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# Effect of Plasma Activated Water on the Degradation of Bifenazate and Spirodiclofen Residues on *Cuimi kumquat* and Impact on Its Quality

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**Abstract:** With the development of plasma-activated water (PAW) technology, its applications in the fields of food, agriculture, and biomedicine are becoming increasingly widespread. PAW has sterilization, pesticide residue reduction, anti-cancer, and blood clotting functions. Traditional methods for pesticide degradation include home processing, baking and freeze-drying, and UV treatment; however, they generally suffer from poor degradation efficiency and adverse effects on fruit quality. This study found that PAW treatment is a green and efficient environmental technology with the advantages of simple operation, good treatment effect, and no secondary pollution. This paper investigated the efficiency of PAW on the reduction of two acaricides, namely, bifenazate and spirodiclofen, and the effect of PAW treatment on the quality of *Cuimi kumquat*. The results showed that after PAW treatment, the residual amounts of bifenazate and spirodiclofen were reduced to a minimum of 1.19 mg·kg$^{-1}$ and 0.23 mg·kg$^{-1}$, with a reduction of 74.35% and 59.37% respectively compared to the control. Moreover, PAW treatment did not have any negative effects on the storage quality of *Cuimi kumquat*.

**Keywords:** *Cuimi kumquat*; plasma-activated water (PAW); bifenazate; spirodiclofen; storage quality



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## 1. Introduction

*Cuimi kumquat* is the fruit of the kumquat genus in the Rutaceae family. It has a unique flavor and can be eaten with the peel. The flesh is sweet and the skin is thin and crisp [1]. Research has shown that the peel of *Cuimi kumquat* is rich in various flavonoid functional components, which have anti-oxidant, anti-tumor, and anti-cancer effects [2].

*Cuimi kumquat* is heavily damaged by *Tetranychus cinnbarinus* due to the high sugar content of branches, leaves and fruits. The kumquats in northern Guangxi need to be covered with film to protect them from the cold, rain, and sun after ripening. Farmers often spray acaricides to control the population of *Tetranychus cinnbarinus* in orchards before applying film; however, they frequently apply the film before the safe period of acaricides is met. As a result, the population of *Tetranychus cinnbarinus* increases after the application of the film, which prompts the farmers to use acaricides again. This cycle often leads to more than ten *Tetranychus cinnbarinus* controls per year, increasing the risk of acaricide residues in *Cuimi kumquat* and posing a significant risk to consumers. Although traditional household processing methods, such as washing, peeling, and boiling, can reduce pesticide residues in fruits and vegetables [3], the washing treatment is not effective, while peeling and boiling are not suitable for fresh fruits such as *Cuimi kumquat*. Currently, the most widely used methods for pesticide residue degradation are baking and freeze-drying [4], ultraviolet treatment, ultrasound, and ozone. However, baking and freeze-drying techniques are not suitable for fresh food products, while ultraviolet treatment requires chemical reagents to

achieve good degradation results, which may cause chemical residues and require further research [5]. Ultrasound treatment may cause pesticide residues on the surface of fruits and vegetables to penetrate into the interior, affecting the quality of fruits [6]. With ozone treatment, degradation takes a long time for to occur and produces too many oxidation products that adhere to the surface of the sample, shielding the effect of ozone [7]. In addition, the concentration and exposure times of ozone are often too long, which will have adverse effects on the color and skin of the sample [8]. However, PAW treatment, as a green and efficient environmental protection technology, is suitable for the degradation of pesticide residues on fresh fruits and vegetables. It is simple to operate, has good treatment effects, and does not cause secondary pollution.

PAW, as an emerging technology applied in the field of pesticide residue degradation in fruits and vegetables, has shown in many studies that its rich oxidation groups can effectively degrade pesticide residues in fruits and vegetables without negative impacts on their taste and quality [9–12]. For example, previous studies have found that after 240 s of PAW treatment, the degradation rates of metribuzin and metobromuron in *Chrysanthemum morifolium* reached 38.2% and 74.3%, respectively, without affecting its color and quality [10]. And another study reported that PAW treatment can effectively degrade the residues of chlorothalonil and thiamethoxam in tomatoes without affecting their quality [9]. Furthermore, due to the transient nature of reactive oxygen species (ROS) and reactive nitrogen species (RNS) in PAW, it will eventually revert back to ordinary deionized water after a certain period of time. Therefore, there will be no chemical residues in the treated fruits and vegetables [13].

Currently, research on the effects of PAW treatment on kumquats mainly focuses on its antibacterial properties [14], while there is limited research on its ability to degrade pesticide residues in kumquats. Thus, this study aimed to investigate the degradation of bifenazate and spirodiclofen in *Cuimi kumquat* treated with PAW generated at different excitation voltages, as well as the impact on the storage quality of the fruits. The *Cuimi kumquat* was chosen as the study object. The goal of this research was to provide a theoretical basis and reference for the further application of PAW in the preservation and processing of *Cuimi kumquat*.

