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THE OPERATIONAL PARAMETERS EFFECT ON PHOTOCATALYTIC DEGRADATION OF DIAZINON USING CARBON AND NITROGEN MODIFIED TiO_2

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ABSTRACT

Diazinon is one of the most active compounds containing in commercial pesticides used for agriculture application. The photocatalytic degradation of commercial emulsion diazinon using nanoparticles photocatalyst C,N-codoped TiO_2 under UV irradiation was investigated. The operational parameters, i.e., the modified titania, catalyst dose, initial pH, the concentration of diazinon, H_2O_2, and humic acid as an additive were examined. Under optimal parameters, the diazinon with initial concentration 18 mg L^{-1} at pH 6 in the presence of 12 mg C,N-codoped TiO_2 catalyst can be degraded 76% after 180 minutes irradiation. Whereas the mineralization of diazinon reached 37% as analyzed by total organic carbon analyzer (TOC). The additive compounds containing diazinon commercial give no effect under the photocatalysis process.

Keywords: C,N-codoped TiO_2, Diazinon, Photocatalysis, Mineralization

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INTRODUCTION

Diazinon is an organophosphate pesticide extensively used as pest control in plantation country such as Indonesia.[1] It is effective in an application for various kinds of cultivations such as horticultural plants, tobacco, rice, corn, fruit trees, sugarcane, and palm.[2] These activities cause the diazinon residues concentration to increase in the environment. On the other hand, this organic compound is a highly toxic pesticide, nonspecific target, low persistence in the environment[3], immunotoxic[4], cytotoxic and genotoxic [5-7] and categorized as moderately hazardous class II by the World Health Organization (WHO). Thus, the removal and reduction of diazinon concentration from the water represent an emerging environmental concern. The pure diazinon is mostly used in the investigation rather than commercial ones. However, the application is more in the form of commercial insecticide emulsion which contains the organic solvent, additive, and impurities for its solubility and stability in water. The presence of those organic compounds mentioned above in emulsion can cause additional complications such as possible reactions among them and their degradation byproducts in the photocatalytic process.[1]

Titania (TiO_2) is one of the selected photocatalyst used for organic pollutant degradation such as diazinon into H_2O and CO_2 because it is effective, stable against photo-corrosion, photoactive, and environment-friendly.[8-10] However, the wide bandgap (3.2 eV) of titania causes limitations in an extensive application under photocatalysis. Recently, modified TiO_2 by codoping with non-metals (C, N, and S) is one of the most efficient techniques. Its product will have higher photocatalytic activity and special characteristics compared with single doped TiO_2. Synergistic effect of dopants results in narrow bandgaps (redshift) leading to higher photoresponse and photocatalytic activity under high energy source (UV-light)[11] and low energy (visible-light).[12,13] Nanoparticles of C,N-codoped TiO_2 have been synthesized by using water solvent and reported single doped and un-doped ones.[14,15]

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The pure diazinon was degraded by the photocatalysis process using modified titania such as FeFNS-TiO_2[16], N-doped TiO_2[17], Fe-doped TiO_2[18]. While the commercial form of diazinon was studied using TiO_2 PC-102[19]. This present work investigates the effect of the operational parameters on photocatalytic degradation of formulation diazinon using C,N-codoped TiO_2 as a photocatalyst. The parameters are; effects of modified titania, catalyst dose, initial pH, the concentration of diazinon, H_2O_2, and humic acid as an additive.

EXPERIMENTAL

Material and Methods

A commercial emulsion containing 600 g L^{-1} diazinon, (Code Name Diazinon 600 EC) was used as organic pollutant insecticide in water. A diazinon standard (CAS No. 333-41-5) was purchased from Sigma-Aldrich. Ethanol 95%, a solvent for diazinon stock solution was purchased from Sigma-Aldrich. Preparation steps and full characterization of the C,N-codoped TiO_2 nanoparticles were conducted according to the previous publication [14].

The change of diazinon concentration was analyzed by and DR600™ UV-vis spectrophotometer (Hach, USA). The total organic carbon of degraded diazinon was analyzed by the TOC analyzer (Shimadzu, Serial No. H571049). The pH of diazinon was measured by using Prolab 2000 pH meter (SCHOTT Instruments GmbH, Germany). The UV light intensity was measured by IL1400A Radiometer/Photometer (International Light Technologies, Inc).

