hydrazide increases with the increase in treatment time. When the discharge voltage is 20 kV and the treatment time is 10 min, the degradation rate of bifenazate is 49.24%, and when the treatment time is increased to 20 min, the degradation rate increases to 80.67%. However, unlike avermectin, the degradation rate of bifenazate is lower when the discharge voltage is lower. When the discharge voltage is 10 kV and the treatment time is 10 min, the degradation rate of bifenazate is only 13.41%, and when the treatment time is increased to 20 min, the degradation rate is only 16.18%. This indicates that the degradation effect of bifenazate is not significant when the discharge voltage is low, and the influence of discharge voltage is more significant compared to treatment time.

The effects of voltage and treatment time on the degradation of spiromesifen are shown in Figure 3C. The results of variance analysis indicate that both discharge voltage and treatment time have significant effects on the degradation rate of spiromesifen ($p < 0.05$). As shown in the figure, the degradation rate of spiromesifen generally increases with increasing discharge voltage. When the voltage is 20 kV, discharge phenomena are significant, and the degradation rate is 62.4% after plasma treatment for 20 min. However, the degradation rate at 10 kV is almost the same as that at 0 kV. The main reason for this phenomenon may be that after the active substances in the plasma decompose spiromesifen into smaller molecules, the presence of these smaller molecules in the solution inhibits the further degradation of larger molecules.

When the discharge voltage is 15 kV or 20 kV, the degradation rate of spiromesifen increases with the increase in treatment time. When the discharge voltage is 20 kV, the degradation rate of spiromesifen is 44.17% after 10 min of treatment and 62.40% after 20 min of treatment. This is because with the increase in processing time, there is a greater presence of active substances in the plasma, resulting in a higher degradation rate of spiromesifen. When the discharge voltage is 0 kV or 10 kV, the degradation rate after 20 min of treatment is lower than that after 15 min of treatment, as explained in the previous paragraph.

The effects of voltage and processing time on the degradation of etoxazole are shown in Figure 3D. The results of the variance analysis indicate that both discharge voltage and processing time have a significant effect on the degradation rate of etoxazole ($p < 0.05$). As can be seen from the figure, the degradation rate of etoxazole increases with increasing discharge voltage. When the voltage is 20 kV, significant discharge phenomena occur, and after plasma treatment for 20 min, the degradation rate reaches 62.4%. However, when the processing time is 10 min or 15 min, the residual amount of etoxazole at 0 kV discharge voltage is smaller than that at 10 kV discharge voltage. The main reason for this phenomenon may be that when the discharge voltage is 0 kV, etoxazole is mainly dissolved in water, resulting in a decrease in the residual amount. When the discharge voltage is 10 kV, a small amount of active substance is produced, which attacks some etoxazole molecules, causing them to decompose into small molecules. The increase in the concentration of

small molecules in the solution then inhibits the degradation of large molecules, leading to this phenomenon.

The degradation rate of etoxazole increases with the increase in treatment time. When the discharge voltage is 20 kV and the treatment time is 10 min, the degradation rate of etoxazole is 21.84%. When the treatment time is increased to 20 min, the degradation rate increases to 48.93%. This is because with the increase in treatment time, there is a greater presence of active substances in the plasma, which leads to an increase in the degradation rate of etoxazole. However, when the discharge voltage is 0 kV or 10 kV, the degradation rate after 20 min of treatment is lower than that after 15 min of treatment, as explained in the previous paragraph.

The effects of discharge voltage and treatment time on the degradation of lufenuron are shown in Figure 3E. The results of the variance analysis indicate that both discharge voltage and treatment time have significant effects on the degradation rate of lufenuron ($p < 0.05$). As can be seen from Figure, the degradation rate of lufenuron generally increases with increasing discharge voltage. When the treatment time is 20 min and the discharge voltage is 15 kV, the degradation rate of lufenuron is higher than that when the discharge voltage is 20 kV. The main reason for this may be that when the discharge voltage is 20 kV, there are more active substances in the plasma, and the speed of decomposition of small molecules produced by the degradation of lufenuron is faster, which in turn inhibits the degradation of large molecules of lufenuron, resulting in this situation.

The degradation rate of lufenuron increases with the increase in treatment time. However, overall, the degradation effect of lufenuron is not ideal, which indicates that the effects of active species and high-energy groups in the plasma on lufenuron are not significant. This may be related to the molecular structure of lufenuron. When the discharge voltage is 15 kV and the treatment time is 20 min, the degradation rate of lufenuron is the highest, reaching 23.11%. When the discharge voltage is 0 kV and the treatment time is 20 min, the degradation rate of lufenuron is only 4.52%, which is about 20% higher, indicating that although the degradation rate of lufenuron after plasma treatment is not high, the active groups and high-energy particles in the plasma still cause the degradation of lufenuron.

