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Degradation of Imidacloprid Residues on Unripe Tomatoes (*Solanum lycopersicum*) by AOPs and Its Analysis using Spectrophotometer and HPLC

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Abstract

Imidacloprid is an insecticide-active ingredient used by farmers to kill and control insects. Imidacloprid residue can be found in unripe tomatoes. Consuming unripe tomatoes contaminated with imidacloprid can cause human health problems such as cancer, chronic kidney disease, neurological disorders, and reproductive issues. In this study, imidacloprid pesticide residues on unripe tomatoes were degraded by the Advanced Oxidation Processes (AOPs) method, namely ozonolysis, sonolysis, and sonozolysis at various processing times (5, 10, 15, 20, and 25 minutes) in 50 g sample mass and 100 mL water volume. The changes in imidacloprid concentration before and after degradation were measured using a UV-Vis spectrophotometer and HPLC. The results of imidacloprid residue degradation by sonolysis was 66.99%, ozonolysis was 74.87%, and sonozolysis was 66.00%. The degradation kinetics of the imidacloprid residue was then studied. Kinetic study of all AOPs methods found that imidacloprid degradation followed a first-order kinetic model. The kinetics data showed that ozonolysis degradation is faster than sonolysis and sonozolysis, with a half-life ($t_{1/2}$) of 16.90 minutes.

1. Introduction

Unripe tomatoes (*Solanum lycopersicum*) are one of the food sources for Indonesian people because they contain antioxidants, vitamins, potassium, and folate. [1]. Farmers use insecticides such as imidacloprid to improve the production and quality of unripe tomatoes while also controlling pests. Imidacloprid is a systemic and water-soluble pesticide. Imidacloprid has a water solubility of 610 mg/L and log Kow of 0.57. From this characteristic, imidacloprid is challenging to remove from tomatoes containing 90–95% water [2]. The use of imidacloprid is harmful to the environment and dangerous to human health. Excessive intake of imidacloprid residues causes neurotoxicity, carcinogenic, and reproductive disorders [3, 4, 5]. The World Health Organization (WHO) categorizes imidacloprid as a class II (moderately hazardous) pesticide [6]. As a result of this case, consumers are becoming more concerned and selective about the food to be consumed, so the government issued a regulation regarding the Maximum Residue Limit (MRL) of imidacloprid residue. One of the regulations issued by the government is the Indonesian National Standard (SNI) 7313:2008. SNI sets the MRL for imidacloprid in unripe tomatoes is 0.5 ppm [7].

Post-harvest, washing, boiling, and adding chemical compounds such as sodium bicarbonate and detergent solutions have been employed to remove imidacloprid residues. [7, 8, 9]. Washing with tap water takes a long time and can pollute the aquatic environment. The addition of chemical substances can affect the taste and make the product more harmful.

The alternative method to solve this problem is the Advanced Oxidation Processes (AOPs) method. The AOPs method is an effective method that has been used to degrade organic compounds such as dyes [10, 11, 12], medicines [13, 14], and pesticides [15, 16, 17]. AOPs

methods such as ozonolysis, sonolysis, and sonozolysis can generate hydroxyl radicals (•OH) that can be used to degrade pesticide residues into (CO_2 and H_2O) because they are more environmentally friendly [18, 19, 20, 21, 22] so that unripe tomatoes become less dangerous to consume. This study aims to compare the ability of each AOP method to imidacloprid residues in unripe tomatoes, such as ozonolysis, sonolysis, and sonozolysis. Ozonolysis is the selective and slow-reacting use of ozone as an oxidant. Ozone dissolves in water to produce •OH as a non-selective and fast oxidant.

