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 (per-sulphate ions, \( S_2O_8^{2-} \) and hydrogen peroxide \( (H_2O_2) \)), transition metal (including \( Co^{2+}, Ag^{+} \) and \( Fe^{3+} \)), 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=O 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, \( C_{12}H_{21}N_{2}O_{3}PS \)), 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 \( Fe^{3+} \) increases the toxicity of treated wastewater and the formation of ferric hydroxide sludge, many researchers have tried replacing \( H_2O_2 \) and \( Fe^{3+} \) 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\(^{2+} + H_2O_2 + \)) → Fe\(^{3+} + *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\(_2O_2\)) 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, Fe\(_{3}SO_{4}\cdot7H_2O\), AgNO\(_3\), Co\((NO_3)_2\cdot6H_2O\), (NH\(_4)_2SO_4\), 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 (Micronson 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\(_2O_2\)\(_6\) (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 heater 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 mm, 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, *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 *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 *OOH (Eq. (4)) and the isolated Fe\(^{2+}\) can react subsequently with H\(_2O_2\) produce *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.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + *\text{OH} + \text{OH}^{-} \quad (2) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}–\text{OOH}^{2+} + \text{H}^+ \quad (3) \\
\text{Fe}–\text{OOH}^{2+} + \)) & \rightarrow \text{Fe}^{2+} + *\text{OOH} \quad (fast) \quad (4)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Methods</th>
<th>Diazinon degradation (%)</th>
<th>TOC removal (%)</th>
<th>TOC removal/Diazinon degradation</th>
</tr>
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<tr>
<td>Ultrasound</td>
<td>22</td>
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</tr>
<tr>
<td>Ultrasound/Fe(^{2+})</td>
<td>25</td>
<td>5</td>
<td>0.19</td>
</tr>
<tr>
<td>Ultrasound/H(_2O_2)</td>
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<td>5</td>
<td>0.20</td>
</tr>
<tr>
<td>Fenton(^{1})</td>
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<tr>
<td>Sono-Fenton(^{1,2})</td>
<td>96</td>
<td>13</td>
<td>0.14</td>
</tr>
</tbody>
</table>

\(^{1}\) Fe\(^{2+}\) concentration was 10 mg L\(^{-1}\).

\(^{2}\) H\(_2O_2\) concentration was 100 mg L\(^{-1}\).
3.2. Effect of oxidants

Recently, the use of sulphate radical-based advanced oxidation processes (AOPs) produced by \( \text{S}_2\text{O}_8^2^- \) has been proven to be a promising method for oxidising organic pollutants [16]. Sulphate radicals (\( \text{SO}_4^2^- \)) have a high standard redox potential (\( E_0 = 2.6 \) V), which makes them very strong oxidants, and are capable of more selective oxidation than \( \cdot \text{OH} \) radicals at acidic pH. Consequently, \( \text{SO}_4^2^- \) can degrade and mineralize contaminants more efficiently. When \( \text{S}_2\text{O}_8^2^- \) and transition metals react, \( \text{SO}_4^2^- \) can be formed (Eq. (5)) and degrade organic compounds. In addition, \( \text{SO}_4^2^- \) can undergo hydrolysis or react with \( \text{OH}^- \) to form \( \cdot \text{OH} \) (Eqs. (6) and (7)). This process is an improvement upon the disadvantage(s) of traditional AOPs, which must be carried out at low pH [16]. Ultrasonic irradiation converts \( \text{S}_2\text{O}_8^2^- \) to two \( \text{SO}_4^2^- \) molecules (Eq. (8)). Thus, \( \text{S}_2\text{O}_8^2^- \) can be considered a suitable oxidant when used with ultrasound and transition metals to develop a sono-Fenton-like process [20].

\[
\text{S}_2\text{O}_8^2^- + \text{Me}^{n+} \rightarrow \text{SO}_4^2^- + \text{SO}_2^- + \text{Me}^{(n+1)+} \quad (5)
\]

\[
\text{SO}_4^2^- + \text{H}_2\text{O} \rightarrow \text{SO}_2^- + \cdot \text{OH} + \cdot \text{H} \quad (6)
\]

\[
\text{SO}_4^2^- + \text{OH}^- \rightarrow \text{SO}_2^- + \cdot \text{OH} \quad (7)
\]

\[
\text{S}_2\text{O}_8^2^- + \cdot \text{OH} \rightarrow 2\cdot \text{SO}_4^2^- \quad (8)
\]

