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Original research article

Facilitated ultrasonic irradiation in the degradation of diazinon insecticide

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ABSTRACT

In this study, the degradation of diazinon insecticide was investigated using ultrasound facilitated by Fenton's and Fenton-like reagents under various experimental conditions. The effects of oxidant (persulphate ions, $S_2O_8^{2-}$ and hydrogen peroxide (H_2O_2)), transition metal (including Co^{2+}, Ag^+ and Fe^{2+}), Fenton's reagent concentration and temperature on diazinon degradation were examined. A solution with an initial diazinon concentration of 50 mg L^{-1} was used in this study. Ultrasonic irradiation in combination with Fenton's and Fenton-like reagents not only effectively degraded diazinon but also rapidly reduced its toxicity. The optimal experimental conditions were determined as follows: 20 mg L^{-1} Fe^{2+}, 150 mg L^{-1} H_2O_2, 25 °C and pH 3. After reacting for 60 min, the diazinon removal efficiency reached 98%, with a mineralization efficiency of 30%. Degradation occurred primarily via oxidation and resulted in the substitution of sulphur with oxygen in the diazinon P═S bond.

1. Introduction

The widespread presence of pesticides in the environment is a noteworthy problem, particularly given the broad use of pesticides in agriculture and hygiene throughout the world. Organophosphorus pesticides are among the most frequently encountered pesticides around the world [1]. They inhibit acetylcholinesterase in insects, producing toxic conditions, and are toxic to humans [2]. Therefore, studies should be conducted to identify and implement methods for removing organophosphorus pesticides. One commonly used insecticide in the organophosphate chemical family, diazinon (O,O-diethyl O-(2-isopropyl-6-methylpyrimidin-4-yl)thiophosphate, $C_{12}H_{21}N_2O_3PS$), was commercially introduced in 1952 [3]. Diazinon is used worldwide in agricultural production to protect plants by controlling a variety of sucking and leaf-eating insects and has been classified by the World Health Organization as a moderately hazardous Class II chemical [3]. Diazinon is stable at pH 7 and is not easily volatilised from soil or water. Thus, it can persist in the environment for up to six months [4]. Furthermore, the degradation by-products of diazinon pose health risks for humans and the environment.

Several technologies, such as ionised gamma irradiation, ozonation, UV, photo-TiO_2, X-ray and ultrasound, have been used to degrade diazinon [5–8]. In most cases, treatment of 120 min was required to achieve complete diazinon degradation. Ultrasonic methods have been widely used in such studies and have mainly been applied to synthetic solutions spiked with one or several contaminants [9]. However, ultrasound alone was unable to fully degrade the organic compounds [3]. Consequently, methods for enhancing the degradation efficiency and reducing the necessary time required for oxidation were investigated.

Processes combining ultrasound and other chemicals or oxidation processes are referred to as sonochemical processes and represent unique and advanced oxidation methods for degrading refractory compounds [10]. For example, the sono-Fenton process combines ultrasound and Fenton's reagent (Eq. (1)) and is a proven innovative method for degrading different types of pollutants, such as carbofuran [11], ethylenediamine [12], and tetracycline [13], over short reaction durations. Additionally, the sono-Fenton process has been used to reduce the toxicity of wastewater. However, because adding H_2O_2 and Fe^{2+} increases the toxicity of treated wastewater and the formation of ferric hydroxide sludge, many researchers have tried replacing H_2O_2 and Fe^{2+} with different chemicals, such as $S_2O_8^{2-}$, Ag^+ and Co^{2+} [14–16]. Consequently, these chemicals have been referred to as Fenton-like reagents.

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$$Fe^{2+} + H_2O_2 +))) \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

This study attempted to degrade diazinon and reduce its toxicity using ultrasonic irradiation facilitated by Fenton's and Fenton-like reagents. Three transition metals (Fe^{2+}, Ag^+ and Co^{2+}) and two oxidants (H_2O_2 and $S_2O_8^{2-}$) were used in different combinations for diazinon degradation. The effects of transition metals, oxidants, Fenton's reagent dosages and temperature on the degradation of diazinon were investigated. Additionally, the toxicity based on cell viability was measured before and after treatments, and possible degradation by-products and oxidation pathways were proposed.

2. Materials and methods

2.1. Standards and reagents

Diazinon (analytical standard) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The purest grade commercially available chemical reagents including H_2SO_4, NaOH, $FeSO_4{\cdot}7H_2O$, $AgNO_3$, $Co(NO_3)_2{\cdot}6H_2O$, $(NH_4)_2S_2O_8$, and an aqueous solution of H_2O_2 (30%, w/w in water) were used in this study.

2.2. Experimental apparatus and designs

A 20 kHz sonicator (Microson VCX 750, USA) equipped with a titanium probe tip was carried out in this study. The detailed information of ultrasonic treatment unit was summarized in our earlier study [11], and the output ultrasonic power was maintained at 100 W in this study. The working volume of ultrasonic reactor was 1 L. A circulating temperature controller was used to maintain the desired reaction temperature (15–55 °C). Other reaction parameters included H_2O_2 concentrations of 0–150 mg L^{-1} (0–4.41 mM) and Fe^{2+} concentrations of 0–20 mg L^{-1} (0–0.306 mM). In addition to H_2O_2 and Fe^{2+}, $S_2O_8^{2-}$ (100 mg L^{-1}, 0.521 mM), Co^{2+} (10 mg L^{-1}, 0.170 mM) and Ag^+ (10 mg L^{-1}, 0.093 mM) were used to investigate the effects of reaction parameter on the degradation of diazinon. During the reaction, the reactor was aerated at 0.2 L min^{-1} to provide sufficient dissolved oxygen. The reactor was equipped with pH and ORP (oxidation-reduction potential) meters (Suntex PC-3200, Taiwan) to monitor the profiles of pH and ORP values.