General Procedure

Photocatalytic reactions were performed in a batch system under 13 Watt UV lamps irradiation (Germicidal CEG13 Base BFC 11004, λ=254 nm). The solution of diazinon with concentration 18 mg L^{-1} was added by photocatalyst (10 at.% C,N-codoped TiO_2 after calcination at 500 ^oC) and irradiated under 1.7 mW cm^{-2} UV-lamp. During the photocatalytic reaction, the optimal C,N-codoped TiO_2 dose was set at experiments with different diazinon concentrations, initial diazinon pH, H_2O_2, and humic acid addition were conducted to investigate their effects on the degradation efficiencies of diazinon. Aliquots were sampled every interval times (30, 60, 120, and 180 minutes) and diazinon residue was detected by a DR600™ UV-vis spectrophotometer at 247 nm. The degraded diazinon solution under optimal condition was also measured by SCL-10A VP HPLC (Shimadzu) equipped with Poroshell 120 SB-Aq 2.7 (4.6 x 150 mm) column, using 80/20 (methanol/water, v/v), volume injection and flow rates were 20 µL and 0.5 mL min^{-1}, respectively. The mineralization percentage of degraded diazinon was analyzed by using a TOC analyzer (Shimadzu, Serial No. H571049).

RESULTS AND DISCUSSION

The Effect of Modified Titania on Diazinon Degradation

Figure-1 represents the effect of carbon and nitrogen as dopant on the degradation of diazinon. Photocatalysis also conducted using single doped TiO_2 carbon, nitrogen, and un-doped as a control. As seen in Fig.-3 diazinon efficiency is greater under photocatalysis using carbon and nitrogen modified titania than single doped. This result can be elucidated by the small band gap and high crystalline of C,N-codoped TiO_2 than C-doped TiO_2, N-doped TiO_2 and un-doped TiO_2 with the bandgap is 2.87 eV, 2.97 eV, 3.02 eV, and 3.09 eV respectively as reported in our previous research.[14] Carbon and nitrogen give synergy effect on modified titania with having high crystallinity and low bandgap. Three opinions regard to the mechanism of modified TiO_2 by doping using non-metals:

1. The dopant incorporates into the TiO_2 crystalline lattice and alters the structure of TiO_2 electronic band which leads the level of the dopant above the O 2p valence band and the bandgap of TiO_2 becomes narrower. Some Ti^{4+} are converted to be Ti^{3+} by non-metal dopant through charge compensation and generated Ti^{3+} forms donor energy below the conduction band of TiO_2.
2. The co-doped carbon produces a photosensitizer by forming carbonaceous species on the surface of TiO_2.
3. Nitrogen dopant substitutes the oxygen site of TiO_2 and forms the impurity energy level above the valence band [12].

The Effect of Catalyst Dose on Diazinon Degradation

Catalyst dose is one of the most factor influences photocatalysis degradations. To optimize C,N-codoped TiO_2 dose, the catalyst with an amount (0, 6, 12, 18, and 24 mg) was added into the diazinon solution while

another parameter is keeping constant. The experiment was also carried out under UV photolysis without catalyst addition as a control. Diazinon was removed 11% for 180 min irradiation times indicating the direct photolysis is not effective. As presented in Fig.-2 the efficiency increases significantly in the presence of 6-18 mg catalyst and decreases at amount 24 mg. The improvement in degradation at higher photocatalyst concentration can be explained by increasing the catalyst providing a higher active site and more photons adsorbed on catalyst surface for the photocatalytic reaction which increased in the oxidative species formation. Further increase in TiO_2 concentration at 24 mg addition, however, gives a negative effect. The exceeded optimal catalyst dose causes increasing turbidity, lower light penetration, and resulting agglomeration causes difficulty in the suspension homogenous form and lowering the number of active sites.[20] Thus, the chosen catalyst as an optimal condition for the degradation process was 12 mg.

