Photocatalytic Degradation of Commercial Diazinon Pesticide Using C,N-codoped TiO₂ as Photocatalyst

Khoiriah Khoiriah[1], Diana Vanda Wellia[1], Jarnuzi Gunlazuardi[2], and Safni Safni[1,*]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Limau Manis, Padang 25163, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Kampus UI, Depok 16424, Indonesia*

Abstract: *Diazinon ($C_{12}H_{21}N_2O_3PS$) is an effective pest controller that has been frequently used by farmers in agriculture. It is a nonspecific and highly toxic pesticide having low persistence in the environment and categorized as moderately hazardous class II. The degradation of commercial diazinon in aqueous solution was investigated by photocatalysis using low-energy activated C,N-codoped TiO_2 as catalyst under visible-light. The influence of some parameters, i.e., catalyst concentration, the initial concentration of diazinon, initial pH of diazinon, and irradiation time on the diazinon degradation was studied. The amount of diazinon degradation was strongly influenced by all the above parameters. The results show that titania-modified enhanced the degradation percentage of diazinon, from 44.08% without a catalyst to 86.93% by adding 12 mg of C,N-codoped TiO_2 catalyst after 30 min visible-light irradiation. UV-visible spectrophotometer, HPLC, and COD analysis verified that diazinon was successfully degraded under photocatalysis visible.*

Keywords: *degradation; photocatalysis; diazinon; C,N-codoped TiO_2*

■ INTRODUCTION

Diazinon(*O, O*-diethyl*O*-[6-methyl-2-(1-methyl ethyl)-4-pyrimidinyl]phosphorothioate (Fig. 1), an effective organophosphate chemical family and commercially introduced in 1952, is frequently used in Indonesia as an insecticide for various types of cultivation such as fruit trees, rice, palm, sugarcane, corn, tobacco, and horticultural plants. It is a nonspecific and highly toxic pesticide which has low persistence in the environment [1], immunotoxic [2] cytotoxic and genotoxic [3-5] and categorized as moderately hazardous class II by the World Health Organization (WHO) [6].

Diazinon at concentration 350 ng/L [7], 4.4 mg/L, 90–444 mg/kg may cause toxic for aquatic organisms, fish (48 h), and human, respectively. Inhibiting the enzyme acetylcholinesterase activity by overstimulation of nicotinic, muscarinic receptors [8] and increasing TNF-a production in rat serum and brain [9-10] are some toxic effects of

diazinon. The continuous application may lead to the common occurrence of diazinon residues in food crops, natural water systems, and soil [11]. Therefore, treating several water systems contaminated by diazinon is urgently demanded to protect human health. The use of advanced oxidation processes (AOPs) is essential because conventional treatment methods have high operational costs, longer reaction time, and producing secondary pollutant [12]. AOPs process produces and uses •OH and •O_2 radicals as reducing agents and strong oxidant to degrade organic pollutants to be environmentally friendly
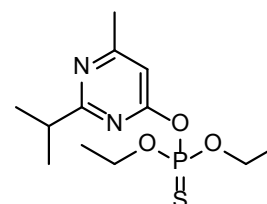

Fig 1. Structure of diazinon

compounds such as H_2O and CO_2 [13-14]. Photocatalysis, the use of light and semiconductor catalyst as reactive species source and having advantages such as non-selectivity, quickly completed oxidation and oxidation of pollutants in the ppb range, is one of the most promising AOPs for wastewater treatment [15].

The selected photocatalyst often used in the degradation process is titania (TiO_2) because of its abundance, effectiveness, stability against photo-corrosion, photoactive, and nontoxic to living things [16-17]. However, it has a fairly high band gap (3.2 eV), and a lot of research has reduced its band gap by modifying TiO_2 with metal, or non-metal elements [18].

Modified titania by the codoping method has higher photocatalytic activity than doping with only one element in the visible-light region [19]. The potential elements that can be used as dopants are carbon and nitrogen because their size is not much different from oxygen [20]. Several methods of synthesis of C,N-codoped TiO_2 have been reported such as sol-gel [21-23], and solvothermal [24-27], but these methods still use organic solvents which are less environmentally friendly and require high costs.

The modified titania with carbon and nitrogen (C,N-codoped TiO_2) has been successfully synthesized by the peroxo sol-gel method using environmentally friendly, water, as solvent [19,28] and reported that the presence of dopants carbon and nitrogen had been shown to provide a synergistic effect in absorbing visible-light to increase titania photocatalytic activity. The application has also been carried out on several organic pollutants [20,29-32] and inorganic pollutant [28]. In the present work, C,N-codoped TiO_2 synthesized by the peroxo sol-gel method was applied on photocatalysis of commercial diazinon pesticide under visible-light. Parameters affecting the degradation process, i.e., catalyst mass, doping on titania, pH of the initial solution, and irradiation time were studied.

■ EXPERIMENTAL SECTION

Materials

Materials used were commercial pesticide Diazinon 60 EC (600 g/L) manufactured by Petrokimia Kayaku, Co (Indonesia), double distilled water and ethanol 96% were from Dwipraga Chemical, Co (Indonesia), acetonitrile chromatography grade, Whatman filter (θ: 0.45 μm), undoped-TiO_2, and C,N-codoped TiO_2 catalyst were obtained from applied analytical chemistry laboratory of Andalas University with particle size about 44 nm.

Instrumentation

Centrifuge Nesco 80-2, analytical balance, UV-Vis spectrophotometer (Shimadzu Corp, serial A116352), HPLC (Hitachi-Trimaide, serial1202-005, Japan) and the Halogen lamp 500 Watt (Philips) were used in this investigation.

