International Journal on Advanced Science Engineering Information Technology

Vol.12 (2022) No. 1
ISSN: 2088-5334

Degradation of Imidacloprid Residue in Cabbage (*Brassica oleracea*) Using Advanced Oxidation Processes and Its Analyzing by Spectrophotometer and HPLC

Safni Safni [a,*], Trisna Ollinovela [a], Syukri Syukri [b]

[a] *Laboratory of Applied Analytical-Chemistry, Andalas University, Padang, 25163, Indonesia*
[b] *Laboratory of Material-Chemistry, Andalas University, Padang, 25163, Indonesia*
Corresponding author: [*]safni@sci.unand.ac.id

Abstract*—Imidacloprid is a synthetic pesticide used to kill and control insects by cabbage farmers. Consuming cabbage contaminated with imidacloprid can cause health problems such as chronic kidney, reproductive disorders and cancer. The parameters for degradation of imidacloprid residue in cabbage were processing time (5, 10, 15, 20, and 25 min), water volume (50, 100, 150, and 200 mL), and sample mass (25, 50, 75, and 100 g). Degradation of imidacloprid residue in cabbage using Advanced Oxidation Processes (AOPs) methods such as ozonolysis, sonolysis, and sonozolysis were compared. Methods of ozonolysis, sonolysis, and sonozolysis have performed using an ozonicator (ozone dose: 400 mg h^{-1}), sonicator (35 kHz), and a combination of both. Using spectrophotometers UV-Vis and High-Performance Liquid Chromatography (HPLC) measurements showed a decrease in imidacloprid concentration after degradation. The degradation percentage of the imidacloprid residue with ozonolysis was higher than that of sonolysis and sonozolysis. The percentage of imidacloprid degradation by ozonolysis in 50 g cabbage at 100 mL of water increased to 82.53% for 15 min. The HPLC chromatogram showed no new peaks that formed after degradation. The imidacloprid residue's degradation kinetics were then investigated. For all AOPs methods, the kinetic analysis demonstrated that imidacloprid degradation fit within a first-order kinetic model. The kinetic data showed that ozonolysis degraded imidacloprid with a half-life (t1/2) of 15.22 min, shorter than sonolysis and sonozolysis.

***Keywords*—Cabbage; imidacloprid; AOPs; ozonolysis; spectrophotometer; HPLC.**

Manuscript received 30 Apr. 2021; revised 21 May 2021; accepted 26 Jun. 2021. Date of publication 28 Feb. 2022.

I. INTRODUCTION

In modern agriculture, pesticides are important for increasing vegetable output since they monitor and eliminate pests, including mosquitoes, rats, fungi, weeds, and bacteria. However, as pesticide use has increased, concern about adverse effects on non-target organisms, such as humans, has grown. Pesticide residues are detrimental to human health, inducing tumors, chronic kidney failure, psychiatric conditions, and reproductive disorders [1]–[5]. 1-(6-chloro-3-pyridinylmethyl)-N-nitro-2-imidazolidinimin is the molecular name for (imidacloprid) and is one of the pesticides that is mostly used. World Health Organization (WHO) states that imidacloprid is a pesticide rated as a Class II (moderately hazardous) [6]. As a result, consumers are becoming more conscious of food quality and safety concerns and the importance of being selective about the foods they eat. As a result, several governments have enacted laws to prevent only nutritious, acceptable-quality food is marketed, reducing the risk of food-borne illness [7]. Since 2008, the Indonesian National Standard, the overall residual limit of imidacloprid is 0.5 mg kg^{-1} [8].

Cabbage (*Brassica oleracea*) is one of Indonesia's most popular vegetable crops. Cabbage is high in antioxidants, enzymes, potassium, folate, and dietary fiber, both of which are beneficial to human health [9]–[12]. Indonesians consumed their cabbages raw. Pesticides residue removal by tap water, boiling, using sodium bicarbonate solution, acetic acid, and detergent solution have been reported in a previous study [13]–[16]. Traditional processes, such as removing them with tap water, are thought to take a long time and offer new pollutants to the environment, whereas removing pesticide residue by boiling cannot be reduced significantly.