Meanwhile, ultrasonic waves are used in sonolysis to produce •OH, and sonozolysis is a process that combines ozonolysis with sonolysis. The effects of processing time, water volume, and sample mass were investigated. To the best of our knowledge, pesticide degradation in raw agricultural commodities such as tomatoes with variations in processing time, sample mass, and water volume parameters has received less attention. The concentrations of imidacloprid in unripe tomatoes after degradation were analyzed using a UV-Vis Spectrophotometer and a High Performance Liquid Chromatography (HPLC). The absorbance, whose value is directly proportional to the concentration of the analyzed sample, results from a UV-Vis Spectrophotometer analysis. HPLC analyzes changes in chromatogram peaks before and after degradation to detect the formation of intermediate compounds during the degradation process. In addition, the first-order kinetics in ozonolysis, sonolysis, and sonozolysis were evaluated.

2. Methodology

2.1. Materials dan Instrumentations

The materials were commercial imidacloprid insecticide 10 WP (PT. Mitra Kreasidharma, Indonesia), acetonitrile (HPLC grade), distilled water, tap water, and fresh unripe tomatoes from Aia Angek (Sepuluh Koto, West Sumatra). The structure of imidacloprid is shown in Figure 1.

The instrumentations for imidacloprid analysis were UV-Vis spectrophotometry (Shimadzu, Japan) and HPLC (Shimadzu, Japan). Ozone (O_3) and ultrasonic waves were obtained by an ozonizer (Hanaco TSH-278, China) with an ozone dose of 400 mg/h and a sonicator (Krisbow CD-4862) with a frequency of 35 kHz.

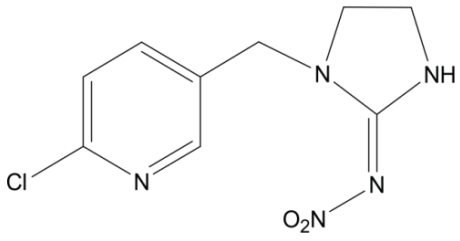

Figure 1. Structure of imidacloprid

2.2. Imidacloprid Residue Degradation in Unripe Tomatoes

2.2.1. Effect of Processing Time

The degradation of imidacloprid residues in unripe tomatoes by ozonolysis, sonolysis, and sonozolysis were carried out using an ozonizer, a sonicator, and a combination of both, respectively. Every 50 g of unripe tomatoes were immersed in 100 mL of water. The processing time was set at 5, 10, 15, 20, and 25 minutes for all of AOPs methods.

2.2.2. Effect of Water Volume

Fresh unripe tomatoes were weighed 50 g, then immersed in 50, 100, 150, and 200 mL of water, respectively. The samples were then processed at the optimal time.

2.2.3. Effect of Sample Mass

Four fresh unripe tomatoes weighing 25, 50, 75, and 100 g were immersed in water according to the optimum volume obtained. Furthermore, the samples were processed according to the optimum time received.

2.3. Imidacloprid Residues Analysis

Fresh unripe tomatoes that have been homogenized were weighed 25, 50, 75, and 100 g and mashed, respectively. The imidacloprid residue extraction in unripe tomatoes was carried out using 100 mL of water. The sample was filtered with Whatman filter paper, and a UV-Vis spectrophotometer analyzed the filtrate at 270 nm. The absorbance value obtained is indicated as the initial absorbance (before degradation).

Unripe tomatoes that have been treated with each variation of parameters (processing time, water volume, sample mass, and AOPs method) were each mashed and added 100 mL of water. The sample was filtered with Whatman filter paper, and UV-Vis Spectrophotometer analyzed the filtrate at 270 nm. The absorbance value obtained was expressed as the final absorbance (after degradation). The percentage of degradation (% degradation) was calculated using the equation:

$$degradation = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where A_0 = absorbance of imidacloprid before degradation and A_t = absorbance of imidacloprid after degradation.

2.4. Statistical Analysis

The method was repeated three times (n=3). The RSD evaluated the results of the method repetition in % value of each method using the equation:

$$RSD = 100\frac{SD}{\bar{x}} \quad (2)$$

Where RSD= relative standard deviation, SD= standard deviation and $\bar{x}$ = the average percent degradation of each method.