Procedure

Photodegradation experiments were conducted in 10 cm internal diameter Petridish as photoreactor that contained 20 mL of 18 mg/L diazinon pesticide in room temperature. The pesticide was treated by photocatalysis under visible-light irradiation using 12 mg TiO_2 and C,N-codoped TiO_2 for 5–30 min to investigate the doping effect on titania catalyst. C,N-codoped TiO_2 (0, 6, 12, 18, and 24 mg) was added into the photocatalysis system to study the effect of catalyst concentration. The effect of initial pH (3, 5, 7, 11) and initial concentration of diazinon over 9, 18, 36, 54, 72 and 90 mg/L were also studied. The pH of the solution was adjusted to 3, 5, 7, 11 by adding NaOH 0.01 N or HCl 0.01 N. The photolysis without catalyst and adsorption of catalyst (in dark place) were also investigated as a control. The degraded solution was collected and centrifuged for 20 min at 3000 rpm and then filtered through a Whatman 0.22 μm filter to separate the catalyst from the solution. The solution was kept in the dark bottles and measured with UV-Vis spectrophotometer. Degradation percentage of pesticide was calculated from spectrophotometric data using Eq. 1:

$$\frac{A_i - A_f}{A_i} \times 100\% \tag{1}$$

where A_i and A_f correspond to initial and final diazinon pesticide absorbance.

The untreated and treated diazinon by visible-light photocatalysis degradation was also analyzed by HPLC packed with a C18 column (150 mm × 4.6 mm) and detected by a UV detector at a wavelength of 247 nm to

identify the formed intermediates. The mobile phase was a mixture of acetonitrile and water, with a volumetric ratio of 75/25 with an injection flow rate of 0.6 mL/min. An injection volume of diazinon solution was 20 μL. The COD (chemical oxygen demand) of samples was determined by closed reflux, colorimetric methods (SNI 06-6989.2-2004).

■ RESULTS AND DISCUSSION

The Effect of Catalyst Concentration on Diazinon Degradation

The effect of C,N-codoped TiO_2 concentration (0–24 mg) was investigated for 18 mg/L diazinon degradation. As shown in Fig. 2, the increase of C,N-codoped TiO_2 addition from 0 to 12 mg improved the diazinon degradation percentage from 31.79% to 67.98% under visible-light photocatalysis for 15 min.

This preliminary improving diazinon degradation percentage with an increasing catalyst (0–12 mg) can be due to the increase in catalyst surface area, the easy light penetration, the enhanced amount of photon absorption on the catalyst surface, and consequently higher production of active species •OH radical by C,N-codoped TiO_2 [33]. However, using C,N-codoped TiO_2 catalyst up to 12 mg reduces degradation percentage. This phenomenon is caused by the higher suspension turbidity, which diminishes the amount of light to reach active surfaces [33-34]. Also, the agglomeration of C,N-codoped TiO_2 may deactivate the active sites [34-38]. Therefore, 12 mg of C,N-codoped TiO_2 is selected as the most efficient catalyst concentration for diazinon removal and used for other experiments.

The Effect of Titania Doping on Diazinon Degradation

The photocatalytic performance of the TiO_2 photocatalysts for the photodegradation of diazinon under visible-light was evaluated, as shown in Fig. 3. At first, catalyst adsorption and photolysis are performed as control with removal percentage 4.48%, 44.08%, respectively for 30 min reaction time. Under photolysis, a photon from the light source may break down the organic
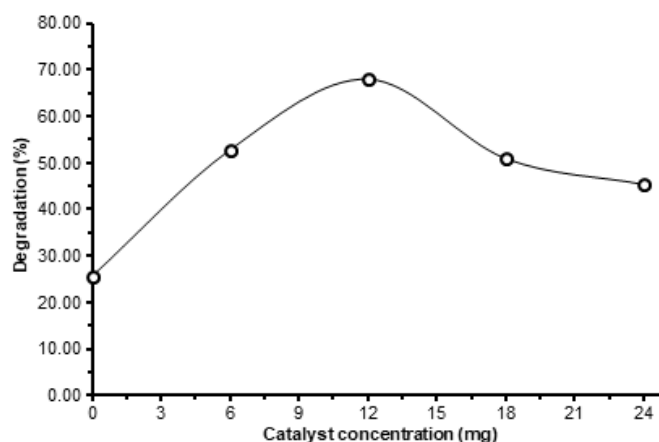
Fig 2. The effect of catalyst mass on photocatalysis of diazinon using C,N-codoped TiO_2 catalyst ([diazinon]$_o$ = 18 mg/L, catalyst = 0, 6, 12, 18, 24 mg, t = 15 min)
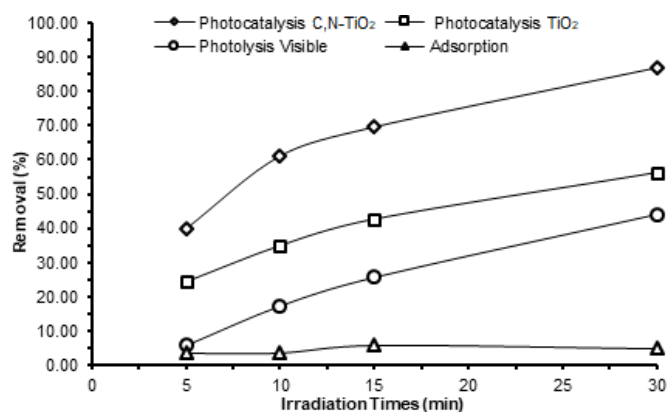
Fig 3. The effect of the catalyst on diazinon degradation by adsorption, photocatalysis using 12 mg C,N-codoped TiO_2 catalyst ([diazinon]$_o$ =18 mg/L, t = 5–30 min)