The uses of other chemicals are thought to affect the taste and make food more harmful when consumed.

Advanced Oxidation Processes (AOPs) are a promising method to reduce organic compounds like dyes [17], [18], medicines [19], and pesticides [20], [21]. AOPs methods such as ozonolysis, sonolysis, and sonozolysis can produce hydroxyl radicals (•OH) that can be used to breakdown compounds into the more simple and environmentally friendly compounds (into H_2O and CO_2) [22], [23]. In this study, the imidacloprid residue in cabbage was degraded using ozonolysis, sonolysis, and sonozolysis. Processing time, water volume, and sample mass were both investigated as contributing factors. After each step, the concentrations of pesticide residues in the cabbage were analyzed using Spectrophotometer UV-Vis and High-Performance Liquid Chromatography (HPLC) to see the changes in the concentration of imidacloprid residues left.

II. Materials and Method

A. Reagents and Materials

Cabbage samples were obtained in Aia Angek (Sepuluh Koto, West Sumatra), wrapped in dark containers, and stored in the laboratory refrigerator. Imidacloprid was obtained from Klopindo 10 WP (PT. Mitra Kreasidharma, Indonesia), acetonitrile HPLC grade (Sigma-Aldrich), and distilled water. The structure of imidacloprid is shown in Fig. 1.

B. Instrumentation

The spectrophotometer UV-Vis (Shimadzu, Japan) and the HPLC (Shimadzu, Japan) were used in this investigation. Ozone (O_3) was generated using an ozonicator (Hanaco TSH-278, China) with a 400 mg h^{-1} ozone dose and a 35 kHz sonicator (Krisbow CD-4862, China).

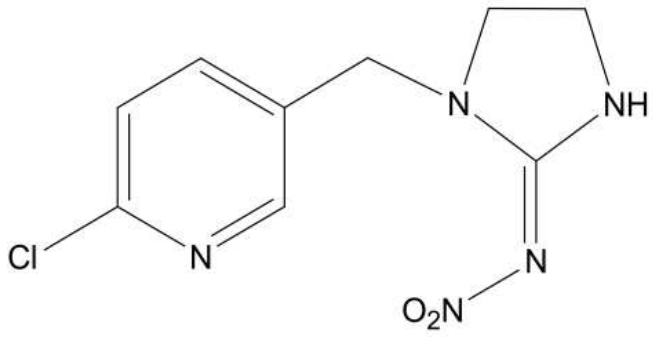

Fig. 1 The structure of imidacloprid

C. Degradation Treatment

Imidacloprid residues were degraded by ozonolysis (by ozonicator), sonolysis (by sonicator), and sonozolysis (combination of ozonicator and sonicator). 100 mL water was used to immerse per 50 g of cabbages. The ozonicator and sonicator processing times were set at 5, 10, 15, 20, and 25 min. In the sonozolysis process, ozonicator and sonicator start at the same time.

The optimal volume was measured by immersing 50 g samples in 50, 100, 150, and 200 mL of water. The time of degradation was adjusted to the optimum time. After that, the optimum mass was measured by immersing samples weighing 25, 50, 75, and 100 g in water for the optimum volume. The time of degradation was adjusted following the optimal time.

The residual was determined before degradation by refining each sample. The sample was filtered using Whatman filter paper and analyzed with a spectrophotometer UV-Vis at a wavelength of 270 nm. The same method was used to determine the residual concentration after degradation. The percentage of degradation was calculated using the absorbance value obtained from the spectrophotometer UV-Vis, using the equation:

$$\%Degradation = \frac{A0-At}{A0} \times 100\% \quad (1)$$

Where A_0= the initial absorbance of imidacloprid, A_t= absorbance of imidacloprid after the degradation process.

