OXIDATION OF DIAZINON BY HOMOGENEOUS FENTON PROCESS

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ABSTRACT

The degradation of aqueous diazinon from an aqueous solution using H₂O₂/Fe²⁺ process is performed in a 1L batch chemical reactor. The extent of diazinon degradation (20 mg/L) has been investigated from a known initial pH solution, temperature and catalyst type (Fe²⁺, Fe³⁺) and for various initial concentrations of diazinon, H₂O₂ and Fe²⁺. The degradation efficiency was obtained (90.82% and 90.63%) at pH 3 and 4 of the initial solution respectively while catalyst type and reaction temperature have a slight impact on the final degradation of diazinon. Efficiency of diazinon removal can be enhanced by increasing initial H₂O₂ concentration in the range of 70 to 150 mg/L and initial Fe²⁺ concentration in the range of 2 to 5 mg/L. The highest degradation efficiency obtained was 90.95% at initial diazinon concentration of 10 mg/L, H₂O₂=150 mg/L and Fe²⁺ = 5 mg/L. This study proved that Fenton process can be used for pretreatment of pesticide wastewater contaminated by diazinon before a biological treatment.

Keywords: diazinon, homogeneous Fenton, oxidation.

1. Introduction

Agriculture is critical to the economy of Vietnam, in which export-oriented agricultural production is a significant source of foreign exchange earnings. The agricultural sector provides approximately 16% of the gross national product (Laiprakobsup & Chorkaew, 2018). Therefore, the production and consumption of pesticide products have drastically increased due to the considerable usage of pesticide products (Van Toan, Sebesvari, Bläsing, Rosendahl, & Renaud, 2013).

Thuy, Van Geluwe, Nguyen, and Van der Bruggen (2012) had indicated that agricultural pesticides in Vietnam are not always reaching target organisms and are consequently posing an environmental threat due to large quantities of wastewaters proportionally generated in pesticide industries. The relevant wastes are characterized by a high chemical oxygen demand (COD), total suspended solids (TSS) and toxicity. Besides, the effluents contain a great amount of toxic and persistent compounds such as organic solvents, catalyst, reactants and raw materials (Köck-Schulmeyer et al., 2013; Münze et al., 2017).

Organophosphates are among the most widely used pesticides for the treatment of pest. In particular, diazinon stands out for its high production and worldwide distribution (Lerro et al., 2015). Diazinon is used as an insecticide, acaricide, and nematicide in...
aquaculture which first registered in the United States in 1956. Therefore, it is possible to find these compounds in the environment and the concentration of diazinon detected in surface water is up to 11.24 µg/L (Van Toan et al., 2013). Pham and Bui (2018) found that diazinon was moderately toxic to tropical freshwater daphnia species (48-h-LC50 3.41 µg/L). Werner et al. (2002) also reported that diazinon could be the main cause for human diseases in Glenn County, California, USA. Therefore, it is necessary to use appropriate techniques for the removal of these pollutants to preserve the environment from contaminated water.

Biological processes are quite economical for the treatment of wastewaters and they are widely used. But, they have been proven to be ineffective in the removal of persistent or non-biodegradable compounds (Feng, van Hullebusch, Rodrigo, Esposito, & Oturan, 2013). For instance, biological treatment processes have not been successful in effectively removing pesticide wastewater (Briceño, Fuentes, Saez, Diez, & Benimeli, 2018). Alternatively, physico-chemical techniques such as reverse osmosis, adsorption, ultrafiltration and coagulation are also used for the treatment of wastewater, whereas these treatments transfer only the pollution, from one phase to another, which subsequently requires further treatment (Feng et al., 2013; Oller, Malato, & Sánchez-Pérez, 2011). Therefore, it is important to develop more effective treatment methods such as chemical and photochemical degradation to remove completely contaminants.

For instance, advanced oxidation processes (AOPs) are proven to be the most effective technique for the degradation of a wide range of refractory pollutants in aqueous solution such as polymers (Hamad, Mehrvar, & Dhib, 2014), phenol (Maleki, Mahvi, Mesdaghinia, & Naddafi, 2007), pharmaceuticals and dyes (Akmehmet Balcioglu et al., 2003). This technique is based on the generation of highly reactive radicals, such as hydroxyl radicals (‘OH) and hydroperoxyl radicals (HO2’) which can react effectively with organic pollutants and reduce intermediate reaction species to CO2 and H2O without producing harmful by-products or sludges that must require further processing (He, Mezyk, Michael, Fatta-Kassinos, & Dionysiou, 2014; Klavarioti, Mantzavinos, & Kassinos, 2009).