## 2. Materials and Methods

### 2.1. Instrumentation and Reagents

The EXPEC 5210 liquid chromatography–triple quadrupole mass spectrometry system (LC-MS/MS, Spectrum Technology Development Co., Ltd., Hangzhou, China), atmospheric pressure plasma (APPJ) devices, ultrasonic cleaner (YL-080S, Shenzhen Jietai Ultrasonic Cleaning Equipment Co., Ltd., Shenzhen, China), analytical balance (BSA124S, Mettler Toledo, Beijing, China), sugar acid meter (PAL-BX/ACID1, ATO, Japan), trace analysis ultra-pure water system (WP-UP-WF-30, Sichuan Water Treatment Equipment Co., Ltd., Sichuan, China), and color difference meter (CM-205, Shanghai Precision Instrument Co., Ltd., Shanghai, China) were used in this study.

Bifenazate solution in methanol (1.2 mL, 100 μg/mL, Wuhan Rhodes Biotechnology Co., Ltd., Wuhan, China), bifenazate suspension (43%, Foshan Daxing Biochemical Co., Ltd., Foshan, China), spirodiclofen (1.2 mL, 100 μg/mL, Wuhan Rhodes Biotechnology Co., Ltd.), spirodiclofen suspension (29%, Jinan Zhongke Green Biological Engineering Co., Ltd., Jinan, China), acetonitrile (chromatographic grade, Sigma-Aldrich Corporation, St. Louis, MO, USA), CNWBOND PSA QuEChERS Special Ultra Clean Filler (CNWBOND PSA, 40–63 μm, item:SBEQCA2401-10g, Shanghai Anpu Cuishi Standard Technical Service Co., Ltd., Shanghai, China), and sodium chloride (analytical grade, Hangzhou Pyron Chemical Co., Ltd., Hangzhou, China) were used as reagents.

### 2.2. Sample Preparation

The *Cuimi kumquat* tangerines were harvested 180 days after flowering from the Hongwei Xia Tun nursery in Chang'an Town, Rongan County, Liuzhou City, Guangxi Zhuang Autonomous Region, China. The trees were 7 years old, while the samples were collected in early December. The fruits with uniform size and color were selected for

analysis. The harvested tangerines were cleaned using an ultrasonic cleaner (90 W, 5 min), while a standard solution of bifenazate and spirodiclofen at a concentration of 1000 ppb was prepared using reverse osmosis (RO) water. Approximately 100 g of the cleaned tangerines was soaked in 1 L of bifenazate and spirodiclofen standard solution for 30 s and air-dried for subsequent analysis.

### *2.3. Preparation of PAW and Sample Handling*

Atmospheric pressure plasma jet (APPJ) was used to activate deionized water and produce PAW. The APPJ plasma device is shown in Figure 1. The plasma experimental device consists of a plasma reactor, a high voltage AC power supply, an air collector, and a measurement device. The plasma reactor adopts a coaxial needle–ring discharge structure, which is mainly composed of a high-voltage electrode, a dielectric tube, and a ground electrode. The high-voltage electrode is a tungsten needle with a diameter of 2 mm; 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, while the plasma excitation region is located between the tungsten needle and the gap covered by the copper foil. The high-voltage AC power supply is composed of a low-voltage DC power supply and a high-frequency inverter, which is used to generate an excitation voltage range of 0–20 kV. The air collector is composed of a brushless diaphragm pump (D50H-42H, Chengdu Hailin Technology Co., Ltd. Chengdu, China) and a flow meter, which provide air as the discharge gas and control the flow rate at 3.5 L·min$^{-1}$. The measurement device is composed of a voltage probe (P6015A, Tektronix, Aerial Survey Technology Co., Ltd., Tianjin, China), a current probe (H-FCT-200, Shanghai Pinyan Measurement and Control Technology Co., Ltd., Shanghai, China), and an oscilloscope (TDS2024C, Tektronix), which are used to monitor real-time voltage and current waveforms. When the voltage is 10 kV, 15 kV, and 20 kV, respectively, the real-time voltage and current waveforms are as shown in Figure 2.

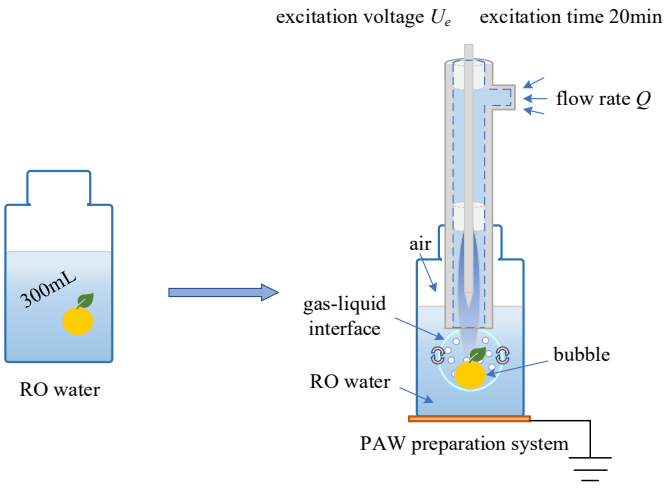


**Figure 1.** Preparation of PAW and sample handling.

A 300 mL beaker was filled with RO water, and the nozzle of the plasma jet device was immersed in the RO water. The plasma excitation region was located in the RO water between the high-voltage electrode and the copper foil. The flow rate was controlled to Q via a flow meter, and the RO water was excited with a voltage Ue (10 kV, 15 kV, 20 kV) for 20 min to produce a certain activity of 300 mL activated water, which were, respectively, referred to as PAW10, PAW15, and PAW20. While the PAW was being generated, the sample was placed in RO water. RO water was used as the control. The experiment was repeated three times.