pollutant through chemical reaction [39]. Hence, the removal percentage increased significantly by adding the catalyst. The C,N-codoped TiO_2 photocatalysts were able to reduce 86.93% diazinon, which is higher than that is obtained in the presence of un-doped TiO_2 with 56.33% removal percentage of diazinon. Modification of titania using nonmetal elements such as carbon and nitrogen can lower its band gap, hasten the electron-hole process, and produce more •OH and •O_2^- radicals, which resulted in more degraded diazinon pesticide. This result was attributed by the shifting edge of modification TiO_2, which can be attributed to the increased of TiO_2 optical absorption [28].

The Effect of Initial pH of Pesticide on Diazinon Degradation

pH is one of the most important parameters influencing the photocatalytic degradation behavior since it determines the photocatalyst surface charge and the size of the aggregate formed. The effect of initial pH in acidic, neutral, and alkaline (3, 5, 7, 11) on photocatalysis degradation of 18 mg/L diazinon using 12 mg C,N-codoped TiO_2 was investigated. As observed in Fig. 4, the percentage of diazinon degradation was 45.82, 69.46, 67.98, and 48.58% at pH 3, 5, 7, and 11, respectively. The maximum degradation of diazinon was achieved at pH 5. This term can be explained by electrostatic interaction between the catalyst surface and the target compound. In this study, the catalyst used was on the nanoscale, with a size of about 44 nm [28]. The zero point charge (zpc), pH_{zpc}, of nano-sized titania is reported around 6.3–6.9 [15, 40]. The TiO_2 surface is positively charged at a low pH (< pH_{zpc}), and negatively charged at a higher pH (> pH_{pzc}). On the other hand, the given pKa for diazinon is 2.6. It will be negatively charged above pH 2.6. Therefore, the optimal condition is found at pKa diazinon < pH < pH_{zpc} C,N-codoped TiO_2 (between 2 < pH < 6.9) at which the positively charged catalyst and negatively charged diazinon should readily attract each other. The same result is also obtained by some researchers that degrade diazinon by photocatalysis using Pt-TiO_2 [34], and ZnO [35], TiO_2 [36] as catalysts.

The Effect of Initial Pesticide Concentration on Diazinon Degradation

The effect of initial pesticide concentration on diazinon degradation percentage is conducted with a dose of 9, 18, 36, 54, 72, and 90 mg/L at a constant condition; 15 min reaction time and 12 mg C,N-codoped TiO_2 catalyst dosage. The diazinon degradation decreases slightly with the higher initial concentrations of pesticides. The percentage of degradation diazinon at initial concentrations of 9, 18, 36, 54, 72 and 90 mg/L sequentially was achieved 72.43, 67.98, 66.07, 57.31, 49.38, and 22.91%, as illustrated in Fig. 5. The decrease in percentage degradation at high concentrations is caused by the competition between diazinon molecules each other
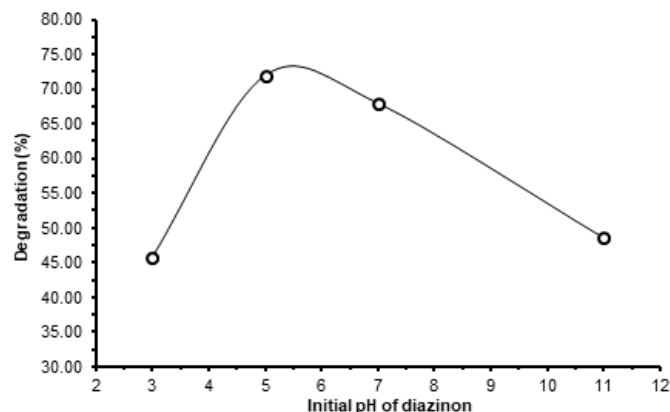