Several researchers have studied the degradation of diazinon by different AOPs methods such as UV/H2O2 (Li, Liu, Duan, van Leeuwen, & Saint, 2015), photo-Fenton (Leila, Yasaman, Majid, Mahdi, & Ayoub, 2016), gamma radiation (Mohamed, Basfar, & Al-Shahrami, 2009), Sonication (C.-K. Wang & Shih, 2016), Ozone process (Ku, Chang, Shen, & Lin, 1998), etc. However, a few studies focus on the mineralization and biodegradability of diazinon using Fenton process.

In the present work, the degradation of diazinon solution is investigated using Fenton process in a batch chemical reactor. The main aim of this study is to analyze how the
degradation process of diazinon can be affected by initial concentrations of diazinon, H$_2$O$_2$, Fe$^{2+}$, and pH as well as temperature and catalyst type.

2. Materials and methods

2.1. Reagents

Diazinon (O,O-diethyl-O-[2-isopropyl-6-methyl-4-pyrimidinyl] phosphorothioate) with >95% purity was purchased from Sigma-Aldrich and was used without further purification. 50% (w/w) of hydrogen peroxide (H$_2$O$_2$) was purchased from Merck, Germany and was used by diluting it to 35%. Analytical grade ferrous sulfate heptahydrate (FeSO$_4$ $\cdot$7H$_2$O) was purchased from Biochem, France. Ferric sulfate (Fe$_2$(SO$_4$)$_3$) with purity exceeding 90% was obtained from Prolabo. The pH of the solution was at first adjusted with either dilute H$_2$SO$_4$ (0.5N) and NaOH (0.1N).

2.2. Experimental setup and analysis

All experiments were carried out in a double jacket 1L stirred batch reactor as shown in Fig. 1. The reactor was covered with aluminum paper to prevent the degradation of diazinon by the photo-Fenton system. The reactor was connected to a thermostatic bath to maintain a constant temperature of 25 °C. The reactor was also equipped with a magnetic stirrer to ensure homogeneity of the reaction medium and maintain a uniform concentration distribution in the reactor. A thermometer was placed in the reactor for temperature measurement and a port for sampling. The pH level was adjusted using a pH-meter (HANNA pH 209) at the onset of each experiment and no further pH adjustment was made during the reaction. According to previous studies (Li et al., 2015; Real, Benitez, Acero, & Gonzalez, 2007; N. Wang, Zheng, Zhang, & Wang, 2016), the suitable concentrations of Fenton reagent and diazinon were prepared. The description and operating conditions of the reactor are given in Table 1.

![Fig. 1. Schematic diagram of the H$_2$O$_2$/Fe$^{2+}$ system](image-url)
Table 1. Reactor operating conditions

<table>
<thead>
<tr>
<th>Item</th>
<th>Experimental operating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume</td>
<td>1L</td>
</tr>
<tr>
<td>Temperature</td>
<td>25-50 °C</td>
</tr>
<tr>
<td>pH</td>
<td>3-7</td>
</tr>
<tr>
<td>Diazinon</td>
<td>10-40 mg/L</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>70-200 mg/L</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>2-10 mg/L</td>
</tr>
</tbody>
</table>

For each experiment, diazinon solution was prepared by dissolving 10 mg of diazinon in a 500 mL flask containing distilled water. The mixture was stirred at 600 rpm for 20 minutes to make a homogenous stable solution. The desired concentration of Fe²⁺ was added to the solution of diazinon. Specific amounts of H₂SO₄ or NaOH were injected for pH solution adjustment. The desired amount of H₂O₂ was poured into the reactor and the temperature was kept constant at 25°C.

Samples were taken from the reactor at different time intervals and were immediately analyzed using a syringe equipped with a 0.2-micron filter. The concentration of diazinon was measured using High Performance Liquid Chromatography (HPLC), the following specifications were used; wavelength was 260 nm, C18 column, length and diameter of the column were 4.6 × 250 mm and the volume of injection sample = 20 µL. The percentage of diazinon removal was calculated as follows:

\[ \text{Diazinon removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \] (1)

C₀ is the initial concentration of diazinon and Cₜ is the concentration of diazinon at reaction time.

