PHOTOCATALYTIC OZONATION USING C,N-CODOPED TiO$_2$ FOR DIAZINON DEGRADATION

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ABSTRACT

Degradation of the diazinon pesticide by photocatalytic ozonation under visible-light irradiation using C,N-codoped TiO$_2$ as a catalyst was investigated. Effects of initial pH, initial concentration of diazinon, and energy sources on the degradation process were studied. The combination of photocatalysis and ozonation processes can lead to the effective degradation of diazinon in comparison to every one of the individual processes. The degradation percentage obtained from the photocatalytic ozonation of 18 mg L$^{-1}$ diazinon was 98 % and the COD removal reached 70 % after 25 minutes irradiation. The diazinon was transformed to less toxic compounds. Based on the results obtained, the photocatalytic ozonation is a potential process to treat wastewater containing the pesticide diazinon.

Keywords: diazinon, photocatalytic ozonation, C,N-codoped TiO$_2$, degradation.

INTRODUCTION

Diazinon, an organophosphate pesticide, is widely used by Indonesian farmers. Even though the use of pesticide has been banned by EPA, the farmers still select this pesticide as an insecticide for various types of cultivation such as fruit trees, rice, palm, sugarcane, corn, tobacco, and horticultural plants [1]. The continuous and excessive application may lead to the common occurrence of diazinon residues in food crops, milk, natural water systems, and soil. On the other hand, this organic compound is categorized as moderately hazardous class II by the World Health Organization (WHO). It is an immunotoxic [2], nonspecific target [3], cytotoxic and genotoxic [4 - 6]. Thus, it is of great importance to find an effective process for the reduction of the diazinon concentration.

The advanced oxidation processes (AOPs) techniques such as the cavitation process (produced by ultrasonic irradiation) [7], the photocatalytic oxidation (using near UV radiation/UV light/sunlight in the presence of semiconductor catalysts) [8], Fenton (utilization of iron sulphate reactions with hydrogen peroxide), and ozonation (in basic condition) can produce non-selective oxidizing agents such as hydroxyl radicals for toxic and refractory pollutants degradation in wastewaters [9]. The use of ozone alone to the treatment of wastewater samples has disadvantages, i.e., high production cost, relatively low solubility and stability in water, selective reaction with organic compounds at acidic pH, and incomplete mineralization [10]. Although photocatalysis alone is of great potential for the treatment of persistent non-biodegradable organic pollutants, it has a low oxidation rate and slow mineralization [11]. Therefore, a combination of these two AOPs techniques (photocatalysis together with ozonation), namely photocatalytic ozonation, can improve the oxidation process efficiency and can overcome the limitations and difficulties found in AOPs-alone for some specific pollutants via producing increased hydroxyl radicals concentration. In particular, this hybrid process is applicable to poorly-biodegradable organic compounds such as pesticides for their transformation to less toxic compounds and more biodegradable compounds with higher mineralization efficiency [10].

The carbon and nitrogen (C,N-codoped TiO$_2$) modified titania has been successfully synthesized by peroxy
sol-gel. The presence of carbon and nitrogen dopants provide a synergistic effect in absorbing visible-light thus increasing the titania photocatalytic activity [12]. The C,N-codoped TiO$_2$ was an effective catalyst on the degradation of organic pollutants by photocatalysis process [13, 14].

The aim of our study is the investigation on the degradation of diazinon using photocatalytic ozonation system and C,N-codoped TiO$_2$ as a catalyst. In this study, commercially available diazinon in commercial form was selected because of its extensive application to agricultural fields. Influences of parameters such as initial pH, the concentration of diazinon, and energy sources on diazinon degradation were investigated.

EXPERIMENTAL

Materials and Equipment

A commercial emulsion containing 600 g L$^{-1}$ diazinon (insecticide), (Code Name Diazinon 600 EC) was used as organic pollutant in water. A diazinon standard was purchased from Sigma-Aldrich. Ethanol 96 %, a solvent for diazinon stock solution, was purchased from Dwipraga Chemical. Dichloromethane (Merck), anhydrous sodium sulfate (Merck) and acetone (Merck) were used as extraction reagents of diazinon. Acetonitrile, chromatography grade (Sigma-Aldrich), and double distilled water were used for the mobile phase on HPLC analysis. Preparation steps and full characterization of the C$_x$N$_y$-codoped TiO$_2$ nanoparticles were conducted according to our previous publication [12]. Meanwhile, the equipment used was HPLC with a C18 column (150 mm × 4.6 mm) packed by a UV detector (Hitachi-Trimaide, serial1202-005, Japan), GC-MS QP2010 (Shimadzu, Japan), Whatman filter (Ω: 0.45 μm), ozonizer (HANACO, 15 W), Halogen lamp 500 Watt (Philips) and analytical balance.