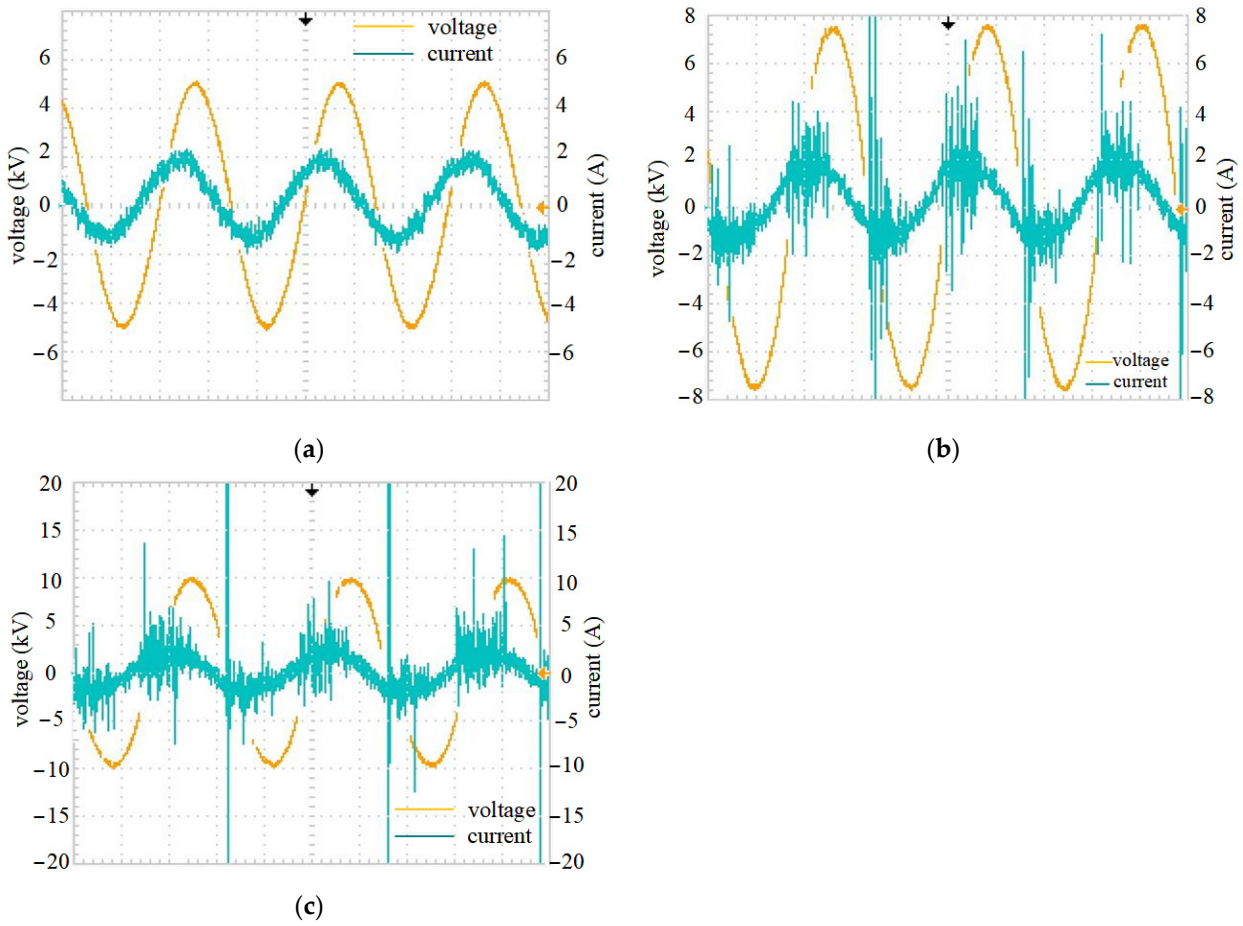


**Figure 2.** Real-time voltage–current waveform diagrams at voltage levels of (**a**) 10 kV, (**b**) 15 kV, and (**c**) 20 kV. The arrow markings in the figure indicate the locations of horizontal trigger positions.

### *2.4. Physicochemical Properties of PAW*

A volume of 300 mL of RO water was transferred to a 1 L beaker. High-voltage electrodes with diameters of d = 2 mm and lengths of 150 mm were used to activate the water at a flow rate of 3.5 L·min$^{-1}$. The nozzle end was immersed in the liquid to study the changes in pH value and EC value of PAW at different activation voltages. Immediately after activation, the pH value of PAW was measured using a benchtop pH meter (STARTER 3100), while the EC value was measured using a portable conductivity meter (DDB-303A). The measurement time did not exceed 2 min, and the experiment was repeated three times.

### *2.5. Analysis of Residual Amounts of Fenamiphos*

#### 2.5.1. Pretreatment Method

Sample preparation process: We weighed 10 g of the sample (accurate to 0.01 g) in a 50 mL centrifuge tube. We then added 10 mL of acetonitrile, vortex, and sonicate for 15 min. We added 2 g of sodium chloride, vortex, and centrifuge for 5 min at 4000 r/min. We then quantitatively transferred the supernatant to a centrifuge tube containing the dehydrating agent and purification material (use 25 mg CNWBOND PSA for each milliliter of extraction solution), vortexed for 1 min, and filtered the supernatant through a 0.22 μm filter membrane, diluting it if necessary, and then measured.