3. Results and discussion

3.1. Role of OH radicals in diazinon degradation

The degradation rate of diazinon was much higher in H₂O₂/Fe²⁺ system than in H₂O₂ alone, which is probably due to the production of substantial amount of highly reactive radicals (°OH) that are mainly responsible for the degradation of the most amount of diazinon antibiotic since the hydroxyl radicals have a high oxidation potential (E⁰ = 2.8 V).

The results shown in Fig.2 clearly exhibit the impact of H₂O₂ and Fe²⁺ in the degradation of diazinon when they are used separately or combined. The contribution of Fe²⁺ in the generation of °OH radicals leads to the oxidation of 90.67% of diazinon compared to 4.10% when H₂O₂ is alone. Hence, these results indicate the significant role of °OH radicals in the elimination of diazinon in H₂O₂/Fe²⁺ process.
3.2. Effect of initial H$_2$O$_2$ concentration

Hydrogen peroxide dosage is an important parameter to evaluate the performance of Fenton process. Thus, the concentration of H$_2$O$_2$ was varied from 70 mg/L to 200 mg/L for an invariant initial concentration of diazinon and ferrous ion of 20 mg/L and 5 mg/L, respectively.

Plots in Fig. 3 describe the degradation of diazinon at various initial concentrations of H$_2$O$_2$ and show that the rate of degradation of diazinon increases with higher concentration of H$_2$O$_2$. In the presence of Fe$^{2+}$, hydrogen peroxide decomposes more efficiently and produces more free radicals, which react immediately with diazinon. It is obvious that with higher H$_2$O$_2$ concentrations, more hydroxyl radicals are produced in the reacting system.

However, no enhancement was observed when the initial concentration of H$_2$O$_2$ exceeded 150 mg/L beyond a reaction time of 40 min. This result, therefore, can be explained by the excess of hydrogen peroxide in the solution which leads to a scavenging phenomenon on hydroxyl radicals as shown in reaction (2).

$$\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^+ + \text{H}_2\text{O}$$  \hspace{1cm} (2)

This reaction produces hydroperoxyl radical (HO$_2^+$) which has an oxidation potential $E^0=1.7V$. Therefore, it is much less reactive than $\cdot \text{OH}$ radicals. Consequently, the rate of diazinon consumption is lowered which explains the decrease in diazinon removal. The highest consumption of H$_2$O$_2$ occurred during the first 30 min of degradation for all tests with different H$_2$O$_2$ initial concentrations.
3.3. Effect of initial $\text{Fe}^{2+}$ concentration

The amount of catalyst plays an important role in Fenton processes; reaction (3) highlights the role of the catalyst for the generation of hydroxyl radicals in the presence of adequate amount of $\text{H}_2\text{O}_2$.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (3)$$

In this work, the impact of the catalyst $\text{Fe}^{2+}$ was studied in the range of 2 at 10 mg/L. In fact, an increase of $\text{Fe}^{2+}$ facilitates the generation of $\cdot\text{OH}$ radicals and consequently improves the degradation of diazinon. As shown in Fig. 4, the degradation efficiency increased for higher concentration of $\text{Fe}^{2+}$. Beyond the threshold of 10 mg/L, it becomes insignificant and the degradation rate remains constant until the end of the reaction. The highest degradation efficiency, in this case, was achieved at a concentration of $\text{Fe}^{2+} = 5\text{mg/L}$.

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**Fig. 3.** Effect of initial $\text{H}_2\text{O}_2$ concentration on diazinon degradation with $[\text{diazinon}]_0 = 20\text{mg/L}$, $[\text{Fe}^{2+}]_0 = 5\text{mg/L}$, at $\text{pH} = 3$ and $T = 25^\circ\text{C}$

**Fig. 4.** Effect of initial $\text{Fe}^{2+}$ concentration on diazinon degradation with $[\text{diazinon}]_0 = 20\text{mg/L}$, $[\text{H}_2\text{O}_2]_0 = 200\text{mg/L}$, at $\text{pH} = 3$ and $T = 25^\circ\text{C}$
3.4. Effect of initial diazinon concentration

The dependence of diazinon degradation on its initial concentration has been studied in an interval between 10 and 40 mg/L with an optimum \( \text{H}_2\text{O}_2 \) concentration of 150 mg/L and \( \text{Fe}^{2+} \) concentration of 5 mg/L.