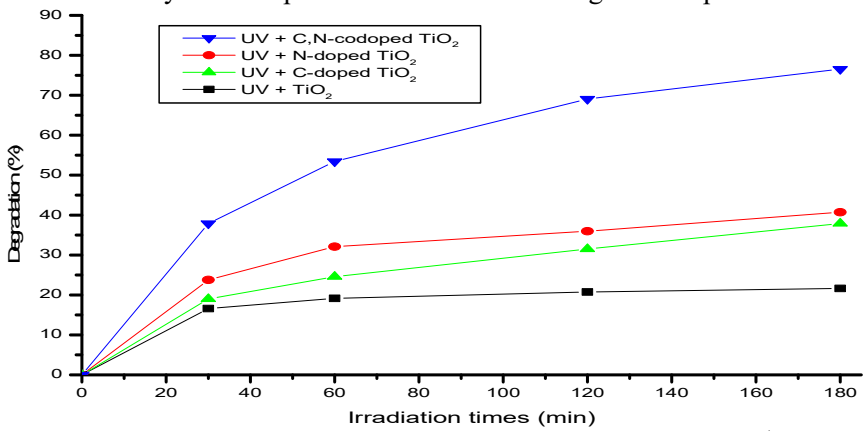

Fig.-1: The Effect of Doping Titania on Photocatalysis of Diazinon [Diazinon = 18 mg L^{-1}, Catalyst = 12 mg, t= 0-180 min, using TiO_2, N-Doped TiO_2, C-Doped TiO_2 and C,N-codoped TiO_2]

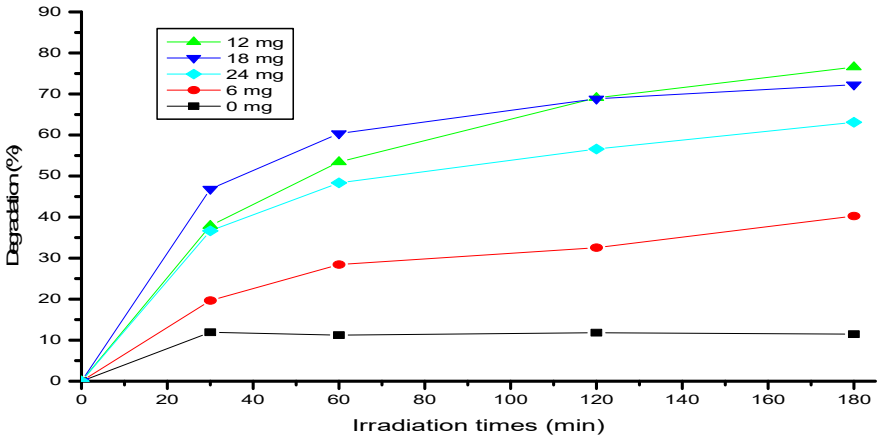

Fig.-2: The Effect of Catalyst Dose on Photocatalysis of Diazinon Using C,N-codoped TiO_2 [Diazinon = 18 mg L^{-1}, Catalyst = 0, 6, 12, 18 and 24 mg, t= 0-180 min]

The Effect of Initial pH on Diazinon Degradation

The effect of pH on the photocatalysis degradation of diazinon using 12 mg C,N-codoped TiO_2 was investigated at pH 3, 5, 6, 7, and 9 for 180 min irradiation. The results are shown in Fig. 3. As observed the optimal diazinon degradation was achieved at pH 6. It is reported that the pH_{zpc} of nano-titania is at range 6.3-6.9.[21] The titania surface will be positive at lower the pH_{zpc} and negative at higher the pH_{zpc}. On the other hand, the pKa of diazinon is 2.6 which is negatively charged above pH 2.6. Low diazinon degradation at higher pH is caused by the negatively charged of nano-titania catalyst preventing the negatively charged diazinon and hydroxide anion to adsorp in catalyst surface. Conversely, there is an electrostatic attraction between positive diazinon and catalyst in acidic conditions leading to a low degradation of diazinon. Therefore, the optimal condition is found at pKa diazinon < pH < pH_{zpc} catalyst.