2.5. HPLC Analysis

HPLC analyzed the Imidacloprid solution and imidacloprid residue on unripe tomatoes before and after degradation. HPLC analysis was performed using acetonitrile: water (60:40 v/v) as mobile phase, C18 column (250 mm × 4.6mm id × 5µm particle size), UV detector with wavelength: 270 nm, flow rate: 1 mL/min and injection volume: 10 µL.

3. Results and Discussion

3.1. Effect of Processing Time

Qualitative assay of imidacloprid with a UV-Vis Spectrophotometer showed a maximum wavelength of 270 nm as shown in Figure 2, so the measurements of imidacloprid before and after degradation were measured with a UV-Vis Spectrophotometer at 270 nm.

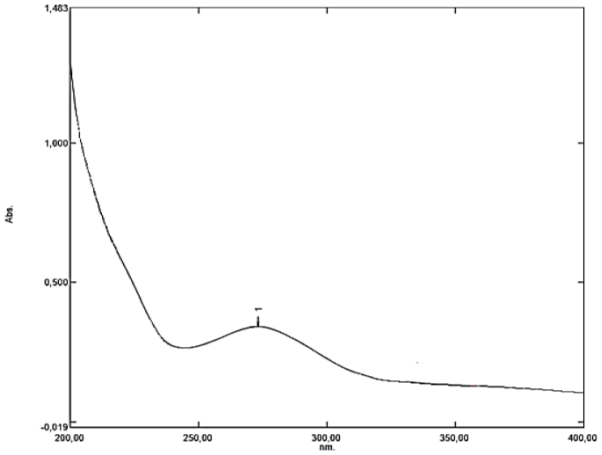

Figure 2. Spectrum of imidacloprid

Figure 3 shows the degradation of imidacloprid residues by ozonolysis, sonolysis, and sonozolysis at various times (5, 10, 15, 20, and 25 minutes). The data show that more imidacloprid residues are degraded with increasing processing time. Compared to other methods, ozonolysis had the highest imidacloprid residue degradation. The percentage of imidacloprid residue degradation in unripe tomatoes by ozonolysis was 74.87%.

The time of the ozonolysis process is dependent on the concentration of O_3. Ozone output of 400 mg/h could generate 333.34 to 1666.67 ppm O_3 for 5 to 25 minutes (as optimum time). Along with the high ozone concentration, O_3 can make more ·OH indirectly by breaking down H_2O molecules. ·OH had a higher oxidation potential (2.07 V) than other oxidants, such as O_3 (2.80 V). As a result, the imidacloprid residue was degraded by ozonolysis, dominated by ·OH. Baghirzade *et al.* (2020) investigated and found that the chloro-pyridine ring on imidacloprid is more easily oxidized by ·OH [23]. It should be noted that the longer the processing time, make dissolved O_3 more unstable and saturated, resulting in a non-significant increase in the production of ·OH and the percentage of degradation [24].

An ultrasonic bath (UB) with a frequency of 35 kHz was used in this study. UB is more easily degrades Non-systemic pesticides than systemic pesticides, such as imidacloprid. The shape of the vessel in the UB influences the waveform and results in relatively low ultrasonic power during sonolysis. [25]. Fatih *et al.* reported and compared the ability of an ultrasonic bath (UB) and an ultrasonic probe (UP) in degrading captan, thiamethoxam, and metalaxyl. UB is more easily degrades captan (non-systemic) than thiamethoxam and metalaxyl (systemic) [26].

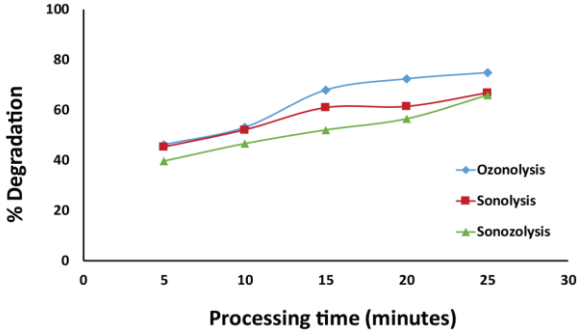

Figure 3. Effect of processing time on imidacloprid residue degradation in unripe tomatoes. Note: water volume= 100 mL, sample mass= 50 g