D. Statistical analysis

For each method, mean values were calculated from three replicate samples (n=3). To calculate Standard Deviation (SD) and Relative Standard Deviation (%RSD), values were used equation:

$$SD = \sqrt{\frac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+(x_3-\bar{x})^2}{n-1}} \quad (2)$$

$$\%RSD = 100\frac{SD}{\bar{x}} \quad (3)$$

E. HPLC Conditions

HPLC was used to determine the changes of imidacloprid concentration after degradation. On the reversed-phase Shim Pack C18 column (250 mm × 4.6 mm i.d), 10 µL of each sample was injected. The mobile phase was acetonitrile: water (60:40, v/v), with a flow rate of 1 mL min^{-1} and UV detector wavelength of 270 nm.

F. Kinetics Calculation

The following integral first-order kinetics equation was used to measure the degradation kinetics:

$$ln\frac{A}{A_0} = -kt \quad (4)$$

The reaction-rate constant is determined by the slope of the linear regression line of ln (A/A_0) against time. The half-life ($t_{1/2}$) of imidacloprid can be calculated using equation:

$$t_{1/2} = \frac{ln\,2}{k} \quad (5)$$

Where A_0= initial imidacloprid concentration, A= imidacloprid concentration after degradation process, t= reaction time and k= rate constant.

III. Results and Discussion

A. Effect of Processing Time

In 50 g of sample and 100 mL of water, the effect of processing time (5 - 25 min) was studied. All methods show an increase in the percentage of imidacloprid degradation in cabbage by increasing the processing time, as describe in Fig. 2. The sonozolysis method results in the least amount of degradation percentage. The sonolysis process has a higher percentage of degradation than sonozolysis, and the

ozonolysis method has the highest percentage of imidacloprid degradation in cabbage. The percentage of imidacloprid degradation in cabbage by ozonolysis before 15 min increased to 82.50%, but after 15 min the increase was not significant.

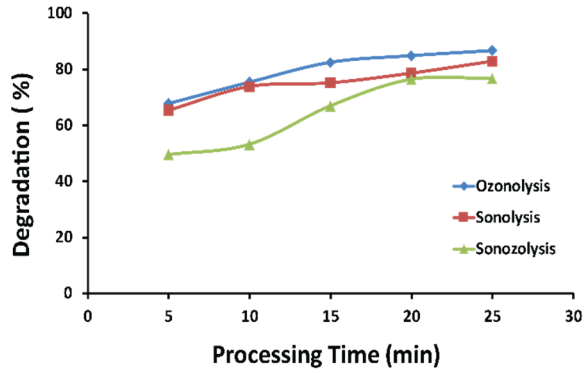

Fig. 2 The effect of processing time on imidacloprid degradation in cabbage (volume= 100 mL, mass= 50 g, ozone dose= 400 mg h^{-1}, ultrasonic frequency= 35 kHz)

Two species (O_3 and •OH) influence degradation, but •OH is more dominant in imidacloprid degradation than O_3. •OH is a non-selective strong oxidant that can oxidize any organic compounds. The chloro-pyridine ring in imidacloprid has also been shown to be readily oxidized by •OH [24]. Since the more unstable dissolved O_3 becomes with, the longer processing period, the •OH amount and percentage of imidacloprid degradation in cabbage did not increase significantly.

B. Effect of Water Volume

By 400 mg/h ozone dose in ozonolysis, the effect of water volume on imidacloprid degradation in cabbage with 50 g of cabbage for 15 min was investigated. With the addition of water, the percentage of imidacloprid degradation in cabbage initially increased and decreased after reaching the optimum condition. According to Fig. 3, the optimum volume is 100 mL, and the percentage of imidacloprid degradation in cabbage obtained was 82.01%. The addition of water reduces imidacloprid concentration while increasing •OH production. Electron-rich compounds (such as imidacloprid) contribute to the formation of a significant amount of •OH. As imidacloprid was degraded, this has been generated in competition with other reactions [25].