Standard curve preparation process: The standard stock solution (100 μg/mL) was diluted with acetonitrile to prepare a series of standard solutions with gradient concentrations of 1.0, 2.0, 5.0, 10, 20, 50, 100, 200, and 500 ng/mL.

#### 2.5.2. High Performance Liquid Chroma-Mass Spectrography (HPLC-MS) Analysis

1. Liquid chromatography conditions

Waters ACQUITY UPLC BEH C18 1.7 μm 2.1 × 100 mm was used for separation, with a mobile phase of 0.1% formic acid water (A) and acetonitrile (B), the column temperature set at 40 °C, an injection volume of 5.0 μL, and liquid chromatography gradient elution conditions as shown in Table 1.

**Table 1.** Gradient elution conditions.

| Time/min | Flow Rate/(mL/min) | A/% | 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 |

2. The mass spectrometry (MS) conditions

The ion source was operated using electrospray ionization in positive mode (ESI+). The ion source temperature was set at 105 °C, the capillary voltage was set at 5.0 kV, and the desolvation gas temperature was set at 495 °C with a flow rate of 300 L/h. The scan mode was set to multiple reaction monitoring (MRM) mode. Other mass spectrometry parameters are listed in Table 2.

**Table 2.** Qualitative ion pairs, quantitative ion pairs, and other MS parameters of bifenazate and spirodiclofen.

| Compound | Parent Ion (m/z) | Product Ion (m/z) | Residence Time/s | Tapered Hole Voltage/V | Collision Energy/eV |
|---|---|---|---|---|---|
| bifenazate | 301.1 | 170.1 | 0.05 | 50.00 | 21 |
| | | 198.05 * | 0.05 | 50.00 | 9 * |
| Spirodiclofen | 411.2 | 313.1 | 0.05 | 50.00 | 15 |
| | | 71.1 * | 0.05 | 50.00 | 30 * |

Note: * indicates quantitative ion pair.

### *2.6. Analysis of the Physical and Chemical Properties of Cuimi kumquat*

We selected the treatment with the best effect on degrading pesticide residues for further study in relation to the physicochemical properties of *Cuimi kumquat*. We set air and RO water as control groups. We then took 2 kg of *Cuimi kumquat* for each treatment and stored the samples for seven days at 10 °C. We observed and recorded the changes in the storage quality.

#### 2.6.1. Determination of Skin Color Difference

The skin color difference was measured using a CM-205 colorimeter during storage. Six fruits were selected from each treatment at each sampling point: four points on the equator of the fruit and one point on the top and bottom, respectively, were chosen. The surface brightness L*, red–green difference a*, and yellow–blue difference b* were measured, and the average value of each measurement was taken.

#### 2.6.2. Determination of Intrinsic Quality of Fruit

Eighteen fruits (three biological replicates) were selected from each treatment at each sampling point. The fruits were juiced using a juicer and the juice was filtered. Determination of soluble solids (TSS), titratable acid (TA) via sugar acidity meter, and vitamin C (VC) content via 2,6-dichlorophenol indophenol titration was performed.

### *2.7. Data Processing*

The experimental data were sorted and statistically analyzed using Microsoft Office Excel 2020 and IBM SPSS Statistics 26. Duncan's multiple comparison method was used to analyze the significant differences (different lowercase letters in the figures indicate significant differences between treatments, $p < 0.05$). Origin 2021 was used for plotting.

## 3. Results and Discussion

### *3.1. Physico-Chemical Properties of PAW*

The interaction between APPJ and RO water generates PAW, which is mainly influenced by pH and EC values [15]. Compared to RO water, PAW has stronger acidity (Figure 3), with a pH as low as 2.82. The acidification of PAW is caused through the excitation of $NO_2^-$, $NO_3^-$, and peroxynitrous acid (ONOOH) [16]. Several studies have shown that this acidic solution exhibits high oxidation potential at a pH range of 2–3 and can promote the degradation of organic compounds [17–19]. Therefore, the acidity of PAW may play an important role in reducing the residues of bifenazate and spirodiclofen in *Cuimi kumquat*. It is worth noting that the large amount of reactive oxygen and nitrogen species (RONS) in PAW can cause lipid peroxidation in cell membranes, leading to a decrease in membrane selectivity. RONS and a large number of protons ($H^+$) can enter the cells, disrupting the redox and pH homeostasis in the cells, ultimately causing physiological dysfunction and cell death [15], which may cause damage to the *Cuimi kumquat* peel; this process requires further investigation.

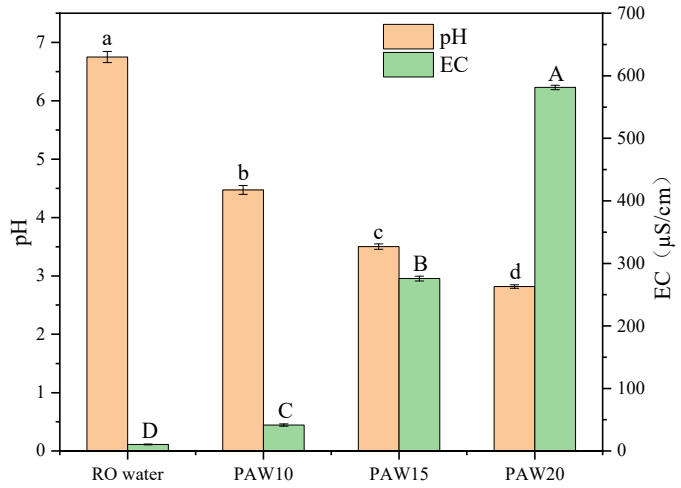


**Figure 3.** pH and EC of RO water and PAW. Different lowercase letters indicate statistical differences between pH values, while different uppercase letters indicate statistical differences between EC values ($p < 0.05$).