Fig 4. The effect of pesticide initial pH (3, 5, 7, 9) on photocatalysis of diazinon using 12 mg C,N-codoped TiO_2 catalyst ([diazinon]$_o$ = 18 mg/L, t = 15 min)
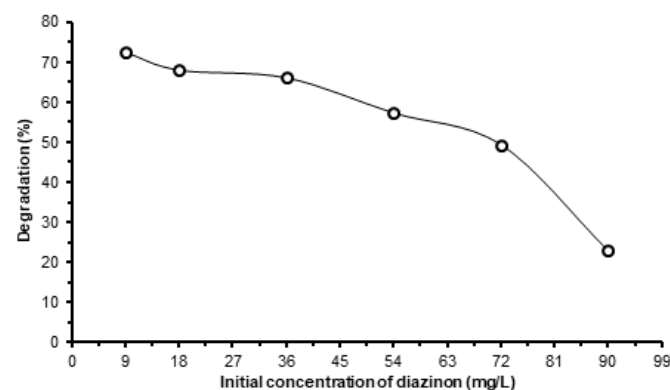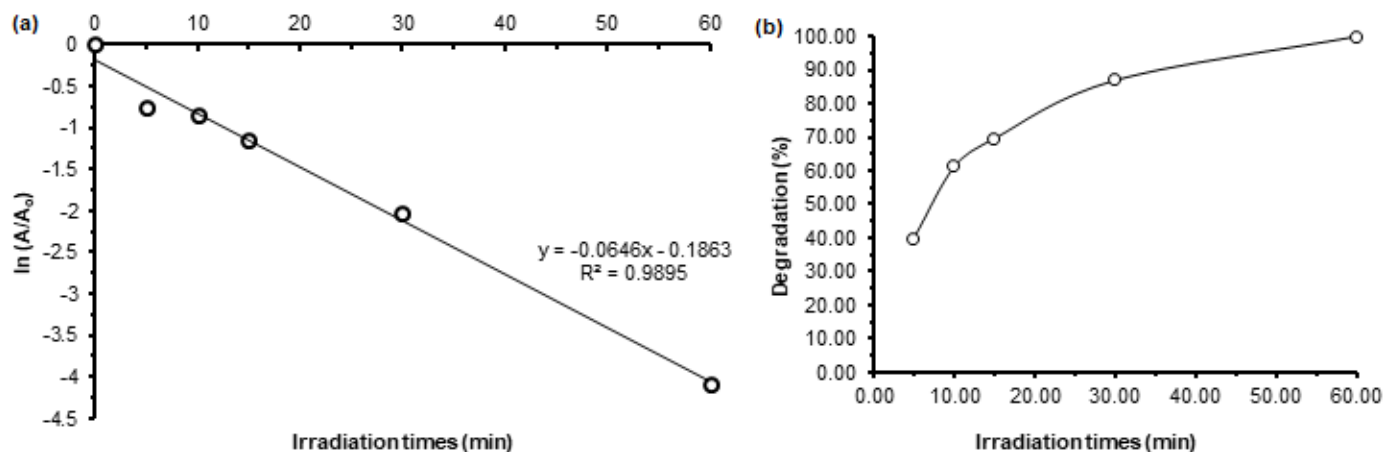

Fig 5. The effect of initial pesticide concentration on photocatalysis of diazinon using 12 mg C,N-codoped TiO_2 catalyst ([diazinon]$_o$ = 9 - 90 mg/L, t = 15 min)

to be absorbed on the C,N-codoped TiO_2 catalyst surface with the result reducing both of the availability of active sites and the pollutant oxidizing agents concentration (•OH and •O_2^- radicals) [33]. More intermediates are generated and consumed the reactive species in the systems. In addition, the generated intermediates may adsorb on the catalyst surface, which causes deactivate of the active sites of photocatalyst and leads to a decrease in the degradation percentage. In contrast, at low concentrations, there is no lack of catalytic sites number, and the rate of degradation will be proportional to the substrate concentration [37].

Two kinds of terms regard to the effect of the initial concentration on degradation process, 1) the efficiency degradation decreases by increasing diazinon concentration [40-42] and 2) there is an optimum point

Fig 6. (a) The effect of irradiation times and (b) the first order model on photocatalysis of diazinon using 12 mg C,N-codoped TiO₂ catalyst ([diazinon]ₒ = 18 mg/L, t = 5–60 min)

of efficiency degradation at a certain concentration [43-45]. This discrepancy may come from being the differences in the catalyst, organic pollutant properties, and experimental conditions.

## The Effect of Irradiation Time on Diazinon Degradation

Time is one of the important parameters affecting the amount of organic pollutant degraded. The pesticide photocatalysis degradation was conducted over the range 5–60 min with constant catalyst weight. As can be seen in Fig. 6(a), the degradation of diazinon steadily improves by increasing time in the photocatalysis process. Diazinon was degraded from 39.86% to 100% when the radiation times were from 5 to 60 min. The contact between photon and C,N-codoped TiO₂ increases at a longer time, leading more number of radical actives species production, which improves diazinon degradation [30,46]. In addition, reactive species and pesticides react perfectly with increasing irradiation time [47].

In order to obtain kinetic information, experimental results were fitted with zero, first and second order equations. The linearity value of those order equations shows that the photocatalytic degradation of 18 mg/L diazinon is well fitted with the first-order model (R = 0.9893) as can be seen in Fig. 6(b). The rate constant calculated from the slope between ln ([diazinon]ₜ/[diazinon]ₒ) versus reaction time Eq. 2 is 0.0646 min⁻¹.

$$\ln\frac{A_t}{A_0} = -kt \tag{2}$$

where A_t = diazinon concentration after irradiation, A_0 = initial concentration of diazinon, k = rate constant [48].

Fig. 7 represents the progressive degradation of diazinon after exposure under photocatalysis visible using C,N-codoped TiO₂. The UV–visible absorption spectrum of diazinon shows a peak at 247 nm. Its peak diminished gradually as exposure time increased, which confirm the progressive degradation of diazinon. The
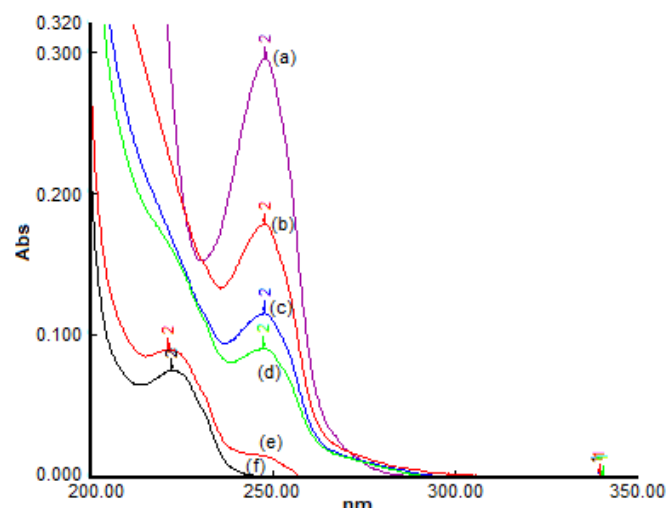