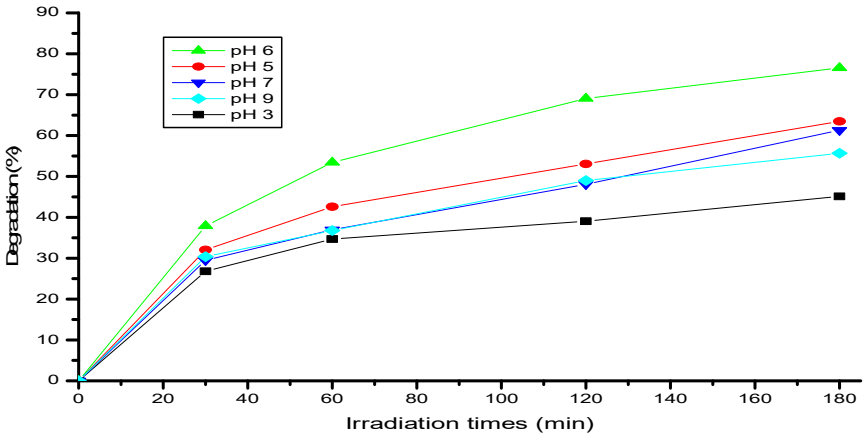

Fig.-3:The Effect of Initial pH on Photocatalysis of Diazinon Using C,N-codoped TiO_2 [Diazinon = 18 mg L^{-1}, Catalyst = 12 mg, pH = 3, 5, 6, 7, and 9; t= 0-180 min]

The Effect of Initial Concentration on Diazinon Degradation

To investigate the effect of the initial concentration of diazinon under photocatalysis degradation, four different concentrations (9, 18, 36 and 54 mg L^{-1}) were selected. The reason for the chosen range of concentrations because of uncontrolled pesticides in the application for improving crop yielding by farmers in developing countries such as Indonesia.[18,22] As shown in Fig.-4 the diazinon degradation increases by increasing the diazinon concentration over 18 mg L^{-1} followed by a decline pattern. The possible reason for decreasing photocatalytic degradation at a higher initial concentration of diazinon is more reactant molecules adsorbed on the catalyst surface which block active sites of the catalyst [23]. Another reason is at a higher concentration of diazinon generates higher intermediate that adsorbs, blocks, and deactivates the active sites of the catalyst.[21]

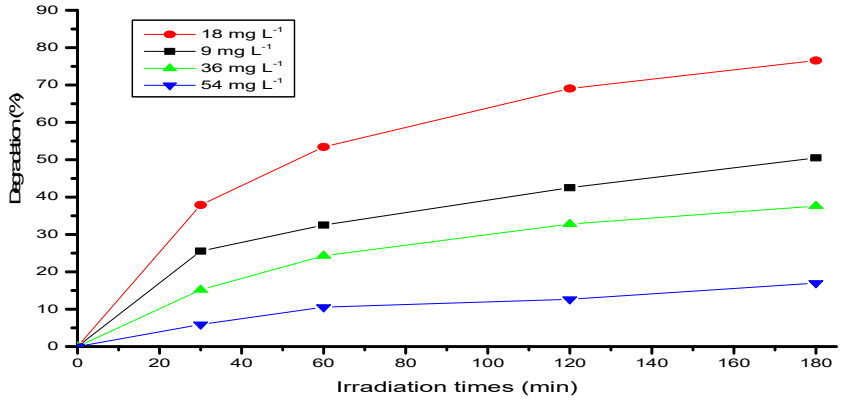

Fig.-4: The Effect of Initial Concentration on Photocatalysis of Diazinon [Diazinon = 9, 18, 36, and 54 mg L^{-1}, Catalyst = 12 mg; t= 0-180 min]