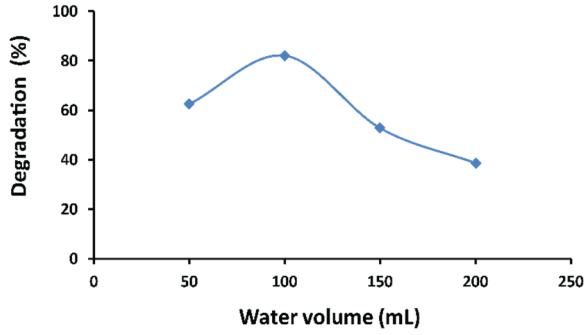

Fig. 3 The effect of water volume on the degradation of imidacloprid in cabbage (method = ozonolysis, t = 15 min, mass = 50 g, ozone dose = 400 mg h^{-1})

C. Effect of Sample Mass

Fig. 4 demonstrates the influence of sample mass variance on 100 mL of water with 400 mg/h ozone dose by ozonolysis for 15 min on the percentage of imidacloprid degradation in cabbage. The percentage of imidacloprid degradation increased for sample mass of 25 to 50 g.

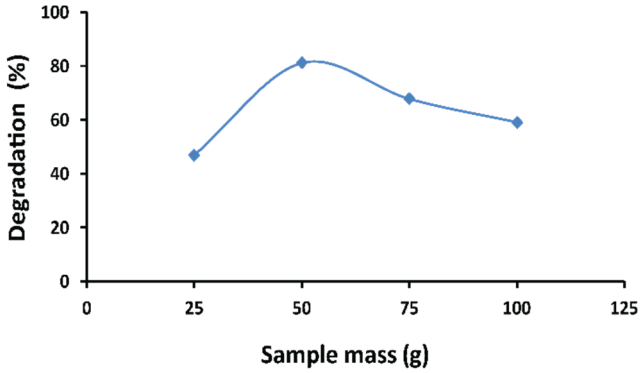

Fig. 4 The effect of vegetable mass on the degradation of imidacloprid in cabbage (method = ozonolysis, t = 15 min, volume = 100 mL, ozone dose = 400 mg h^{-1})

The largest percentage of imidacloprid degradation in cabbage was found to be 81.21%. An increase in sample mass means that the pesticide concentration also increased. Large pesticide concentrations could raise the molar ratio of pesticides, thus decreasing the dissolved O_3 concentration. Khoiriah *et al.* (2020) found that the percentage degradation of diazinon decreased at high concentrations [26].

D. Effect of AOPs Methods

Fig. 5 shows the percentage of imidacloprid degradation in 50 g cabbage on 100 mL of water using ozonolysis (ozone dose = 400 mg/h), sonolysis (ultrasonic frequency= 35 kHz), and sonozolysis (combine 400 mg/h ozone dose and 35 kHz ultrasonic frequency) processes for 15 min. Ozonolysis resulted in the highest imidacloprid degradation than other methods. The AOPs methods produce •OH to degrade imidacloprid. Ozonolysis produces •OH by breaking down H_2O molecules with O_3, while sonolysis produces •OH by breaking down H_2O molecules with ultrasound. Sonozolysis is a process that combines ozonolysis and sonolysis to obtain •OH. The oxidation performance of single oxidizers including sonolysis is lower than that of ozonolysis. The degradation of pesticides by the AOPs method was assessed similarly to the study of Patil et. al. (2014), where a single oxidation method like sonolysis is less efficient than other AOPs methods. Degradation of imidacloprid using sonication was only 66,80% [27]. In contrast to multiple reactions, such as sonozolysis, must be considered since it may result in competition for degrading depend on pH or the presence of other inorganic and organic compounds [28]. Following ozonolysis, the residual imidacloprid concentrations in cabbage were 0.15 mg kg^{-1}. This concentration conforms to Indonesian Standard 7313:2008, which states that the maximum limit of imidacloprid residue is 0.5 mg kg^{-1}.