Fig 7. The change in UV-visible spectrum of Diazinon (a) before (0 min) and (b-f) after photocatalysis for 5–60 min, using 12 mg C,N-codoped TiO₂ catalyst ([diazinon]ₒ = 18 mg/L, t = 5–60 min)

complete degradation was reached at 60 min irradiation by vanishing diazinon peak at 247 nm and appearing the new peak at 230 nm. The possible compound formed from this process is 2-isopropyl-6-methyl-4-pyrimidinol (IMP) as a less byproduct of diazinon degradation [49]. The IMP has UV-Vis absorbance spectra at 230 nm, as reported by Žabar [50]. Yielding IMP from diazinon occurs probably by two mechanisms; through oxidative desulfuration of hydroxyl radical attack on the thiono group to form diazoxon followed by hydrolysis, or through a directly oxidative mechanism on diazinon [49].
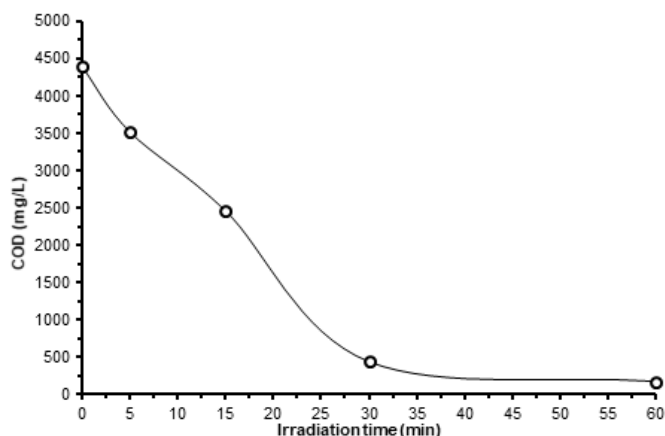
The HPLC Analysis of Degraded Diazinon

Generally, some intermediates and by-products will be produced during the degradation process. Sometimes they are more toxic than the initial target contaminants. Fig. 8 shows that diazinon concentration reduces after treatment indicating by the decrease in its peak at a retention time of 8.7 min. Diazinon almost completely disappears and transforms into other compounds after 60 min photocatalysis. This result is a good agreement with the UV-visible spectrophotometric data reaching 100% degradation percentage by disappearing diazinon spectrum and forming a new spectrum at 230 nm, as shown in Fig. 7. The existence of a new peak at retention time t_R = 1.67 min and t_R = 2.76 min in chromatogram signifies the possible formation of new compounds as the diazinon degradation products that need to be analyzed further.
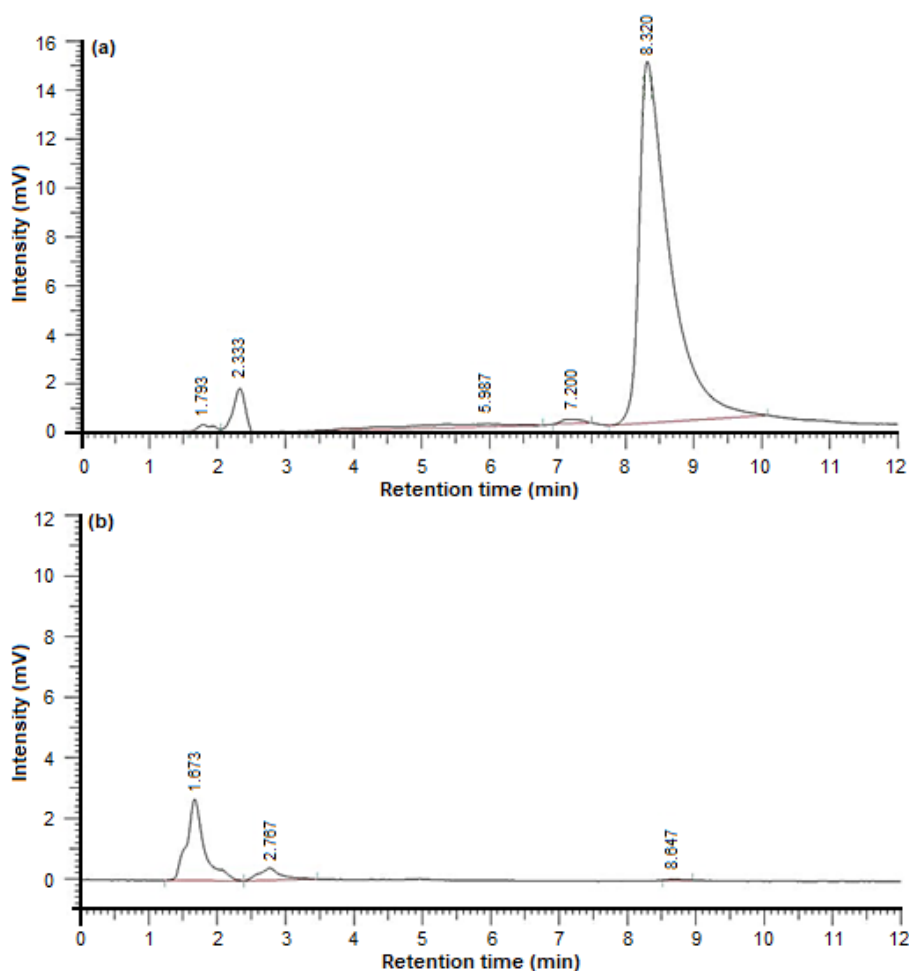
Fig 8. Chromatogram of (a) un-treated diazinon solution (b) treated diazinon by visible photocatalysis using 12 C,N-codoped TiO_2 catalyst ([diazinon]$_o$ =18 mg/L, t = 60 min)