The Effect of H_2O_2 Addition on Diazinon Degradation

The effect of H_2O_2 addition on diazinon degradation efficiency was examined at a series of hydrogen peroxide concentrations in range 0 mmol L^{-1} - 0.5 mmol L^{-1} as exhibited in Table 1. The H_2O_2 addition gives a positive effect on the diazinon degradation at 30-60 minutes photocatalysis. The degradation efficiency decreases with increasing initial H_2O_2 concentration and the optimal concentration is found at 0.25 mmol L^{-1} H_2O_2 addition. The diazinon degradation is 37.91% without H_2O_2 and increases to be 51.85% at 0.25 mmol L^{-1} H_2O_2 addition. However, the addition of 0.5 mmol L^{-1} H_2O_2 causes the descent of diazinon degradation to be 35.77%. The presence of H_2O_2 at low concentration on the photocatalytic system could be an option electron acceptor to oxygen which inhibits the recombination process [24, 25]. Also, H_2O_2 is can be as an additional free radical source through direct photolysis of H_2O_2 by UV-light as shown [26]. Those reactions would improve the efficiency of diazinon degradation. While H_2O_2 may act as a powerful

scavenger of HO• and hole-less effective on HO•$_2$ production at overdose addition on photocatalytic system leading to the reduction of diazinon degradation.[27]

Table-1: The Effect of H_2O_2 Addition on Photocatalysis of Diazinon

Irradiation Times (min)	Diazinon Degradation on H_2O_2 Addition (%)			
	0 mmol L^{-1}	0.125 mmol L^{-1}	0.25 mmol L^{-1}	0.50 mmol L^{-1}
30	37.91	51.851	35.769	48.589
60	53.426	55.452	41.618	55.789
120	69.057	69.033	45.419	61.531
180	76.552	75.823	49.610	65.617

The Effect of Humic Acid Addition on Diazinon Degradation

The effect of humic acid is important to be studied as its occurrence in natural water is in range 0.03-30 mgCL^{-1}.[28] The effect of humic acid effect on diazinon degradation was investigated at concentrations of 0-18 mg L^1. The diazinon removal decreases from 76.55% to be 29.41% in the presence of humic acid at concentration 3-18 mg L^{-1}. This decline could be attributed to the occupied catalyst surface by humic acid blocking the active sites for the access of diazinon.[26, 27] Besides, humic acid can be an optical filter as it has strong absorbance at 190 to 800 nm and competitively absorbs light and photons.[28]

HPLC Analysis and Mineralization of Diazinon

Figure-5 reports the HPLC chromatogram of diazinon solution before and after degradation for 180 minutes recorded at 247 nm. There are three peaks detected; at retention time 3.7 min, 4.7 min, and 5.3 min in the chromatogram of the initial solution. The first two peaks can be attributed to the organic solvent in the commercial diazinon emulsion.[1] The intensity of those peaks keeps constant as increasing irradiation times, suggesting there is no degradation of those compounds. At the same time, the peak of diazinon at t_R = 5.3 min decreases in prolonging irradiation time, indicating the reduction and degradation of diazinon. As shown in Fig.-5b, the process produces a new peak at t_R = 3.3 min and its intensity raises with decreasing diazinon concentration in longer photocatalysis. This result suggests that the photocatalysis process may transform diazinon and forms a new compound as degradation products. This compound peak appears at shorter retention times than that the diazinon, implying that the generated intermediate is smaller molecular weight and less polarity than that of diazinon.[1]

Figure-5c shows that the degradation and mineralization degree of diazinon increase as the reaction time increased with efficiency 76% and 37 %, respectively. The amount of degraded diazinon is higher than that of the mineralized. This much difference indicated that the degradation processes produced transient organic intermediates on the photocatalysis system caused un-complete mineralization.[29] This result is confirmed by the HPLC analysis that found a diazinon intermediate during photocatalytic degradation. When the titania catalyst was irradiated by photon, its electron will excite from valence band to conduction band which generates electron-hole. The reaction of oxygen and water with the generated electron-hole will form the strong oxidative hydroxyl radical. The radical and hole oxidize the organic pollutant to be CO_2, H_2O, and some intermediates.[26, 30, 31]

Table-2: The Effect of Humic Acid Addition on the Photocatalysis of Diazinon

Irradiation Times (min)	Diazinon Degradation on Humic Acid Addition (%)			
	0 mg L^{-1}	3 mg L^{-1}	9 mg L^{-1}	18 mg L^{-1}
30	37.91	36.83	34.07	6.794
60	53.42	51.06	42.75	16.029
120	69.057	54.98	52.27	29.405
180	76.552	75.823	49.610	65.618