4. Discussion

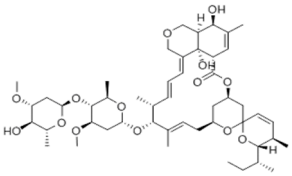
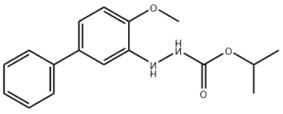
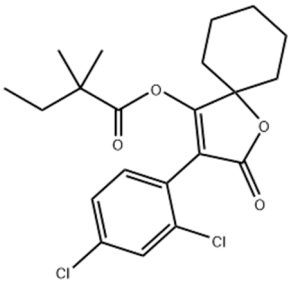
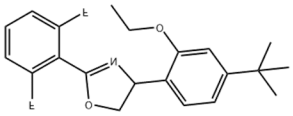
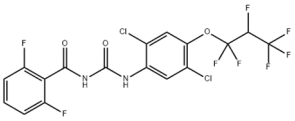
4.1. Chemical Bonds in Pesticide Molecules That Are Prone to Oxidation

When nonthermal plasma is discharged in water, large quantities of strong oxidants such as ozone, hydrogen peroxide, ·OH, and O· are produced [36]. Therefore, when pesticide molecules contain chemically reactive bonds that are easily oxidized, the molecules are more likely to decompose. From the molecular formulas in Table 3, it can be seen that avermectin contains an intramolecular double bond, a ketone group, and a dihydropyridine group; bifenazate contains a hydrazine bond (H-N-N-H) and an ester bond (-COOR); spiromesifen contains two spiro rings, one of which has a ketone group (R-(C=O)-R), and the other has a benzene ring with two double bonds (C=C); methyleneamino is present on the molecule of etoxazole; and lufenuron contains a cis-cyclohexanebisbenzamide group on the phenyl ring. The single bond (-CH2-) between the formylamino group (-CO-NH-) and the bisbenzamide group is easily oxidized. Therefore, nonthermal plasma has a good degradation effect on these five acaricides.

4.2. The Impact of pH on the Degradation of Pesticide Molecules

Taking the discharge voltage of 20 kV in the Figure 4 below as an example, it can be seen that the pH value of the solution gradually decreases with increasing treatment time because the plasma generates ions such as NO^{3-}, NO^{2-}, and H^{+} during the discharge process, causing the solution to become acidic [38]. Li et al. [39] found that the pH value of imidacloprid solution treated with nonthermal plasma gradually decreased during the degradation process, and Lv [40] found that the pH value of abamectin solution decreased by 37.38% after treatment with nonthermal plasma for 240 s.

Table 3. Computed properties of pesticides [37].

Name	Molecular Weight	Molecular Formula	Chemical Structure Depiction	XLogP3-AA
Avermectin	873.1	$C_{48}H_{72}O_{14}$		3.8
Bifenazate	300.35	$C_{17}H_{20}N_2O_3$		4.2
Spiromesifen	411.3	$C_{21}H_{24}Cl_2O_4$		5.9
Etoxazole	359.4	$C_{21}H_{23}F_2NO_2$		5.4
Lufenuron	511.1	$C_{17}H_8Cl_2F_8N_2O_3$		6.4

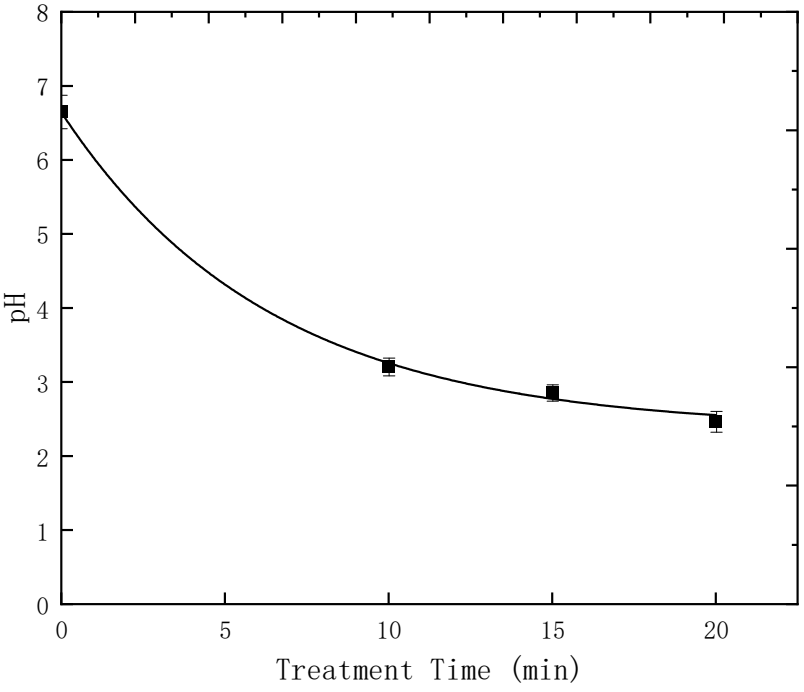


Figure 4. pH changes in the solution during the plasma discharge process.