Methods

Photocatalytic ozonation reactions were performed in a batch system under 500 Watt Halogen lamp irradiation (Philips) with bubbling 400 mg/h ozone. Diazinon solution with initial concentration 18 mg L$^{-1}$ was added by 12 mg photocatalyst (10 at % C$_x$N$_y$-codoped TiO$_2$ after calcination at 500°C) bubbled by gaseous ozone and irradiated under Halogen visible-light. Experiments with the individual system: ozonation (O$_3$), catalytic ozonation (O$_3$/catalyst) and photocatalysis (visible/catalyst) were also carried out. During the photocatalytic ozonation some parameters such as different initial diazinon pH (3, 5, 6, and 11), energy source of irradiation (visible and solar light), and initial concentration of diazinon (9, 18, 36, 54, and 72 mg/L) were conducted to investigate their influence on the degradation efficiency of diazinon. The pH of the solution was adjusted to 3, 5, 7, 11 by adding 0.01 N NaOH or 0.01 N HCl. Aliquots were collected after 5, 10, 15, and 20 minutes and filtered using 0.45 μm to separate the catalyst from the solution. The reduction of diazinon concentration was measured by HPLC packed with a C18 column (150 mm × 4.6 mm) and detected by a UV detector at a wavelength of 247 nm. 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 06-6989.2-2009). Degradation percentage of pesticide was calculated using the equation below:

$$\frac{C_i - C_f}{C_i} \times 100, \%$$

where $C_i$ is an initial concentration of diazinon and $C_f$ is the final concentration. The diazinon byproducts formed after photocatalytic ozonation were analyzed using GC-MS. The degraded solutions of diazinon were extracted three times using 10 mL dichloromethane. The combined organic phases were passed through 2 g of anhydrous sodium sulfate and evaporated with a rotary evaporator to about 1 mL. The residue was dissolved with 5 mL acetone and concentrated in a rotary evaporator to 2 mL [15]. The residue was injected to gas chromatograph-mass spectrometer (GC-MS) for qualitative analysis. The analysis was carried out with a GC–MS QP2010 equipped with a DB-5 MS capillary column (30 m length x 0.32 mm I.D. X 0.25 μm thickness). Helium at a constant flow rate of 1 mL/min was used as a carrier gas. The MS interface and the ion source temperature were 300°C. The oven temperature program was set as follows: Initial temperature 60°C, held for 2 min, ramped to 230°C at 10°C min$^{-1}$ and held for 2 min.

RESULTS AND DISCUSSION

Effect of the combined process

The effect of the hybrid process on diazinon degradation was investigated and the result is shown in Fig. 1(a).
At first, individual AOPs process namely ozonation (O$_3$), ozonolytic (O$_3$ + catalyst) and photocatalysis (visible + catalyst) were performed as a comparison. The amount of degraded diazinon is 68.1 %, 73.73 %, and 85.25 %, respectively. Under the ozonation process, the diazinon was reduced by direct attack molecules since the pH of the initial solution at this experimental is neutral (Eq. 1). Indirect attack of •OH radicals may occur in alkaline condition [16]. Hence, the presence of catalyst in the ozonation process enhances the degradation percentage from 68.1 % to 73.7 %. In addition, during the direct oxidation of ozone in the presence of a catalyst, •OH radicals are produced. Ozone and catalyst surface interact through physical adsorption, formation of weak hydrogen bonds, and dissociative adsorption. Equations 1 - 3 illustrate these processes [10]:

$$\text{O}_3 + \text{pesticide} \rightarrow \text{pesticide’s oxidative products} \quad (1)$$

$$\text{O}_3 + \text{photocatalyst (active surface sites)} \rightarrow \text{•OH + O}_2 \quad (2)$$

$$\text{•OH} + \text{H}_2\text{O} \rightarrow \text{•OH} \quad (3)$$

The degradation’s extent under photocatalysis was considerably higher than that in the previous cases. Under this process, besides the role of •OH radicals, diazinon might also be degraded directly by positive holes (h$^+$) produced, due to the electron excitation process of the catalyst upon light absorption. When C,N-codoped TiO$_2$ catalyst was irradiated by visible-light, its electron will excite from the valence band to conduction band and will generate electron-hole pair (Eq. 4). The generated hole reacts with water to form powerful oxidative •OH radicals (eq. 5 - 6).