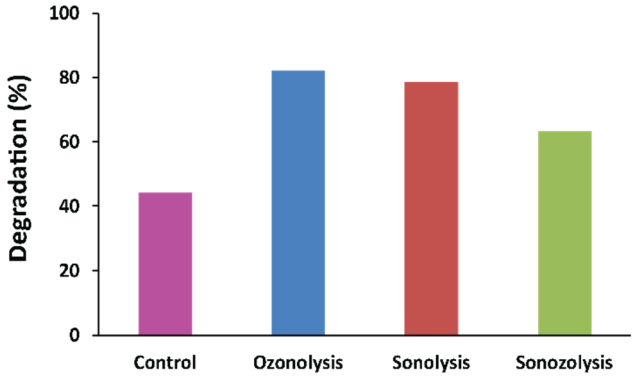

Fig. 5 The effect of AOPs method on the degradation of imidacloprid in cabbage (t = 15 min, volume = 100 mL, mass= 50 g, ozone dose = 400 mg h^{-1}, ultrasonic frequency = 35 kHz)

E. Statistical Analysis

Analyzing these similarly pretreated samples at the same time, with the same equipment, and by the same analyst can be used to verify precision. The mean of imidacloprid degradation in cabbage was found to be 63.22% - 84.18%, according to the statistical result shown in Table 1.

TABLE I
STATISTICAL DATA FROM AOPS METHODS TO DEGRADE IMIDACLOPRID IN CABBAGE (N = 3)

Methods	Mean	SD	RSD (%)
Ozonolysis	82.18	1.68	2.04
Sonolysis	78.65	1.69	2.13
Sonozolysis	63.22	1.37	2.17

Standard Deviation (SD) and Relative Standard Deviation (%RSD) values were 1.37-1.68 and 2.04% - 2.17%, respectively. The AOPs method has high precision based on SD and %RSD values, suggesting that ozonolysis, sonolysis, and sonozolysis are the best methods for degrading imidacloprid in cabbage. According to Simoes *et al* [29], these qualities fulfill the imidacloprid pesticide residue degradation analysis standards.

F. Analysis of HPLC

Fig. 6 shows the HPLC system was used at a detector wavelength of 270 nm to observe the change in the concentration of imidacloprid residue in cabbage before and after degradation. The imidacloprid peaks appeared at a retention time of 3.46 min. The peak intensity decreased for the degraded imidacloprid residue, indicating a reduction in imidacloprid. On the chromatogram, no new peaks were found. This means that no intermediate compounds were detected when the imidacloprid residue in 50 g of cabbage and 100 mL of water was treated by ozonolysis for 15 minutes.

Organic-compounds degradation often assumes the first-order rule [30]–[32]. The coefficient values (R^2) for imidacloprid degradation by ozonolysis, sonolysis, and sonozolysis were 0.9629, 0.9596, and 0.9305, respectively, indicating good linearity (as shown in Fig. 7). As a result, the degradation of imidacloprid can be assumed to follow the first-order rate law.