2.3. Sample extraction and analysis

To isolate the diazinon and its oxidation by-products from aqueous solution, dichloromethane and n-hexane were carried out in a liquid–liquid extraction procedure. Diazinon and oxidation by-products were identified during the oxidation process using a gas chromatography/mass spectrometry detector (GC/MS, Shimadzu GC/MS-GC2010 Plus, Shimadzu, Kyoto, Japan) with a HP-5MS column (length 30 m, thickness 0.25 μm, diameter 0.25 mm) and the concentration of diazinon was detected using a GC/flame ionisation detector (Varian GC 3400, Mulgarve, Victoria, Australia) equipped with a DB-1 fused silica capillary column. The pre-treatment of diazinon solution before analysis and analytic setups were followed the study proposed by Wang and Shih [17].

2.4. TOC and toxicity analysis

Diazinon mineralization was investigated by determining the total organic carbon (TOC) concentration using a TOC analyser (TOC-500, Shimadzu, Japan). Each sample collected during the reaction was analysed in triplicate. The toxicities of the diazinon samples were determined by assessing the cell viability based on cell counting. In all experiments, cells were treated with diazinon water samples for 24 h before and after treatment. The steps for cell counting, including the incubation of rat liver cells and measurement method of cells, have been detailed in our earlier publication [12].

3. Results and discussion

3.1. Degradation of diazinon by various processes

Table 1 shows the preliminary studies involving diazinon degradation and mineralization using the ultrasound, ultrasound/Fe^{2+}, ultrasound/H_2O_2, Fenton and sono-Fenton processes, with the Fe^{2+} and H_2O_2 concentrations of 10 mg L^{-1} and 100 mg L^{-1} in the Fenton and sono-Fenton processes, respectively, and a reaction duration of 60 min. As shown in Table 1, the degradation efficiencies of diazinon subjected to ultrasound, ultrasound/Fe^{2+} and ultrasound/H_2O_2 were 22, 25 and 26%, respectively, which indicated that only unsatisfactory increases in diazinon degradation when Fe^{2+} and H_2O_2 were used independently with ultrasound. Thus, $^{\bullet}OH$-oxidation did not significantly contribute to diazinon degradation, and most of the achieved degradation occurred through the ultrasonic thermal cleavage. During the Fenton process, 62% of the diazinon was degraded and 6% of the TOC was removed. Because sufficient $^{\bullet}OH$ radicals were formed during the Fenton process, the refractory organic compounds could be readily degraded [18]. However, the ratio of TOC removal to diazinon removal by the Fenton process was only 0.1, which is lower than that observed for other ultrasonic processes. This result indicates that most of the degraded diazinon is transformed into other by-products and could not be mineralized as CO_2. Combining ultrasound with the Fenton process resulted in the highest diazinon degradation (96%), which was higher than that obtained using ultrasound or the Fenton process alone. This could be proven that a synergetic effect occurred when combining ultrasound and the Fenton process [12,19]. Eq. (2) shows the Fenton reaction and it is found that the Fe^{2+} is oxidized to Fe^{3+}, then the Fe^{3+} reacts with H_2O_2 to produce a complex intermediate ($Fe{-}OOH^{2+}$) as shown in Eq. (3). The ultrasound spontaneously decomposes the $Fe{-}OOH^{2+}$ to Fe^{2+} and $^{\bullet}OOH$ (Eq. (4)) and the isolated Fe^{2+} can react subsequently with H_2O_2, produce $^{\bullet}OH$ again (Eq. (2)), and thus establishing a cyclic mechanism. Even the degradation of diazinon achieved using the sono-Fenton process was significantly greater than that achieved by each of the other processes shown in Table 1, however, the ratio of TOC removal/diazinon removal was still low when using the sono-Fenton process, which indicated that better experimental designs were necessary.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe{-}OOH^{2+} + H^+ \quad (3)$$

$$Fe{-}OOH^{2+} +))) \rightarrow Fe^{2+} + {}^{\bullet}OOH\ (fast) \quad (4)$$

Table 1
Diazinon degradation and TOC removal results and the ratios of TOC removal/diazinon degradation obtained using different treatment processes.

Methods	Diazinon degradation (%)	TOC removal (%)	TOC removal/Diazinon degradation
Ultrasound	22	4	0.18
Ultrasound/Fe^{2+}[a]	25	5	0.19
Ultrasound/H_2O_2[b]	26	5	0.20
Fenton[a,b]	62	6	0.10
Sono-Fenton[a,b]	96	13	0.14

[a] Fe^{2+} concentration was 10 mg L^{-1}.
[b] H_2O_2 concentration was 100 mg L^{-1}.