EC value is a physical quantity that measures the conductivity of a solution. The higher the EC value, the more electrolytes or ions the solution contains [20]. As shown in Figure 3, the EC value of PAW is significantly higher than that of RO water, increasing linearly from 10.42 μS/cm to 581.37 μS/cm with an increase in excitation voltage. The increase in the EC value of PAW mainly depends on the applied excitation voltage, excitation time, and discharge mode. Ma et al. (2015) found that the EC value of RO water activated using a plasma jet for 20 min with an excitation voltage of 18 kV and Ar (98%)/$O_2$ (2%) as the working gas was 450 μS/cm [21], which is lower than the value obtained in this study (581.37 μS/cm). This may be because this study used direct discharge in liquid, which results in a higher EC value than plasma discharge on the liquid surface [22].

### *3.2. Linear Range and Quantification Limit of HPLC-MS*

A mixed standard working solution of bifenazate and spirodiclofen 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 1.0–500 ng/mL. The obtained standard curves for bifenazate and spirodiclofen were Y = 3931.2446X + 30,000.7846 and Y = 27,198.9796X + 99,277.9849, respectively. The determination coefficients ($R^2$) were 0.9951 and 0.9974, respectively. Under this detection condition, the limit of quantitation (LOQ) was calculated to be 0.0005 mg/kg using the signal-to-noise ratio (S/N) of 10, indicating the high sensitivity of the method.

### *3.3. PAW's Effect on Pesticide Residue Degradation in Cuimi kumquat*

Figure 4 illustrates the effects of different treatments on the residues of bifenazate and spirodiclofen in *Cuimi kumquat* fruit. The results indicate that the concentration of acaricides in *Cuimi kumquat* decreases with an increase in the activated voltage of PAW. The concentrations of bifenazate and spirodiclofen in untreated *Cuimi kumquat* was 5.06 mg·kg$^{-1}$ and 0.57 mg·kg$^{-1}$, respectively. After soaking the fruit in RO water for 20 min, the concentration of bifenazate decreased by 91.69%, while the concentration of spirodiclofen hardly decreased. However, after PAW20 treatment, the concentration of bifenazate and spirodiclofen decreased to the lowest values of 1.19 mg·kg$^{-1}$ and 0.23 mg·kg$^{-1}$, respectively. Compared with the control, the reduction rates were 74.35% and 59.37%, respectively. These results suggest that PAW can effectively degrade acaricides in *Cuimi kumquat* under certain voltages. In this experiment, the lowest residues of spirodiclofen after degradation were below the China maximum residue limit (MRL) of 0.5 mg·kg$^{-1}$ (China MRL is based on fresh kumquat adapted from the State Administration of Market Supervision and Administration). However, the residues of bifenazate did not decrease to below the China MRL of 0.7 mg·kg$^{-1}$. Further studies can investigate the degradation effects of RONS in PAW on different pesticides, which may be related to the physicochemical properties of the pesticides themselves.

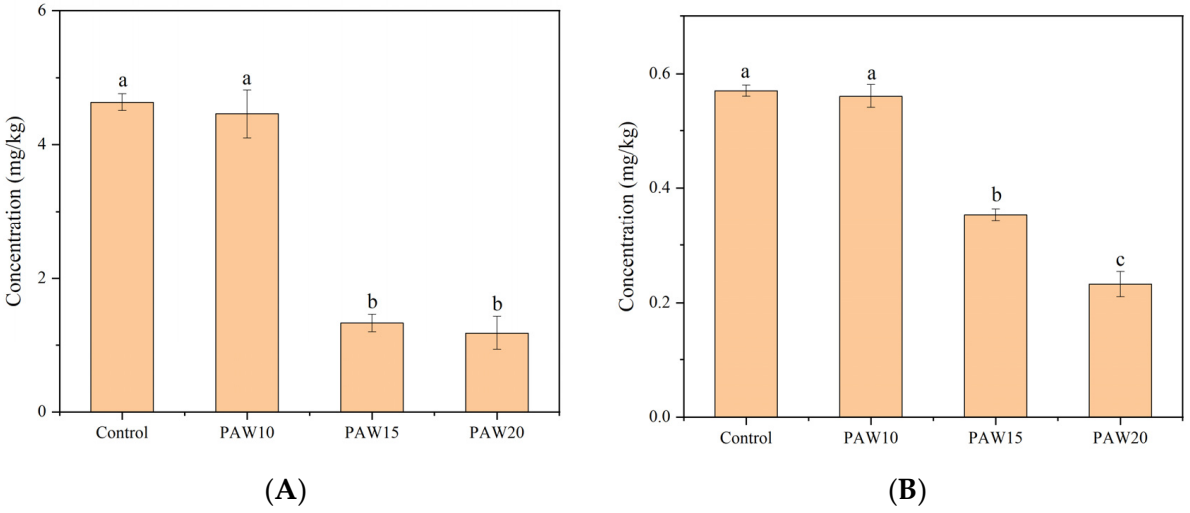


**Figure 4.** Residues of bifenazate (**A**) and spirodiclofen (**B**) in PAW-treated *Cuimi kumquat*. Mean values (n = 3) with lowercase letters indicating significant differences ($p < 0.05$) and lowercase letters being the same indicating no significant differences ($p \geq 0.05$).