3.2. Effect of Water Volume

According to Figure 3, ozonolysis is the AOPs method with the highest degradation percentage. As a result, ozonolysis is used to determine the optimum percentage of water volume degradation. Figure 4 shows the optimum water volume for ozonolysis of imidacloprid residues in unripe tomatoes with various volumes of water (50, 100, 150, and 200 mL). The results showed that the degradation percentage increased with increasing water volume from 50 mL to 100 mL. However, the water volume from 100 mL to 200 mL, the percentage of degradation decreased. The volume required to degrade imidacloprid residues in unripe tomatoes was 100 mL. Decomposition of water molecules by O_3 caused the concentration of imidacloprid to decrease; when in a condition of abundance water, the production of OH increased.

In addition, electron-rich molecules in imidacloprid, such as amines, stimulate the formation of many ·OH. The reaction of O_3 with amines to generate ·OH is shown in equation [27]:

$$R_3N + O_3 \rightarrow R_3N^{\cdot+} + O_3^{\cdot-}$$

In water, $O_3^{\cdot-}$ decays into ·OH, O_2, and OH^- like the chemical reaction below. When degrading imidacloprid, increased production of ·OH competes with other reactions [28].

$$O_3^{\cdot-} \rightarrow O_2 + O^{\cdot-}$$

$$O^{\cdot-} + H_2O \rightarrow \cdot OH + OH^-$$

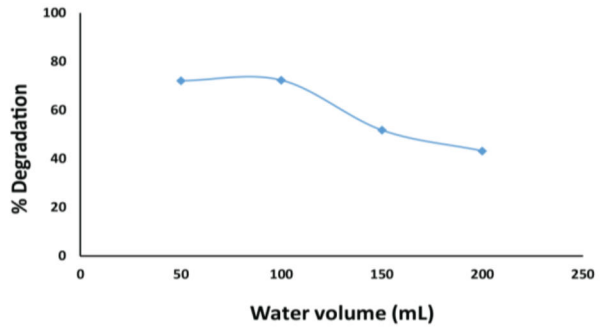

Figure 4. Effect of water volume on imidacloprid residue degradation in unripe tomatoes by ozonolysis. Note: processing time = 25 minutes, sample mass = 50 g

3.3. Effect of Sample Mass

Based on preliminary data, the best condition of two parameters (processing time and water volume) was ozonolysis for 25 minutes with 100 mL water. This condition was then utilized to calculate the percentage of degradation in the sample mass variation. Figure 5 shows that the percentage of degradation of the imidacloprid residue increased from 25 to 50 g, but decreased after passing through 50 g. Unripe tomatoes had the highest value of imidacloprid residue degradation at 71.42%. The pesticide concentration was dependent on the mass of the sample. A large sample mass could increase the pesticide molar ratio, decrease the dissolved ozone concentration and ·OH to generate. It should be noted that as the concentration of imidacloprid increases, the intermediate degradation compound will increases. ·OH degraded intermediate compound as well as imidacloprid. As a result, as the sample mass increased, the percentage of imidacloprid degradation by ozonolysis at constant volume decreased [29].

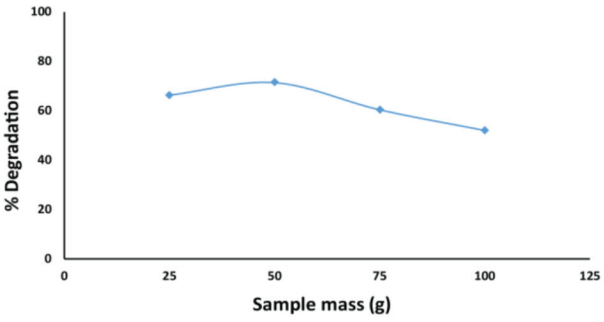

Figure 5. Effect of sample mass on imidacloprid residue degradation in unripe tomatoes by ozonolysis. Note: processing time= 25 minutes, water volume= 100 mL