The results in Fig. 5 show that the diazinon degrades from higher initial diazinon concentrations. For instance, with initial diazinon concentrations of 10, 20, 30 and 40 mg/L, the removal efficiency achieved after 60 minutes were 90.95, 90.82, 88.47 and 85.27%. With given operating conditions, the diazinon degradation rate increased much faster for lower initial diazinon concentration. Also, high concentrations of diazinon resulted an increase of intermediate products which compete with diazinon to react with hydroxyl radicals and can also become limiting reagents. Consequently, a reduction of the rate constants was obtained.

![Graph showing effect of initial diazinon concentration](image)

**Fig. 5.** Effect of different initial diazinon concentration conditions on diazinon degradation with \([\text{H}_2\text{O}_2]_0 = 150 \text{ mg/L}, [\text{Fe}^{2+}]_0 = 5 \text{ mg/L at pH = 3 and T = 25°C} \)**

Moreover, the reduction in degradation yield for an initial concentration of diazinon can be related to a similar amount of \(^{•}\text{OH} \) radicals formed in all solutions considered. These results are in accordance with the data reported by Li et al. (2015), who studied the degradation of diazinon by UV/TiO\(_2\) under solar light.

3.5. Effect of temperature

Three experimental tests were performed at temperatures of 25, 40 and 50 °C to evaluate its effect on the diazinon degradation. Plots in Fig. 6 show that an increase in temperature considerably improves diazinon degradation rate in the first 20 minutes. Under thermal effect, chemical bonds of the diazinon molecules are weakened and start breaking down in accordance with Arrhenius law (Loftin, Adams, Meyer, & Surampalli, 2008). But, beyond 20 minutes, the degree of degradation remains almost invariant for the temperatures used and no improvement is observed. However, hydrogen peroxide decomposing at high temperature and closing to 60°C can produce inactive species like \( \text{H}_2\text{O} \) and \( \text{O}_2 \) and it forms other radicals with less reactivity such as \( \text{HO}_2^{•} \) (Khamaruddin, Bustam, & Omar; Monteagudo, Durán, & San Martín, 2014). In Fenton process, there is no need to increase the temperature; ambient temperature seems to be the best to apply to the diazinon system.
Fig. 6 Diazinon degradation versus time for different reaction temperatures, with $[\text{diazinon}]_0 = 20 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 150 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = 5 \text{ mg/L}$, pH = 3

3.6. Effect of initial pH solution

In several studies on wastewater treatment using AOP processes (Hamad et al., 2014), the pH of the solution being treated an important variable to investigate. In particular, the degradation process by Fenton is generally carried out in an acidic pH medium to preserve the aqueous Fe$^{2+}$ ions in the solution.

An initial pH of the solution was applied in a range of 1 to 7 for initial diazinon concentration of 20 mg/L, H$_2$O$_2$ concentration of 150 mg/L and Fe$^{2+}$ concentration of 5 mg/L. As shown in Fig. 7, the degradation yield obtained was 68.02, 77.17, 90.82, 90.63, 80.13, 68.62 and 42.26% for pH of 1, 2, 3, 4, 5, 6 and 7, respectively. It can be concluded that the optimum pH of the Fenton reaction occurs in the region of 3 to 4. It is also clear that from a pH = 7, the degradation becomes less important. This is due to the precipitation of ferrous ion into Fe(OH)$_3$ and consequently the decrease of H$_2$O$_2$ decomposition to hydroxyl radicals.