At present, PAW has gradually been applied to the degradation of pesticides in fruits and vegetables such as citrus, tomato, and chrysanthemum [9–12]. However, most of these studies soak the samples in PAW after its preparation, whereas this experiment significantly improved the degradation efficiency by placing the samples in RO water while generating PAW. This is because the effective degradation of pesticides requires the synergistic effect of ROS and RNS, while the lifespan of some RONS in PAW, such as ·OH, HOO·, $O_2^-$, is short. Long-lived RONS, such as $H_2O_2$, $NO_2^-$, and $NO_3^-$, cannot act alone and need to form strong oxidants, such as peroxynitrous acid (ONOOH), peroxynitrite, and related nitrogen oxides, resulting in weak pesticide degradation effects [23,24]. Specifically, for example,

the radical ·OH can be related to the presence of $H_2$ in the air discharge, giving rise to an increase in the dissociation processes of the nitrogen, hydrogen, and oxygen molecules, with other species forming (NO, OH, and NH). The OH species are formed according to the following equations:

$$H_2 + e(eV) \rightarrow H + H + e^-, \quad (1)$$

$$H + O_2 \rightarrow \cdot OH + O, \quad (2)$$

Moreover, the high-energy electrons ($e^-$) would bombard the RO water and oxygen molecules in producing ·OH and $H_2O_2$ [24].

$$e^- + H_2O \rightarrow \cdot H + \cdot OH + e^-, \quad (3)$$

$$H_2O + H_2O + e^- \rightarrow H_2O_2 + H_2 + e^-, \quad (4)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2. \quad (5)$$

The low pH value and high oxidation–reduction potential (ORP) environment of PAW enable it to degrade pesticides [10]. In this experiment, PAW mainly degraded pesticides through underwater discharge of APPJ to generate ROS. Multiple studies have shown that $O_3$ in ROS plays a key role in pesticide degradation [25–28]. OH· and $H_2O_2$ generated using $O_3$ in aqueous solution also have a certain effect on pesticide degradation [29].

The degradation rate of bifenazate was higher than that of spirodiclofen after PAW treatment (Figure 4). This is mainly due to the properties of the pesticides themselves. The solubility of bifenazate in water was found to be 2.1 mg/L, which is higher than that of spirodiclofen at 0.05 mg/L [30]. Moreover, pesticides with higher water solubility are easier to degrade [31]. Additionally, the partition coefficient of bifenazate (octanol/water), known as log Pow, was determined to be 3.5, which is lower than the log Pow of spirodiclofen, which was 5.8 [30]. The lower the log Pow value of the pesticide, the higher its affinity for water, making it easier to remove via washing methods [32].

### *3.4. Effect of PAW Treatment on Skin Colour Difference during Storage of Cuimi kumquat*

The surface color of fruit peel is an important attribute used to evaluate fruit quality and commercial value, which directly affects consumers' willingness to purchase. The International Commission on Illumination (CIE) improved the CIE XYZ color model to the CIE L*a*b* model, which is widely used to measure color differences in food [33].

As can be seen from Figure 5, the brightness (L*) and yellow–blue chromaticity (b*) values of fruits in different treatment groups did not exhibit significant changes throughout the storage period. The red–green chromaticity (a*) showed significant differences on the fourth day of storage; however, no significant differences were observed on the fifth to seventh days of storage. Compared with the control group, the L* and b* values of the treatment group fluctuated on the fourth and seventh days of storage, showing a slight decrease in fruit skin brightness and a slightly bluish hue. The a* values fluctuated randomly before storage for the first three days; after treatment for four days, the fading-to-red effect of PAW20 was better than that of the control and RO water. However, overall, no significant color differences were observed among the different treatments in Figure 5. The results indicate that PAW20 treatment had no significant effect on the color of *Cuimi kumquat*, which is similar to the results of Ali et al. [34–37]. PAW treatment did not significantly promote color transformation in tomatoes, grapes, strawberries, and potatoes.