3.4. Comparison of AOPs Methods

The optimum conditions used to compare the three of AOPs methods are the same. The conditions used were 25 minutes of processing time, 100 mL of water, and 50 g of tomatoes. Table 1 shows the results of imidacloprid residue degradation. The degradation of imidacloprid residues in unripe tomatoes were 74.87% by ozonolysis, 66.99% by sonolysis, and 66.00% by sonozolysis. Compared to sonolysis and sonozolysis, ozonolysis had the highest effect on degrading imidacloprid residues in unripe tomatoes.

Table 1 shows the effects of the degradation process by ozonolysis, sonolysis, and sonozolysis, which generates ·OH to initiate the oxidation process. Sonolysis, for example, has a lower degradation efficiency than ozonolysis. This phenomenon is similar to Gonzales *et al.* (2020) that single oxidation processes, such as sonolysis, have lower efficiency than ozonolysis [30]. The design of the bath in the sonicator used in this study results in ultrasonic vibration resistance. The ultrasonic power per unit volume and cavitation bubble intensity in the vessel system is lower than in the probe system [31]. Bagal *et al.* (2012) reported that using an ultrasonic bath and an ultrasonic horn for 60 minutes, the degradation efficiency of alachlor was 55.8 % and 3.5 %, respectively [32].

Sonozolysis is a type of double oxidation; however, it must be considered because it can occur to competition for degrading species [33]. It is because sonozolysis can produce two ·OH during the breakdown of H_2O by O_3 and ultrasonic vibrations simultaneously. Another hypothesis is that the production of large bubbles can decrease the rate of transfer of ozone from the gas phase to the liquid phase [34]. According to results, the residual concentration of imidacloprid in unripe tomatoes after ozonolysis was 0.1 ppm, making it safe for eating because it fulfilled the Indonesian National Standard 7313:2008, which states that the maximum permitted pesticide level is 0.5 ppm.

Tabel. 1 Comparison of 3 methods for degrading imidacloprid in unripe tomatoes (n=3). Note: processing time = 25 minutes, water volume = 100 mL, sample mass = 50 g

Methods	Imidacloprid Absorbance		Degradation Percentage (%)	Mean	SD	RSD (%)
	Before Degradation	After Degradation				
Ozonolysis	0.203	0.058	71.42	72.41	1.30	1.80
		0.057	71.92			
		0.053	73.89			
Sonolysis	0.203	0.071	65.02	66.06	1.66	2.51
		0.070	65.19			
		0.065	67.98			
Sonozolysis	0.203	0.092	54.67	56.81	1.99	3.51
		0.087	57.14			
		0.084	62.43			

Besides that, Table 1 shows the mean, standard deviation (SD), and relative standard deviation (%RSD) of the data obtained. The %RSD value represented the precision of the method at three repetitions. The obtained percentage of RSD ranged from 1.08% to 3.51 %. All methods show a %RSD less than 5%, meaning that the methods had high precision in degrading imidacloprid residues. These data fulfilled the requirements for analyzing imidacloprid pesticide residue degradation [35].

3.5. Analysis of HPLC

Imidacloprid solution, imidacloprid residue in unripe tomatoes before and after degradation were

injected into HPLC. The mobile phase was acetonitrile: water (60:40), the column was a C18 column (250 × 4.6 mm id × 5m particle size), the flow rate was 1 mL/min, the injection volume was 10 µL, and the UV detector was set to 270 nm.

Figure 6 shows the result of HPLC measurements. Imidacloprid had a retention time (t_R) of 3,464 minutes. The peak intensity on the chromatogram before degradation was higher than the peak intensity after degradation. This phenomenon indicates that ozonolysis effectively degrades imidacloprid residues in unripe tomatoes. The absence of new peaks on the chromatogram for the degraded imidacloprid residue samples showed that no new compounds were found as intermediate products in the degradation process. The samples did not need to be analyzed further.