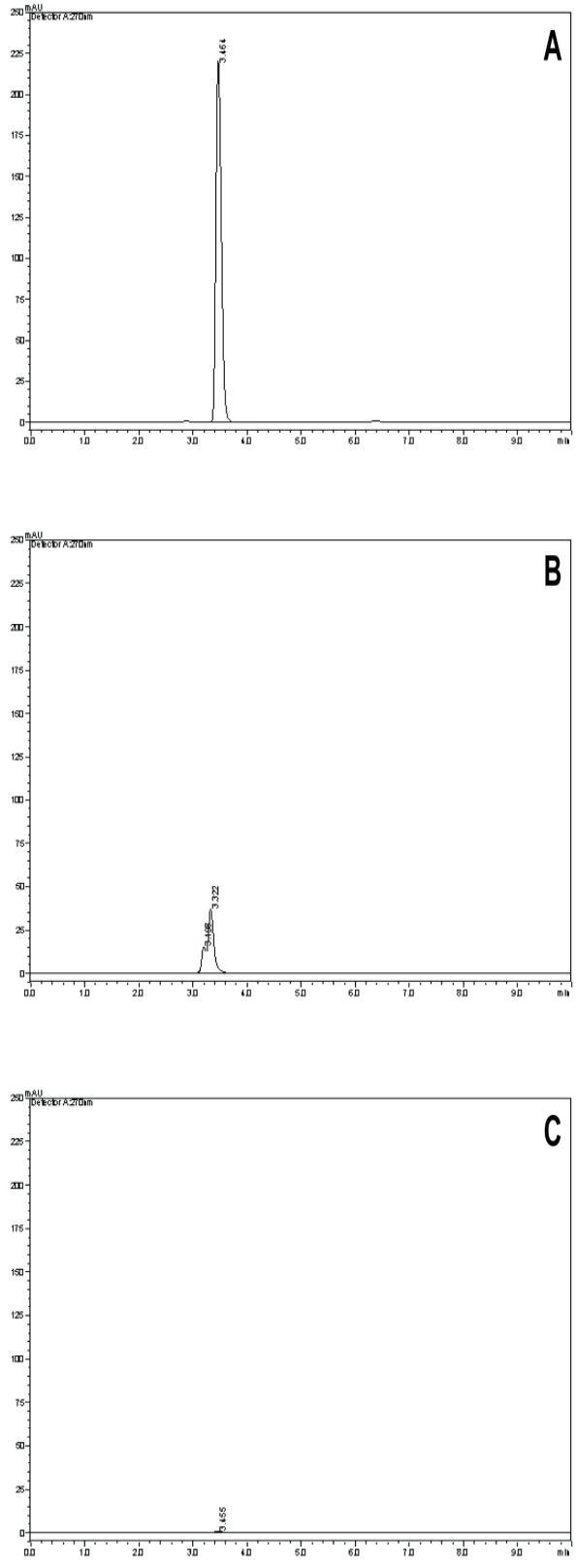

Fig. 6 Chromatogram of (A): imidacloprid, (B): imidacloprid residue in cabbage, (C): imidakloprid residue in cabbage after degradation (method = ozonolysis, mass = 50 g, volume = 100 mL, t = 15 min)

G. Reaction Kinetics

First-order kinetics data for imidacloprid degradation in cabbage are shown in Table 2. The ozonolysis process and the sonolysis samples had the shortest (15.22 min) and longest (21.59 min) half-lives, respectively. This indicates the imidacloprid is very easily degraded chemically by ozonolysis [31]. The rate of degradation of the imidacloprid residue was 0.0321-0.0447 min-1 in this study.

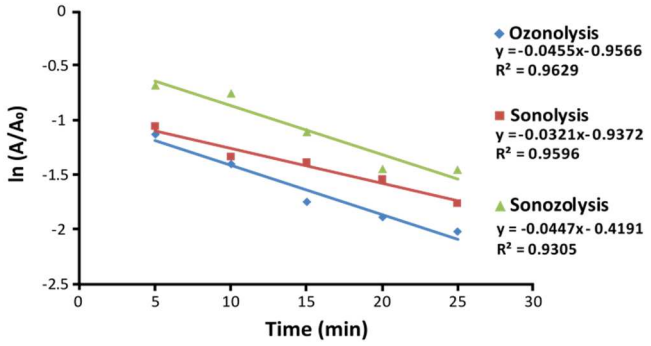

Fig. 7 First-order kinetics model of imidacloprid in cabbage by AOPs

TABLE II
STATISTICAL DATA FROM AOPS METHODS TO DEGRADE IMIDACLOPRID IN CABBAGE (N = 3)

Methods	k (min^{-1})	1/k (min)	$t_{1/2}$ (min)
Ozonolysis	0.0455	21.97	15.22
Sonolysis	0.0321	31.15	21.59
Sonozolysis	0.0447	23.37	15.50

IV. Conclusion

When ozonolysis was used to degrade imidacloprid, it produced a higher percentage of degradation than other AOPs methods such as sonolysis and sonozolysis. The imidacloprid residue in cabbage can be degraded as much 82.53% by ozonolysis for 15 min. The HPLC chromatogram of imidacloprid residues in cabbage after degradation showed a decrease in peak intensity, indicating that it has been degraded and there are no intermediates compounds identified during the degradation process. After 15 min ozonolysis process, the remaining imidacloprid concentration in cabbage is 0.15 ppm, less than the Indonesian National Standard 7313: 2008.

Acknowledgment

The Andalas University Professor Grant provided financial support for this research.