$$\text{C,N-codoped TiO}_2 + \text{visible light} \rightarrow \text{C,N-codoped TiO}_2$$

$$\left( e^-_{\text{cb}} + h^+_{\text{vb}} \right) \quad (4)$$

$$\text{Diazinon + h}^+ \rightarrow \text{products of diazinon oxidation} \quad (5)$$

$$\text{H}_2\text{O (ads)} + h^+ \rightarrow \text{•OH + H}^+ \quad (6)$$

However, the combination of photocatalysis with ozonation, called ‘photocatalytic ozonation (O$_3$ + visible + catalyst)’, could reduce 95 % diazinon, which is higher than that obtained in individual AOPs. This significant increase is attributed to the high free radicals generation. The additional radical source as a complementary and synergistic effect of the three previous processes is the reaction of oxidizing reagents (e.g. •O$_2^•$, •O$_3^-$, H$_2$O$_2$) formed during the process. The possible mechanism is assumed during •OH radical production: 1) the photo-generated electron from catalyst is transferred directly to adsorbed ozone and oxygen molecule and forms an ozonide radical to produce •OH radicals (Eq. 7 - 9); 2) the generated inorganic H$_2$O$_2$ could potentially reform and simultaneously yield more free radicals (Eq. 13 - 16). All of these reactions can inhibit recombination of photo-generated electron-hole pairs, consequently a large number of radicals are produced and as a result, higher diazinon degradation can be achieved (Eq. 17) [10].

$$\text{O}_3 (\text{ads}) + e^- \rightarrow \text{•O}_3^- \quad (7)$$

$$\text{•O}_3^- + \text{H}^+ \rightarrow \text{HO}_2^• \quad (8)$$

$$\text{HO}_2^• \rightarrow \text{O}_2 + \text{•OH} \quad (9)$$

$$\text{O}_2 (\text{ads}) + e^- \rightarrow \text{•O}_2^- \quad (10)$$

$$\text{O}_3 + \text{OH} \leftrightarrow \text{•O}_2^- + \text{HO}_2^• \quad (11)$$

$$\text{O}_3 + \text{•OH} \leftrightarrow \text{HO}_2^• \rightarrow \text{O}_2 + \text{HO}_2^• \quad (12)$$

$$2\text{HO}_2^• \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (13)$$

$$\text{H}_2\text{O}_2 (\text{ads}) + e^- \rightarrow \text{•OH}^• + \text{OH}^- \quad (14)$$

$$\text{H}_2\text{O}_2 (\text{ads}) + \text{•O}_2^- \rightarrow \text{•OH}^• + \text{OH}^• + \text{O}_2 \quad (15)$$

$$\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{•OH}^• + \text{HO}_2^• + \text{O}_2 \quad (16)$$

$$\text{•OH + diazinon} \rightarrow \text{products of diazinon oxidation} \quad (17)$$

When C,N-codoped TiO$_2$ as a modified titania is activated by photon from visible light, the electron of titania will excite from valence to conduction band as illustrated in Eq. 4 in the photocatalysis system. The ozone from bubbling ozonizer and oxygen from the air in the system may lead to the capture of the photoexcited electron and produce active species (•O$_2^•$, •O$_3^-$, H$_2$O$_2$) acting as a source of hydroxyl radical generation as shown in Eqs. 7 - 15. Continuously reactions of those intermediates cause inhibition of electron and hole recombination and result as a greater effectiveness in diazinon degradation compared to ozone, ozonolytic and photocatalysis processes, respectively. This result was consistent with the result reported by Lin on the degradation of organophosphate pesticide by O$_3$/UV/TiO$_2$ system [17].

The coefficient correlation and the degradation rate of diazinon are given in Table 1. The linearity value obtained is near 1 and it shows that the degradation of diazinon by this process is well fitted with the first-order model (Fig. 1(b) and Table 1). The rate constant value for photocatalytic ozonation (O$_3$ + visible + catalyst) is approximately 1.72, 2.38, and 2.84-fold larger than the value for photocatalysis (visible + catalyst), ozonolytic
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The k
value of photocatalytic ozonation is 1.074-fold larger than the summation of ozonation and photocatalysis. This result proves that the combined process enhances the efficiency of diazinon degradation significantly. Once the efficiency of (O
3
 + visible + catalyst) process has been demonstrated, the influence of primary parameters are investigated.