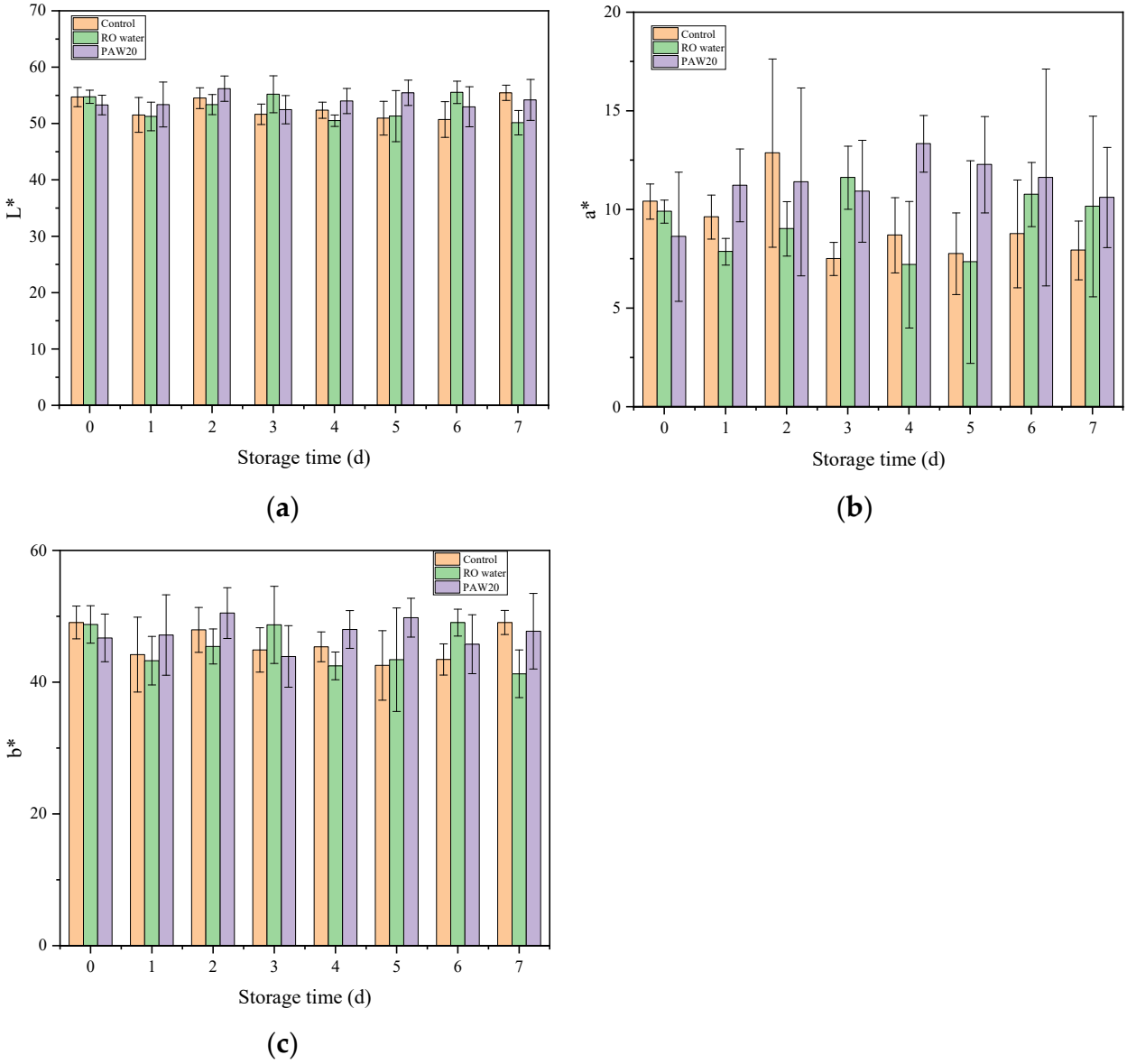


**Figure 5.** PAW-treated *Cuimi kumquat* peel color difference values L* (**a**), a* (**b**), and b* (**c**). Based on the paired sample *t*-tests shown in the three graphs, there is no significant difference between the control group and the treatment group, $p > 0.05$).

### *3.5. The Impact of PAW Treatment on the Intrinsic Quality of Cuimi kumquat Fruit*

The TSS reflects the changes in nutrient content during fruit storage [38]. As shown in Figure 6a, there were no significant differences in TSS content among the treatments during the storage time of *Cuimi kumquat*. However, after 3–4 days of storage, the TSS content of *Cuimi kumquat* treated with PAW20 was slightly lower than the control, which was due to the enhanced respiration rate of *Cuimi kumquat* after water absorption. After 5–7 days of storage, the TSS content of *Cuimi kumquat* treated with PAW20 was slightly higher than the control, which was due to the delayed aging process of the fruit during storage due to PAW treatment [39]. Thus, PAW can maintain the TSS content of *Cuimi kumquat* during storage.

The TA is an important index that is used to evaluate the flavor quality of fruit. As shown in Figure 6b, the TA content of *Cuimi kumquat* showed a trend of first decreasing, then increasing, and finally decreasing again with the increase in storage time. After 5–7 days of storage, the TA content of the mandarin fruit treated with PAW20 was significantly higher than the control. The VC content in *Cuimi kumquat* treated with PAW20 during storage was slightly higher than the control (Figure 6c), indicating that PAW treatment can slow down

the decline of total acid content in the fruit and preserve the nutrients, although the effect was not significant.