References

[1] F. P. Carvalho, 'Pesticides, environment, and food safety', *Food Energy Secur.*, vol. 6, no. 2, pp. 48–60, 2017.

[2] S. Mostafalou and M. Abdollahi, 'Pesticides: an update of human exposure and toxicity', *Arch. Toxicol.*, vol. 91, no. 2, pp. 549–599, 2017.

[3] F. J. R. Paumgartten, 'Pesticides and public health in Brazil', *Curr. Opin. Toxicol.*, vol. 22, pp. 7–11, 2020.

[4] A. M. Aloizou *et al.*, 'Pesticides, cognitive functions and dementia: A review', *Toxicol. Lett.*, vol. 326, pp. 31–51, 2020.

[5] J. R. Richardson, V. Fitsanakis, R. H. S. Westerink, and A. G. Kanthasamy, 'Neurotoxicity of pesticides', *Acta Neuropathol.*, vol. 138, no. 3, pp. 343–362, 2019.

[6] World Health Organization (WHO), *The WHO recommended classification of pesticides by hazard and guidelines to classification*. 2019.

[7] Z. Li and A. Jennings, 'Worldwide regulations of standard values of pesticides for human health risk control: A review', *Int. J. Environ. Res. Public Health*, vol. 14, no. 7, p. 1, 2017.

[8] SNI 7313, *Maksimum limit of pesticide residues on indonesian agricultural products*. 2008.

[9] U. Sahin, M. Ekinci, S. Ors, M. Turan, S. Yildiz, and E. Yildirim, 'Effects of individual and combined effects of salinity and drought on physiological, nutritional and biochemical properties of cabbage (Brassica oleracea var. capitata)', *Sci. Hortic. (Amsterdam).*, vol. 240, no. June, pp. 196–204, 2018.

[10] D. Šamec, I. Pavlović, and B. Salopek-Sondi, 'White cabbage (Brassica oleracea var. capitata f. alba): botanical, phytochemical and pharmacological overview', *Phytochem. Rev.*, vol. 16, no. 1, pp. 117–135, 2017.

[11] Y. Xu *et al.*, 'A comparative evaluation of nutritional properties, antioxidant capacity and physical characteristics of cabbage (Brassica oleracea var. Capitate var L.) subjected to different drying methods', *Food Chem.*, vol. 309, pp. 1–8, 2020.

[12] C. Novotny, V. Schulzova, A. Krmela, J. Hajslova, K. Svobodova, and M. Koudela, 'Ascorbic acid and glucosinolate levels in new czech cabbage cultivars: Effect of production system and fungal infection', *Molecules*, vol. 23, no. 8, pp. 2–12, 2018.

[13] B. Lozowicka, M. Jankowska, I. Hrynko, and P. Kaczynski, 'Removal of 16 pesticide residues from strawberries by washing with tap and ozone water, ultrasonic cleaning and boiling', *Environ. Monit. Assess.*, vol. 188, no. 1, p. 1, 2016.

[14] A. Heshmati, M. Hamidi, and A. Nili-Ahmadabadi, 'Effect of storage, washing, and cooking on the stability of five pesticides in edible fungi of Agaricus bisporus: A degradation kinetic study', *Food Sci. Nutr.*, vol. 7, no. 12, pp. 3993–4000, 2019.

[15] T. Yang, J. Doherty, B. Zhao, A. J. Kinchla, J. M. Clark, and L. He, 'Effectiveness of commercial and homemade washing agents in removing pesticide residues on and in apples', *J. Agric. Food Chem.*, vol. 65, no. 44, pp. 9744–9752, 2017.

[16] S. Ruengprapavut, T. Sophonnithiprasert, and N. Pongpoungphet, 'The effectiveness of chemical solutions on the removal of carbaryl residues from cucumber and chili presoaked in carbaryl using the HPLC technique', *Food Chem.*, vol. 309, pp. 1–4, 2020.

[17] R. A. Putri, S. Safni, N. Jamarun, and U. Septiani, 'Kinetics study and degradation pathway of methyl orange photodegradation in the presence of C-N-codoped TiO2 catalyst', *Egypt. J. Chem.*, vol. 63, no. Part 2, pp. 563–575, 2020.