**Effect of the initial solution pH**

pH value of an aqueous solution is an important factor affecting the ozonation efficiency and the evolution of hydroxyl radicals [18]. Fig. 2 displays the influence of initial pH (3, 5, 6, 8 and 11) with 12 mg catalyst, 18 mg/L diazinon, and 15 min treatment under photocatalytic ozonation. Diazinon was decayed of 79.76 %, 84.42 %, 93.59 % and 82.18 % at pH 3, 5, 8 and 11, respectively. The optimal pH was achieved at neutral pH (6.47) with an efficiency of 94.96 %. This result can be explained by the electrostatic interaction. The catalyst used is nano-sized titania with pH
zpc
 value in the range 6.3 - 6.9 [19]. The catalyst surface may be positively charged at acidic conditions and negatively charged at higher than the pH
zpc
. Hence, the pesticide is adsorbed onto the catalyst surface (diazinon pKa is 2.6), which is negatively charged in acidic solution. Therefore, the optimal condition is found at pKa diazinon < pH < pH
zpc
 catalyst. The similar result was also reported by Rajeswari and Kanmani in their studies on the carbaryl degradation.
Degradation [11]. Obviously, the photocatalytic ozonation is a process with a great potential for wastewater treatment containing diazinon pesticide.

Effect of diazinon initial concentration

Another important factor influencing the efficiency of the photocatalytic ozonation degradation is the initial pollutant concentration [10]. This parameter was set with initial diazinon concentrations 9, 18, 36, 54 and 72 mg/L at constant conditions: 15 min reaction time, 12 mg catalyst dosage, and 400 mg/h ozone. The degradation is efficient at initial diazinon concentrations of 9, 18, 36 mg/L: 87.75 %, 94.96 % and 93.38 %, respectively, as shown in Fig. 3. This improvement can be attributed to the higher availability of pollutant to react with the adsorbed active oxidizing species on the photocatalyst or in the bulk solution [10]. However, there is some decrease in efficiency at concentrations of 54 - 72 mg/L. The possible reason is the scattering effect of the deposited organic substances on the C,N-doped TiO$_2$ surface, which leads to the decrease of photon to reach the catalyst surface [20]. The results exhibit that the combined process is applicable for wastewater treatment containing both low and high diazinon concentration.

Effect of energy source

The photocatalyst is modified titania by carbon and nitrogen. It is activated under solar-light irradiation [21]. Thus, it is important to investigate the effect of energy source on the photocatalytic ozonation process. The amount of degraded diazinon is not significantly different in comparison for both energy sources. The degradation percentage was 71.84 % - 98.32 % at visible and 72.22 % - 96.93 % at solar-light irradiation for 5 - 25 minutes, respectively, as illustrated in Fig. 4. The intensities of solar and visible light measured by Luxmeter were 120589 lux and 47800, respectively. The use of visible light provides better degradation results even though sunlight has greater intensity than visible light. It is the distance between the solution and the light source that might cause the difference in the results. Based on the result obtained, the photocatalytic ozonation using C,N-doped TiO$_2$ can be an economic method for efficient degradation of organic pollutants and to overcome the energy problem.

In addition, according to the previous research, the photocatalysis for 300 minutes under solar light irradiation can remove 90.75 % diazinon [21]. The photocatalytic ozonation can degrade diazinon faster within 25 minutes and can achieve an efficiency of 96.93 % as demonstrated in Fig. 4. A possible explanation of this phenomenon may be due to the contribution of UVA and UVB containing in solar light [22]. These energies would be absorbed by ozone and hydrogen peroxide molecule to produce more active oxidizing reagents [10].

Generally, during the degradation process will be produced some intermediates and by-products. At this experiment, the simulated pollutant used was diazinon in formulation form. The major contain solution is diazinon.
azinon approved by HPLC data. Diazinon appears at 8.7 min with highest peak intensity and almost disappears completely for 25 min reaction times by transforming to some by-products which appear at 1.7 min, 2.7 min, 3.7 min, 5.3 min, and 11.1 min. All of the new peaks except for the compound at 1.7 min, diminish gradually as exposure time increased, which confirms that the process also removes the intermediates. Also, during the degradation process, the pH of the solution decreases with increased irradiation time from 6.47 to 2.38 suggesting the generation and accumulation of acidic products.