Fig. 7. Diazinon degradation efficiency versus initial pH solution, with $[\text{diazinon}]_0 = 20 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 150 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = 5 \text{ mg/L}$, $T = 25^\circ\text{C}$
3.7. Effect of type of catalyst

Figure 8 shows a comparison between two systems of degradation, Fenton system (H$_2$O$_2$/Fe$^{2+}$) and Fenton-like system (H$_2$O$_2$/Fe$^{3+}$) at identical operating conditions (diazinon=20 mg/L, H$_2$O$_2$=150 mg/L, Fe$^{2+}$=Fe$^{3+}$=5 mg/L). The degradation yield achieved was 90.82% and 88.20% in Fenton and Fenton-like systems, respectively. But, in the first 30 minutes, the degradation rate in the Fenton process was much faster than in the Fenton-like process. This could be related to the oxidation of diazinon much more with •OH radicals in Fenton process according to the reaction (3) which has a rate constant of 70 Lmol$^{-1}$S$^{-1}$. Unlike, Fenton-like, the oxidation was carried out much more with hydroperoxyl radicals (HO$_2^•$) which has less power of oxidation than •OH radicals. Moreover, the rate constant (k$_2$=0.02 Lmol$^{-1}$S$^{-1}$) of production of HO$_2^•$ is very slow as defined in reaction (5).

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^• + \text{H}^+ \]  

(5)

From 30 minutes onwards to the end of the reaction, the rate of diazinon degradation was almost the same in both processes. Similar observations are reported by Wang et al. (S. Wang, 2008), who studied the decolourisation of wastewater from an azo dye by Fenton and Fenton-like processes.

**Fig. 8. Performance of Fenton and Fenton-like processes for diazinon degradation,**

*with [diazinon]$_0$ = 20 mg/L, [H$_2$O$_2$]$_0$ = 150 mg/L, [Fe$^{2+}$]$_0$ = 5 mg/L, [Fe$^{3+}$]$_0$ = 5 mg/L, pH = 3, T = 25°C*

4. Conclusion

Oxidation and molecular degradation of diazinon were investigated under different operating conditions in Fenton and Fenton–like processes for 60 min of reaction. A diazinon degradation efficiency of 4.10% was obtained when H$_2$O$_2$ was used alone in the Fenton process. However, the degradation rate of diazinon in the Fenton process (H$_2$O$_2$/Fe$^{2+}$) and Fenton-like process (H$_2$O$_2$/Fe$^{3+}$) was much higher, with a removal efficiency of 90.82% and 88.40%, respectively. An increase of diazinon initial concentration lowered the degradation efficiency, whereas an excess of H$_2$O$_2$ can impede removal efficiency of diazinon. Also, the initial pH is an important parameter in the
degradation of diazinon. A high degradation rate was obtained for a pH of 3 confirming the optimum pH value for Fenton process. The highest value of 90.95% removal efficiency was achieved in the Fenton process operated with 10 mg/L of H₂O₂, 10 mg/L of diazinon, 5 mg/L of Fe²⁺ and pH value of 3 at an ambient temperature of 25°C. This study indicated that Fenton process can be used for pretreatment of wastewater contaminated by diazinon before a biological treatment.

Conflict of Interest: Author have no conflict of interest to declare.

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OXI HÓA DIAZINON BẰNG QUÁ TRÌNH FENTON ĐỒNG THỂ

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TÓM TÀT

Quá trình phân hủy diazinon bằng Fenton đồng thể được khảo sát trong mô hình 1L. Các thông số ảnh hưởng đến hiệu quả loại trừ diazinon như: nồng độ diazinon, pH, nhiệt độ, hàm lượng H₂O₂, sát loại xúc tác (Fe²⁺, Fe³⁺) đều được nghiên cứu. Kết quả cho thấy phản ứng xảy ra hiệu quả tại pH trong khoảng 3 đến 4 (đạt 90,82% và 90,63%), trong khi hiệu quả lại bị ảnh hưởng bởi nhiệt độ hay loại xúc tác. Hiệu suất phản ứng cũng tăng khi tăng nồng độ H₂O₂ từ 70 mg/L tới 150 mg/L và Fe²⁺ từ 2 mg/L lên 5 mg/L. Hiệu suất loại trừ diazinon đạt cao nhất là 90,95% tại nồng độ ban đầu diazinon là 10 mg/l, H₂O₂=150 mg/l and Fe²⁺ = 5 mg/l. Kết quả trên cho thấy Fenton đồng thể có thể sử dụng như quá trình tiền xử lì trước việc dùng xử lì sinh học cho nước thải trước các sinh từ nhiễm diazinon.

Từ khóa: Diazinon, Fenton đồng thể, quá trình oxi hóa.