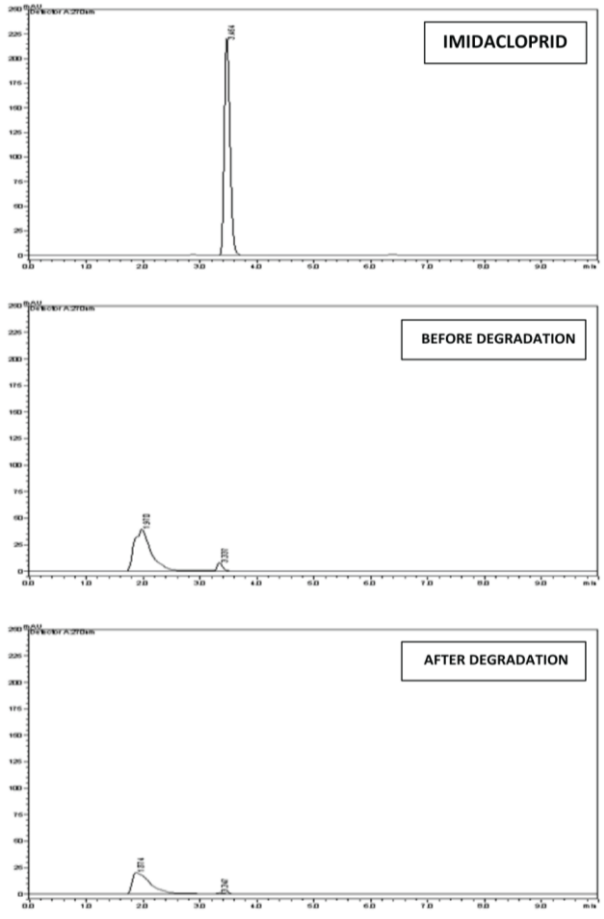

Figure 6. Imidacloprid chromatogram, imidacloprid residues in unripe tomatoes before and after degradation by ozonolysis

However, the degradation process produces intermediates before mineralization into CO_2 and H_2O was completed. ESI(+)-MS was used by Bourgin *et al.* (2011) to identify imidacloprid degradation intermediates. The $[M+H]^+$ ion has a mass ratio of 158 m/z, comparable to 6-chloro nicotinic acid. The ionic precursors produce m/z 140 derivative ions as well as H_2O. According to Bourgin *et al.*(2011), the degradation pathway is as follows (Figure 7):

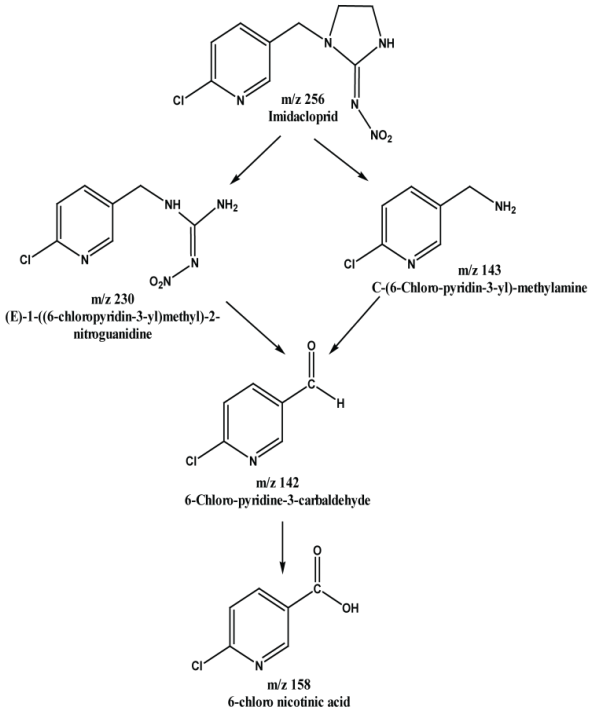

Figure 7. Degradation pathway of imidacloprid adopted from Bourgin et al. (2011) [36]