Fig 9. The chemical oxygen demand (COD) of diazinon after photocatalysis using 12 mg C,N-codoped TiO_2 catalyst ([diazinon]$_o$ = 18 mg/L, t = 5–60 min)

Chemical Oxygen Demand (COD) of Degraded Diazinon

The degree of diazinon mineralization was determined by using COD experiment. It is found that the COD of diazinon solution decreases from 4400 mg/L to 176 mg/L after 60 min of photocatalysis treatment. This indicates that 96% of diazinon was mineralized to carbon dioxide during photocatalysis [51]. When titania catalyst was irradiated by photon, its electron will excite from valence band to conduction gap, and this process generates electron-hole. The reaction between oxygen and water with generated electron-hole would form the strong oxidative hydroxyl radical (•OH). The radical would oxidize the organic pollutant into CO_2 and H_2O [52]. The COD, spectrophotometer UV-Visible, and chromatogram confirmed that photocatalysis using C,N-codoped TiO_2 under visible-light was successfully degraded the diazinon.

■ CONCLUSION

The diazinon degradation is accelerated by titania modified (C,N-codoped TiO_2) under the photocatalysis process. The diazinon can be completely degraded by C,N-codoped TiO_2 catalyzed visible photocatalysis for 60 min irradiation. The degradation was strongly affected by catalyst concentration, initial concentration of diazinon, initial pH of the solution, and irradiation time. UV-visible spectrophotometer, HPLC and COD analysis

verified that diazinon was successfully degraded by photocatalysis visible using 12 mg C,N-codoped TiO_2.

■ REFERENCES

[1] Čolović, M., Krstić, D., Petrović, S., Leskovac, A., Joksić, G., Savić, J., Franko, M., Trebše, P., and Vasić, V., 2010, Toxic effects of diazinon and its photodegradation products, *Toxicol. Lett.*, 193 (1), 9–18.

[2] Neishabouri, E.Z., Hassan, Z.M., Azizi, E., and Ostad, S.N., 2004, Evaluation of immunotoxicity induced by diazinon in C57bl/6 mice, *Toxicology*, 196 (3), 173–179.

[3] Muranli, F.D., Kanev, M., and Ozdemir, K., 2015, Genotoxic effects of diazinon on human peripheral blood lymphocytes, *Arh. Hig. Rada Toksikol.*, 66 (2), 153–158.

[4] Harchegani, A.B., Rahmani, A., Tahmasbpour, E., Kabootaraki, H.B., Rostami, H., and Shahriary, A., 2018, Mechanisms of diazinon effects on impaired spermatogenesis and male infertility, *Toxicol. Ind. Health*, 34 (9), 653–664.

[5] Ezzi, L., Haouas, Z., Salah, I.B., Sakly, A., Grissa, I., Chakroun, S., Kerkeni, E., Hassine, M., Mehdi, M., and Cheikh, H.B., 2016, Toxicopathic changes and genotoxic effects in liver of rat following exposure to diazinon, *Environ. Sci. Pollut. Res.*, 23 (11), 11163–11170.

[6] Jonidi-Jafari, A., Shirzad-Siboni, M., Yang, J.K., Naimi-Joubani, M., and Farrokhi, M., 2015, Photocatalytic degradation of diazinon with illuminated ZnO–TiO$_2$ composite, *J. Taiwan Inst. Chem. Eng.*, 50, 100–107.

[7] Li, P.C.H., Swanson, E.J., and Gobas, F.A.P.C., 2002, Diazinon and its degradation products in

agricultural water courses in British Columbia, Canada, *Bull. Environ. Contam. Toxicol.*, 69 (1), 59–65.

[8] Čolović, M.B., Krstić, D.Z., Ušćumlić, G.S., and Vasić, V.M., 2011, Single and simultaneous exposure of acetylcholinesterase to diazinon, chlorpyrifos and their photodegradation products, *Pestic. Biochem. Physiol.*, 100 (1), 16–22.

[9] Ahmed, M.A.E., Ahmed, H.I., and El-Morsy, E.M., 2013, Melatonin protects against diazinon-induced neurobehavioral changes in rats, *Neurochem. Res.*, 38 (10), 2227–2236.

[10] Hariri, A.T., Moallem, S.A., Mahmoudi, M., Memar, B., and Hosseinzadeh, H., 2010, Sub-acute effects of diazinon on biochemical indices and specific biomarkers in rats: Protective effects of crocin and safranal, *Food Chem. Toxicol.*, 48 (10), 2803–2808.

[11] Wu, J., Lan, C., and Chan, G.Y.S., 2009, Organophosphorus pesticide ozonation and formation of oxon intermediates, *Chemosphere*, 76 (9), 1308–1314.

[12] Yahiat, S., Fourcade, F., Brosillon, S., and Amrane, A., 2011, Photocatalysis as a pre-treatment prior to a biological degradation of cyproconazole, *Desalination*, 281, 61–67.