[18] A. El Nemr, M. A. Hassaan, and F. F. Madkour, 'Advanced Oxidation Process (AOP) for Detoxification of Acid Red 17 Dye Solution and Degradation Mechanism', *Environ. Process.*, vol. 5, no. 1, pp. 95–113, 2018.

[19] E. M. Cuerda-Correa, M. F. Alexandre-Franco, and C. Fernández-González, 'Advanced oxidation processes for the removal of antibiotics from water. An overview', *Water (Switzerland)*, vol. 12, no. 1, pp. 1–51, 2020.

[20] H. Wang, J. Zhan, L. Gao, G. Yu, S. Komarneni, and Y. Wang, 'Kinetics and mechanism of thiamethoxam abatement by ozonation and ozone-based advanced oxidation processes', *J. Hazard. Mater.*, vol. 390, pp. 1–11, 2020.

[21] Khoiriah, Safni, Syukri, and J. Gunlazuardi, 'The operational parameters effect on photocatalytic degradation of diazinon using carbon and nitrogen modified TiO2', *Rasayan J.*, vol. 13, no. 3, pp. 1919–1925, 2020.

[22] X. Jin, S. Peldszus, and P. M. Huck, 'Reaction kinetics of selected micropollutants in ozonation and advanced oxidation processes', *Water Res.*, vol. 46, no. 19, p. 6519, 2012.

[23] E. Kudlek, 'Decomposition of contaminants of emerging concern in advanced oxidation processes', *Water (Switzerland)*, vol. 10, no. 7, pp. 1–18, 2018.

[24] S. Chen, J. Deng, Y. Deng, and N. Gao, 'Influencing Factors and Kinetic Studies of Imidacloprid Degradation by Ozonation Influencing Factors and Kinetic Studies of Imidacloprid Degradation by Ozonation', *Environ. Technol.*, vol. 40, no. 1, p. 1, 2018.

[25] R. Flyunt *et al.*, 'Determination of •OH, O2•- , and Hydroperoxide Yields in Ozone Reactions in Aqueous Solution', *J. Phys. Chem. B*, vol. 107, p. 7242, 2003.

[26] Khoiriah, Safni, Syukri, and J. Gunlazuardi, 'Photocatalytic ozonation using C,N-codoped TiO2 for diazinon degradation', *J. Chem. Technol. Metall.*, vol. 55, no. 6, pp. 2120–2127, 2020.

[27] A. L. Patil, P. N. Patil, and P. R. Gogate, 'Degradation of imidacloprid containing wastewaters using ultrasound based treatment strategies', *Ultrason. Sonochem.*, vol. 21, no. 5, p. 1778, 2014.
[28] K. Ikehata and M. G. El-Din, 'Aqueous Pesticide Degradation by Ozonation and Ozone-Based Advanced Oxidation Processes: A Review (Part II)', *Ozone Sci. Eng.*, vol. 27, no. 3, pp. 173–191, 2005.
[29] A. Simões, M. Miranda, C. Cardoso, F. Veiga, and C. Vitorino, 'Rheology by design: A regulatory tutorial for analytical method validation', *Pharmaceutics*, vol. 12, no. 9, pp. 1–27, 2020.
[30] P. Thanekar, M. Panda, and P. R. Gogate, 'Degradation of carbamazepine using hydrodynamic cavitation combined with advanced oxidation processes', *Ultrason. Sonochem.*, vol. 40, pp. 567–576, 2018.
[31] P. Sintuya, K. Narkprasom, S. Jaturonglumlert, N. Whangchai, D. Peng-Ont, and J. Varith, 'Effect of Gaseous Ozone Fumigation on Organophosphate Pesticide Degradation of Dried Chilies', *Ozone Sci. Eng.*, vol. 40, no. 6, pp. 473–481, 2018.
[32] H. Zhan *et al.*, 'Kinetics and novel degradation pathway of permethrin in Acinetobacter baumannii ZH-14', *Front. Microbiol.*, vol. 9, pp. 1–12, 2018.