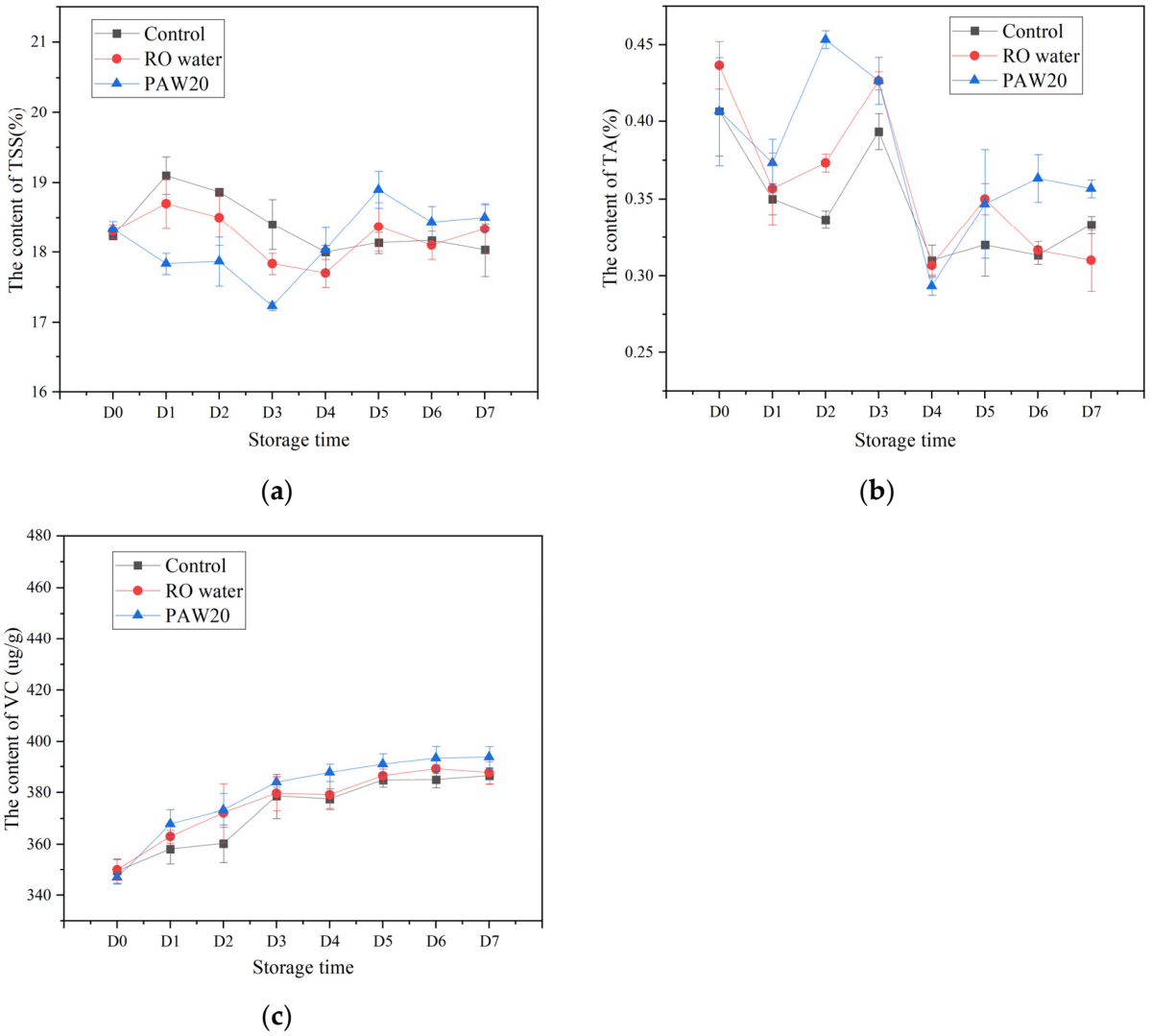


**Figure 6.** Effects of PAW treatment on content of TSS (**a**), TA (**b**), and VC (**c**) in *Cuimi kumquat* fruit.

## 4. Conclusions and Outlook

This study verified the feasibility and effectiveness of PAW treatment of bifenazate and spirodiclofen residues in *Cuimi kumquat*. HPLC results showed that the concentrations of bifenazate and spirodiclofen in *Cuimi kumquat* significantly decreased with increasing voltages of PAW treatment. After PAW20 treatment for 20 min, the residual levels of bifenazate and spirodiclofen in *Cuimi kumquat* decreased to the lowest levels of 1.19 mg·kg$^{-1}$ and 0.23 mg·kg$^{-1}$, respectively. The low pH value (2.82) and high EC value (581.37 µS/cm) of PAW were favorable for the reduction in bifenazate and spirodiclofen levels. In addition, there were no significant differences in fruit peel color, TSS, TA, and VC content of *Cuimi kumquat* compared to the control. In summary, PAW treatment can effectively reduce the residual levels of bifenazate and spirodiclofen in citrus fruits without affecting their storage quality. This treatment provides a new idea for green and efficient reduction in pesticide residues in whole fruit consumption and is a technique with great potential for practical applications.

However, further research is needed to investigate the application of PAW in reducing pesticide residues in food. Firstly, although this study demonstrated that PAW can effectively degrade the residues of bifenazate and spirodiclofen in *Cuimi kumquat* and does not significantly affect the shelf quality of the final product, it is necessary to expand the selection of

agricultural products and pesticides to represent current agricultural practices and the types of products available in the market to ensure that the results are applicable to real scenarios. Secondly, more research is needed to select appropriate plasma parameters, such as discharge power, airflow velocity, and treatment time, to ensure that PAW can effectively remove target pesticide residues without causing any harm to agricultural products. Furthermore, the physicochemical reactions generated by the pesticide residues under these conditions, the damage effects on the pesticide structure, and the degradation products of the pesticides should be studied. Thirdly, the low pH value and high ORP environment created using PAW during pesticide degradation may damage the oxidation–reduction potential and pH stability of fruit and vegetable skin cells, eventually leading to physiological dysfunction and cell death. This may cause damage to fruits and vegetables and requires further research. In addition, it is necessary to improve the technical level of research and carry out research on low-temperature plasma directly applied to agricultural products for sterilization and pesticide residue reduction.

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