[13] Mirmasoomi, S.R., Ghazi, M.M., and Galedari, M., 2017, Photocatalytic degradation of diazinon under visible light using TiO_2/Fe_2O_3 nanocomposite synthesized by ultrasonic-assisted impregnation method, *Sep. Purif. Technol.*, 175, 418–427.

[14] Beduk, F., Aydin, M.E., and Ozcan, S., 2012, Degradation of malathion and parathion by ozonation, photolytic ozonation, and heterogeneous catalytic ozonation processes, *Clean-Soil Air Water*, 40 (2), 179–187.

[15] Chen, H., Shen, M., Chen, R., Dai, K., and Peng, T., 2011, Photocatalytic degradation of commercial methyl parathion in aqueous suspension containing La-doped TiO_2 nanoparticles, *Environ. Technol.*, 32 (13), 1515–1522.

[16] Sakkas, V.A., Dimou, A., Pitarakis, K., Mantis, G., and Albanis, T., 2005, TiO_2 photocatalyzed degradation of diazinon in an aqueous medium, *Environ. Chem. Lett.*, 3 (2), 57–61.

[17] Nadia, E.M., Moustapha, B., and Yahia, A.I., 2018, UV/TiO_2 photocatalytic oxidation of commercial pesticide in aqueous solution, *Am. J. Innov. Res. Appl. Sci.*, 7 (1), 36–43.

[18] Kumar, S.G., and Devi, L.G., 2011, Review on modified TiO_2 photocatalysis under UV/visible light: Selected results and related mechanisms on interfacial charge carrier transfer dynamics, *J. Phys. Chem. A*, 115 (46), 13211–13241.

[19] Xu, Q.C., Wellia, D.V., Yan, S., Liao, D.W., Lim, T.M., and Tan, T.T.Y., 2011, Enhanced photocatalytic activity of C-N-codoped TiO_2 films prepared via an organic-free approach, *J. Hazard. Mater.*, 188 (1-3), 172–180.

[20] Safni, Wellia, D.V., Komala, P.S., and Putri, R.A., 2015, Degradation of yellow-GCN by photolysis with UV-light and solar irradiation using C-N-codoped TiO_2 catalyst, *J. Chem. Pharm. Res.*, 7 (11), 306–311.

[21] Kakroudi, M.A., Kazemi, F., and Kaboudin, B., 2014, Highly efficient photodeoximation under green and blue LEDs catalyzed by mesoporous C-N-codoped nano TiO_2, *J. Mol. Catal. A: Chem.*, 392, 112–119.

[22] Chen, D., Jiang, Z., Geng, J., Wang, Q., and Yang, D., 2007, Carbon and nitrogen co-doped TiO_2 with enhanced visible-light photocatalytic activity, *Ind. Eng. Chem. Res.*, 46 (9), 2741–2746.

[23] Liu, G., Han, C., Pelaez, M., Zhu, D., Liao, S., Likodimos, V., Kontos, A.G., Falaras, P., and Dionysiou, D.D., 2013, Enhanced visible light photocatalytic activity of CN-codoped TiO_2 films for the degradation of microcystin-LR, *J. Mol. Catal. A: Chem.*, 372, 58–65.

[24] Dai, G., Liu, S., Liang, Y., Liu, H., and Zhong, Z., 2013, A simple preparation of carbon and nitrogen co-doped nanoscaled TiO_2 with exposed {001} facets for enhanced visible-light photocatalytic activity, *J. Mol. Catal. A: Chem.*, 368-369, 38–42.

[25] Wu, Y.C., and Ju, L.S., 2014, Annealing-free synthesis of C-N co-doped TiO_2 hierarchical spheres by using amine agents via microwave-assisted solvothermal method and their

photocatalytic activities, *J. Alloys Compd.*, 604, 164–170.

[26] El-Sheikh, S.M., Khedr, T.M., Hakki, A., Ismail, A.A., Badawy, W.A., and Bahnemann, D.W., 2017, Visible light activated carbon and nitrogen co-doped mesoporous TiO_2 as efficient photocatalyst for degradation of ibuprofen, *Sep. Purif. Technol.*, 173, 258–268.

[27] Wang, X., and Lim, T.T., 2010, Solvothermal synthesis of C–N codoped TiO_2 and photocatalytic evaluation for bisphenol A degradation using a visible-light irradiated LED photoreactor, *Appl. Catal., B*, 100 (1-2), 355–364.

[28] Wellia, D.V., Fitria, D., and Safni, 2018, C-N-codoped TiO_2 synthesis by using peroxo sol gel method for photocatalytic reduction of Cr(VI), *J. Pure Appl. Chem. Res.*, 7 (1), 25–31.

[29] Fitriyani, Y.O., Septiani, U., Wellia, D.V., Putri, R.A., Safni, 2017, Degradasi zat warna direct red-23 secara fotolisis dengan katalis C-N-codoped TiO_2, *Valensi*, 3 (2), 152–159.

[30] Safitri, V.Y., Santoni, A., Wellia, D.V., Khoiriah, and Safni, 2017, Degradation of paracetamol by photolysis using C-N-codoped TiO_2, *Molekul*, 12 (2), 189–195.

[31] Safni, Weillia, D.V., Komala, P.S., Putri, R.A., and Deliza, 2016, Photocatalytic degradation of yellow-GCN dye using C-N-codoped TiO_2 thin film in degradation reactor using visible-light irradiation, *Der Pharma Chem.*, 8 (19), 642–646.