The degradation behavior of different types of pesticide molecules can be influenced by pH, which may be one of the factors causing different degradation rates of different pesticide molecules. The degradation rate of avermectin is different under different pH conditions. Under acidic conditions, the stability of avermectin is lower and the degradation rate is faster, leading to a more significant degradation effect. When the pH value is within the neutral range, the stability of avermectin is the highest, and the degradation rate is the slowest. Under alkaline conditions, the degradation rate of avermectin also increases. Bifenazate is relatively stable under neutral or weak acidic conditions but is prone to degradation under alkaline conditions, resulting in a slightly inferior degradation effect compared with avermectin. Spiromesifen is relatively stable under neutral and weak acidic conditions but is easily decomposed under alkaline conditions. The degradation of etoxazole is relatively less affected by pH value, but its degradation rate may be slowed down under acidic conditions. Therefore, the degradation effect on spiromesifen and etoxazole that is inferior to that on bifenazate. Lufenuron degrades faster under neutral or weak alkaline conditions but slower under acidic conditions, resulting in the poorest degradation effect among the four pesticides.

4.3. The Impact of XLogP3-AA on the Degradation of Pesticide Molecules

The water solubility of compounds is an important parameter for studying the degradation of organic matter [41]. The hydrophobicity of organic compounds refers to their affinity for either water or oil when in aqueous solutions. Hydrophobic organic compounds tend to be insoluble in water; thus, their distribution and migration in the environment are often restricted, which may lead to a slower degradation rate. Additionally, hydrophobic organic compounds usually have higher chemical stability as their molecular structure is not easily attacked by water or other solvents, which can also result in a slower degradation rate in the environment. The higher the XLogP3-AA value, the greater the hydrophobicity of the organic compound. Therefore, theoretically, the lower the XLogP3-AA value, the more easily the organic compound can be degraded in water environments. As can be seen from the data in Table 3, the XLogP3-AA values of avermectin, bifenazate, etoxazole, spiromesifen, and lufenuron increase in order, which is almost the same as their degradation rate trend. Therefore, the hydrophobicity of organic compounds may also be one of the important factors causing differences in their degradation rates. In Wang et al.'s study [42], it was found that under a discharge voltage of 160 kV and a treatment time of 10 min, the degradation rate of carbendazim in an aqueous solution was 89.04%. The XLogP3-AA value of carbendazim is 1.5 [43]. In Sang et al.'s study [44], it was found that under a discharge voltage of 3 kV and a treatment time of 12 min, the degradation rate of aniline in the aqueous solution was 90.2%. The XLogP3-AA value of aniline is 0.9 [43]. From these two studies, it can be observed that the XLogP3-AA value of aniline is lower than that of carbendazim, indicating that aniline is relatively easier to degrade compared with carbendazim. This trend aligns with the degradation difficulty observed for the five compounds in this study. Therefore, the hydrophobicity of organic compounds may also be one of the important factors contributing to their different degradation rates.

5. Conclusions

In this study, a nonthermal plasma processing system for acaricides residue degradation was built, and the influence of nonthermal air plasma on the degradation efficiency of five commonly used acaricides (avermectin, bifenazate, etoxazole, spiromesifen, and lufenuron) on the surface of kumquat cuimi was investigated. The main conclusions are as follows:

1. The results show that plasma has a significant degradation effect on the acaricide residues on the surface of kumquat cuimi. The discharge voltage and treatment time have a significant impact on the degradation rate. The degradation efficiency varies for different acaricides and is closely related to their molecular structure, solution pH, and hydrophobicity.

2. Plasma is a high-energy physical state that can degrade acaricide residues through non-elastic collisions of high-energy particles and oxidation of active groups. However, this study indicates that a higher discharge voltage and longer treatment time do not necessarily result in better degradation efficiency. This is because the active species generated in the plasma can decompose the pesticide molecules into smaller ones, leading to an increase in the concentration of small molecules in the solution, which in turn inhibits the degradation of large molecules. This study provides insights into the practical application of nonthermal plasma for the degradation of pesticide residues on fruit and vegetable surfaces.

Therefore, in subsequent research, we intend to investigate the following points:

1. We aim to determine the effective control and optimization of nonthermal plasma parameters for different pesticide residues.
2. Taking a micro-scale approach, we aim to explore the dynamic process of pesticide degradation by plasma-active species.

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