**By-products of degraded diazinon**

The by-products as a result of the degradation of diazinon are identified by GC-MS analysis and are listed in Table 2. The 2-isopropyl-6-methyl-4-pyrimidinone (IMP), the most common of diazinon byproduct formed after AOPs treatment, also is identified in this study. It is yielded from diazinon probably by two mechanisms: through oxidative desulfuration of hydroxyl radical at-tack on the thiono group to form diazoxon followed by hydrolysis, or through a directly oxidative mechanism on diazinon [23]. In general, this process degrades diazinon

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**Table 2. The by-products of diazinon degradation.**

<table>
<thead>
<tr>
<th>No</th>
<th>Retention Times (min)</th>
<th>Name</th>
<th>Structure</th>
<th>Molecular Weight (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.695</td>
<td>2,6-octadien-1-ol,3,7-dimethyl-, (E)-</td>
<td><img src="image1" alt="Structure" /></td>
<td>C_{10}H_{18}O, Mw = 154</td>
</tr>
<tr>
<td>2</td>
<td>12.779</td>
<td>1,1,1,3,5,7,9,11,11,14-decamethyl5-(trimethylsiloxy) hexasiloxane</td>
<td><img src="image2" alt="Structure" /></td>
<td>C_{13}H_{42}O_6Si, Mw = 490</td>
</tr>
<tr>
<td>3</td>
<td>12.910</td>
<td>2-isopropyl-6-methyl-4-pyrimidinone</td>
<td><img src="image3" alt="Structure" /></td>
<td>C_{8}H_{12}N_{2}O, Mw = 152</td>
</tr>
<tr>
<td>4</td>
<td>13.811</td>
<td>dodecanoic acid</td>
<td><img src="image4" alt="Structure" /></td>
<td>C_{12}H_{24}O_{2}, Mw = 200</td>
</tr>
<tr>
<td>5</td>
<td>14.020</td>
<td>diethyl phthalate</td>
<td><img src="image5" alt="Structure" /></td>
<td>C_{12}H_{14}O_{4}, Mw = 222</td>
</tr>
<tr>
<td>6</td>
<td>14.425</td>
<td>Apiol</td>
<td><img src="image6" alt="Structure" /></td>
<td>C_{12}H_{14}O_{4}, Mw = 222</td>
</tr>
<tr>
<td>7</td>
<td>15.260</td>
<td>4-t-butyl-2-(1-methyl-2-nitroethyl)cyclohexanone</td>
<td><img src="image7" alt="Structure" /></td>
<td>C_{13}H_{23}NO_{3}, Mw = 241</td>
</tr>
<tr>
<td>8</td>
<td>16.065</td>
<td>tetradecanoic acid</td>
<td><img src="image8" alt="Structure" /></td>
<td>C_{14}H_{28}O_{2}, Mw = 228</td>
</tr>
</tbody>
</table>
and transforms to less toxic compounds than diazinon and mostly acidic compounds. This result is in good agreement with the change of solution pH during the degradation process. Jonidi-Jafari reported by-product such as Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-, Pentasiloxane, dodecamethyl-, 3-Isopropoxy-1,1,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy) tetrasiloxane, benzoic acid, 2,5-bis(trimethylsiloxy)-, tri-methylsilylst ester, cyclononasiloxane, octadecamethyl-, silane, cyclohexylidimethoxymethyl-, diethyl phthalate, respectively, after photocatalytic treatment of diazinon [24]. Kouloumbos identified photocatalytic products such as 2-isopropyl-6-methylpyrimidin-4-ol (IMP), diazoxon, hydroxydiazinon, hydroxydiazoxon, diazinon methyl ketone, diazinon aldehyde, 2-hydroxydiazinon, 2-hydroxydiazoxon [15].

**COD removal during photocatalytic ozonation process**

Furthermore, COD analysis was conducted to determine the degree of diazinon mineralization. It is found that approximately 70 % of diazinon was mineralized to carbon dioxide for 25 min photocatalytic ozonation (Fig. 5(b)). Incomplete mineralization was correlated to the transient by-product formation during the process. As identified from GC-MS data, this process generates new acidic compounds as intermediates upon the treatment (Table 2) and the mineralization is insufficient.

**CONCLUSIONS**

The study showed that diazinon degradation is enhanced in a combination of photocatalysis and ozonation processes. The results clearly indicate that the photocatalytic ozonation can efficiently degrade diazinon compared to the individual process. The combined process produces more hydroxyl radical (•OH) for diazinon oxidation. The initial pH, initial concentration and the energy sources play a significant role in the degradation process. The photooxidation of 18 mg L\(^{-1}\) diazinon at pH 6.47 for 25 min is quantitatively degraded of 98 % and mineralized of 70 %. HPLC data proved that photocatalysis ozonation is capable to remove both diazinon and formed by-products.

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