CONCLUSION

The degradation of commercial diazinon emulsion using C,N-codoped TiO_2 catalyst under UV-light irradiation was investigated. The diazinon degradation efficiency was strongly influenced by modified titania, catalyst dose, initial pH, the concentration of diazinon, H_2O_2, and humic acid addition. The addition of 0.25 mmol L^{-1} H_2O_2 improves diazinon efficiency at 30-60 minutes photocatalysis. While the presence of humic acid on the system decreases diazinon degradation. Photocatalysis of 18 mg L^{-1} diazinon at pH 6

in the addition of 12 mg C,N-codoped TiO_2 catalyst can be degraded 76% and mineralized 37% after 180 minutes irradiation. The additive compounds containing diazinon commercial give no effect under the photocatalytic process.

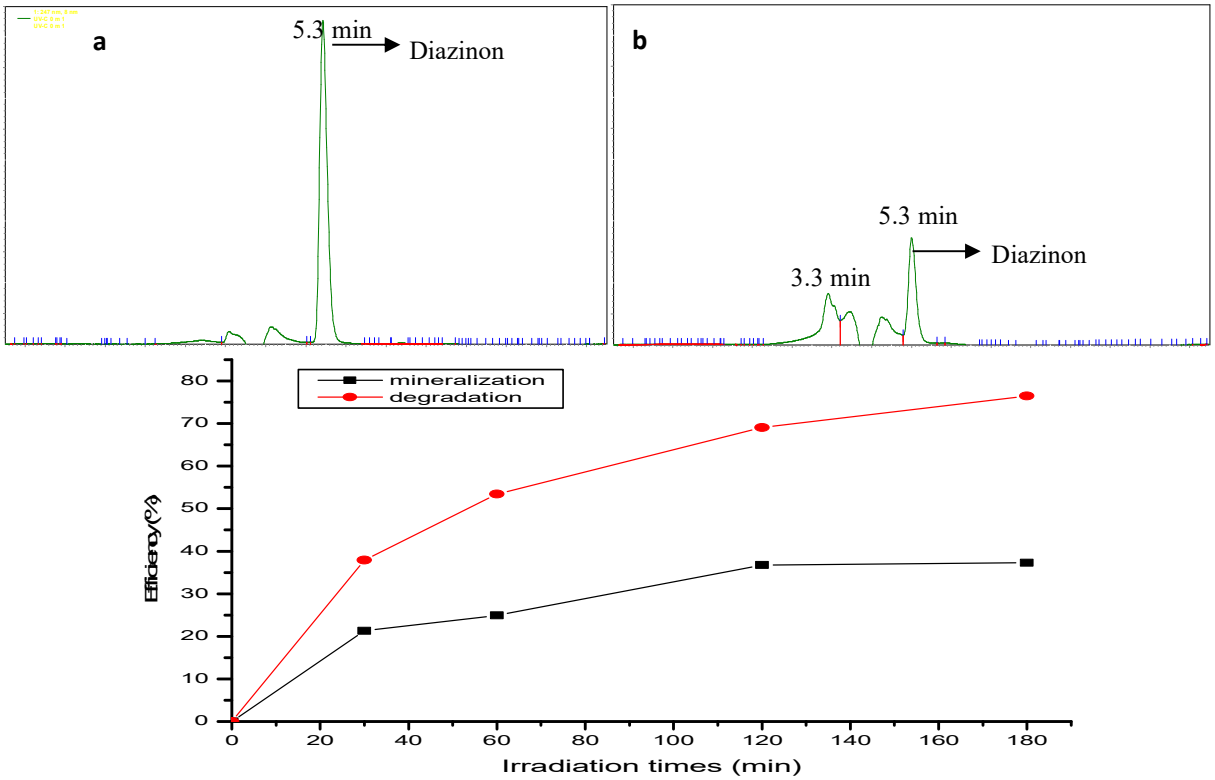

Fig.-5: Chromatogram of Diazinon (a) Before and (b) After Photocatalysis for 180 min (c) Mineralization Efficiency of Diazinon after 180 min Photocatalysis

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