[32] Safni, M., Putri, R.A., Wellia, D.V., and Septiani, U., 2017, Photodegradation of orange F3R dyes: Effect of light sources and the addition of CN-codoped TiO_2 catalyst, *Der Pharma Chem.*, 9 (10), 1–5.

[33] Kumar, A., and Pandey, G., 2017, A review on the factors affecting the photocatalytic degradation of hazardous materials, *Mater. Sci. Eng. Int. J.*, 1 (3), 1–10.

[34] Nakaoka, Y., Katsumata, H., Kaneco, S., Suzuki, T., and Ohta, K., 2012, Photocatalytic degradation of diazinon in aqueous solution by platinized TiO_2, *Desalin. Water Treat.*, 13 (1-3), 427–436.

[35] Daneshvar, N., Aber, S., Seyed Dorraji, M.S., Khataee, A.R., and Rasoulifard, M.H., 2007, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light, *Sep. Purif. Technol.*, 58 (1), 91–98.

[36] Jafari, S.J., Moussavi, G., and Hossaini, H., 2016, Degradation and mineralization of diazinon pesticide in UVC and UVC/TiO_2 process, *Desalin. Water. Treat.*, 57 (8), 3782–3790.

[37] Ahmed, S., Rasul, M.G., Brown, R., and Hashib, M.A., 2011, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review, *J. Environ. Manage.*, 92 (3), 311–330.

[38] Jonidi-Jafari, A., Gholami, M., Farzadkia, M., Esrafili, A., and Shirzad-Siboni, M., 2017, Application of Ni-doped ZnO nanorods for degradation of diazinon: Kinetics and by-products, *Sep. Sci. Technol.*, 52 (15), 2395–2406.

[39] Speight, J.G., 2017, "Transformation of inorganic chemicals in the environment" in *Environmental Inorganic Chemistry for Engineers*, 1st Ed., Butterworth-Heinemann, 333–382.

[40] Kalantary, R.R., Shahamat, Y.D., Farzadkia, M., Esrafili, A., and Asgharnia, H., 2015, Photocatalytic degradation and mineralization of diazinon in aqueous solution using nano-TiO_2 (Degussa, P25): Kinetic and statistical analysis, *Desalin. Water. Treat.*, 55 (2), 555–563.

[41] Shirzad-Siboni, M., Jonidi-Jafari, A., Farzadkia, M., Esrafili, A., and Gholami, M., 2017, Enhancement of photocatalytic activity of Cu-doped ZnO nanorods for the degradation of an insecticide: Kinetics and reaction pathways, *J. Environ. Manage.*, 186 (Pt 1), 1–11.

[42] Mohagheghian, A., Karimi, S.A., Yang, J.K., and Shirzad-Siboni, M., 2016, Photocatalytic degradation of diazinon by illuminated WO_3 nanopowder, *Desalin. Water. Treat.*, 57 (18), 8262–8269.

[43] Baneshi, M.M., Rezaei, S., Sadat, A., Mousavizadeh, A., Barafrashtehpour, M., and Hekmatmanesh, H., 2017, Investigation of photocatalytic degradation of

diazinon using titanium dioxide (TiO₂) nanoparticles doped with iron in the presence of ultraviolet rays from the aqueous solution, *Biosci. Biotechnol. Res. Commun.*, 1, 60–67.

[44] Laoufi, N.A., Tassalit, D., and Bentahar, F., 2008, The degradation of phenol in water solution by TiO₂ photocatalysis in a helical reactor, *Global NEST J.*, 10 (3), 404–418.

[45] Tabasideh, S., Maleki, A., Shahmoradi, B., Ghahremani, E., and McKay, G., 2017, Sonophotocatalytic degradation of diazinon in aqueous solution using iron-doped TiO₂ nanoparticles, *Sep. Purif. Technol.*, 189, 186–192.

[46] Sari, M.I., Agustina, T.E., Melwita, E., and Aprianti, T., 2017, Color and COD degradation in photocatalytic process of procion red by using TiO₂ catalyst under solar irradiation, *AIP Conf. Proc.*, 1903, 040017.

[47] Wardhani, S., Purwonugroho, D., Fitri, C.W., and Prananto, Y.P., 2018, Effect of pH and irradiation time on TiO₂-chitosan activity for phenol photo-degradation, *AIP Conf. Proc.*, 2021, 050009.

[48] Hossaini, H., Moussavi, G., and Farrokhi, M., 2017, Oxidation of diazinon in cns-ZnO/LED photocatalytic process: Catalyst preparation, photocatalytic examination, and toxicity bioassay of oxidation by-products, *Sep. Purif. Technol.*, 174, 320–330.

[49] Shemer, H., and Linden, K.G., 2006, Degradation and by-product formation of diazinon in water during UV and UV/H₂O₂ treatment, *J. Hazard. Mater.*, 136 (3), 553–559.

[50] Žabar, R., 2012, Persistence, degradation and toxicity of transformation products of selected insecticides, *Dissertation*, University of Nova Gorica, Slovenia.

[51] Rajamanickam, D., and Shanthi, M., 2016, Photocatalytic degradation of an organic pollutant by zinc oxide – solar process, *Arabian J. Chem.*, 9 (Suppl. 2), S1858–S1868.

[52] Syafei, D., Sugiarti, S., Darmawan, N., and Khotib, M., 2017, Synthesis of TiO₂/carbon nanoparticle (C-dot) composites as active catalysts for photodegradation of persistent organic pollutant, *Indones. J. Chem.*, 17 (1), 37–42.