3.6. Reaction Kinetics

There are three types of kinetics model reactions: zero-order, first-order, and second-order. In the degradation process, first-order kinetics has been thoroughly characterized. The reason is that the time required by a pollutant to decrease by the same percentage is equal in first-order kinetics. The first-order kinetics occurs because the rate of pollutant degradation is proportional to its concentration [15, 29, 30, 31, 32]. Figure 8 shows the first-order degradation kinetics obtained by plotting ln (A/A_o) versus time. The R^2 value of the acquired regression line was 0.9500 for ozonolysis, 0.9537 for sonolysis, and 0.9639 for sonozolysis. R^2 value close one indicated good linearity.

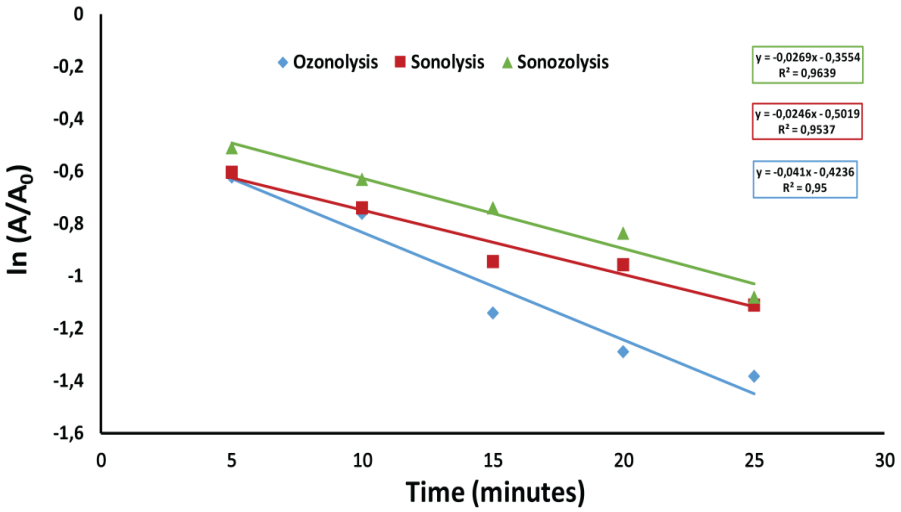

Figure 8. First-order pseudo kinetics model of imidacloprid by ozonolysis, sonolysis, and sonozolysis in unripe tomatoes. Note: water volume = 100 mL, sample mass = 50 g, t = 5–25 minutes

The half-life ($t_{1/2}$) of the imidacloprid residue degradation can be calculated by equation:

$$t_{1/2} = \ln 2/k$$

The results show that ozonolysis has the shortest half-life (16.90 minutes). It means that imidacloprid is easy chemically degraded by ozonolysis [37]. Table 2 shows first-order kinetic data for imidacloprid degradation in unripe tomatoes.

Tabel 2. First-order kinetic data for imidacloprid degradation in unripe tomatoes (n=3)

Methods	k (min^{-1})	1/k (min)	$t_{1/2}$ (min)
Ozonolysis	0.0410	24.39	16.90
Sonoyisis	0.0246	40.65	28.17
Sonozolysis	0.0269	37.17	25.75

4. Conclusion

The percentage of imidacloprid degradation obtained by ozonolysis was more significant than sonolysis and sonozolysis. Ozonolysis for 25 minutes can degrade imidacloprid residue in unripe tomatoes by up to 72.41 %. After degradation, the HPLC chromatogram of imidacloprid residues in unripe tomatoes showed no new peaks. The absence of new peaks on the chromatogram means that no intermediate compounds were detected in the degradation process. The remaining concentration of imidacloprid in unripe tomatoes after degradation by ozonolysis is 0.1 ppm, so it is safe for consumption because it meets the Indonesian National Standard 7313:2008. The degradation of imidacloprid using ozonolysis, sonolysis, and sonozolysis was obeyed the first-order kinetic.

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