Therefore, this study used \( \text{H}_2\text{O}_2, \text{S}_2\text{O}_8^2^- \) and a combination of \( \text{H}_2\text{O}_2/\text{S}_2\text{O}_8^2^- \) with sonolysis to further increase mineralization efficiency. As shown in Fig. 1, 96, 95 and 94% of diazinon was degraded when \( \text{H}_2\text{O}_2, \text{H}_2\text{O}_2/\text{S}_2\text{O}_8^2^- \) and \( \text{S}_2\text{O}_8^2^- \) were added, respectively. The initial ORP value was approximately 276 mV and sharply increased to between 500 and 550 mV once the oxidants were dosed. After 60 min of reaction, the final ORP values were 570, 546 and 530 mV when \( \text{H}_2\text{O}_2, \text{H}_2\text{O}_2/\text{S}_2\text{O}_8^2^- \) and \( \text{S}_2\text{O}_8^2^- \), respectively, were added. The ultrasound/\( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) process resulted in the highest ORP value and diazinon degradation efficiency; however, these measurements were only slightly greater than those of the other two processes. In addition, the amounts of TOC removed by these three processes were 13, 12 and 10%, respectively, which indicated that the degraded diazinon could not be mineralized to \( \text{CO}_2 \). Based on the above discussion, \( \text{H}_2\text{O}_2 \) performed as the best oxidant for degrading diazinon when it was used in conjunction with the sonochemical process.

3.3. Effect of transition metals

In Eq. (9), it is found that adding external \( \text{H}_2\text{O}_2 \) can increase the formation of \( \cdot \text{OH} \) and may increase the oxidation rate, and such effects have been observed in the presence of metallic ions especially \( \text{Cu}^{2+}, \text{Fe}^{3+} \) and \( \text{Ag}^+ \). Ling et al. [21] and He et al. [22] have both proposed that the added \( \text{Co}^{2+} \) or \( \text{Ag}^+ \) would react with \( \text{H}_2\text{O}_2 \) and produce \( \cdot \text{OH} \) radicals. In addition, the \( \cdot \text{OH} \) radicals produced by the ultrasound/\( \text{Co}^{2+}/\text{H}_2\text{O}_2 \) system would react with organic pollutants and result in their degradation and mineralization. Hence, in this study, seven different combinations (\( \text{Fe}^{2+}, \text{Ag}^+, \text{Co}^{2+}, \text{Fe}^{2+}/\text{Ag}^+, \text{Fe}^{2+}/\text{Co}^{2+}, \text{Ag}^+\text{Co}^{2+} \) and \( \text{Fe}^{2+}/\text{Ag}^+/\text{Co}^{2+} \)) were examined, each with 100 mg L \(^{-1} \) \( \text{H}_2\text{O}_2 \). Among these seven combinations, the ultrasound/\( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) was the most effective one.

\[
\text{H}_2\text{O}_2 + \text{metal}^{n+} + \text{H}^+ \rightarrow \cdot \text{OH} + \text{H}_2\text{O} + \text{metal}^{(n+1)+} \quad (9)
\]

When \( \text{Ag}^+ \) was used only, degradation and mineralization of diazinon achieved using the ultrasound/\( \text{Ag}^+/\text{H}_2\text{O}_2 \) process were 41 and 8%, respectively, which were slightly better than those obtained using ultrasound alone or the combined ultrasound/\( \text{H}_2\text{O}_2 \) process (as shown in Table 2). However, in this study, the effects of \( \text{Ag}^+ \) addition were much less significant than those of \( \text{Fe}^{2+} \) addition. This result could be explained by Eqs. (10) and (11), which points out that the \( \text{Ag}^+ \) reacts with \( \cdot \text{OH} \) radicals under acidic conditions to form \( \text{Ag}^{2+} \) or \( \text{Ag}^{3+} \). Thus, the number of \( \cdot \text{OH} \) radicals would become insufficient for degrading the organic matter [23].

\[
\cdot \text{OH} + \text{Ag}^+ + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Ag}^{2+} \quad (10)
\]

\[
2\cdot \text{OH} + \text{Ag}^+ + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{Ag}^{3+} \quad (11)
\]

Similarly, the addition of \( \text{Co}^{2+} \) resulted in a competition effect by reacting with \( \cdot \text{OH} \) radicals and producing \( \cdot \text{OH} \) radicals by sono-Fenton or sono-Fenton-like processes and could not be used to degrade diazinon [17]. Also, degradation and mineralization of diazinon were slightly higher when two or three transition metals were used in the solution than when either \( \text{Ag}^+ \) or \( \text{Co}^{2+} \) was present, as shown in Table 2. Degradation and mineralization in the presence of 2–3 transition metals, however, were slightly lower than the \( \text{Fe}^{2+} \) was used alone, indicating that the addition of \( \text{Fe}^{2+} \) could help the system provide more \( \cdot \text{OH} \) radicals for degrading organic compounds.

### Table 2

<table>
<thead>
<tr>
<th>Factors</th>
<th>Diazinon degradation (%)</th>
<th>TOC removal (%)</th>
<th>TOC removal/Diazinon degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{2+} )</td>
<td>96</td>
<td>130</td>
<td>0.14</td>
</tr>
<tr>
<td>( \text{Ag}^+ )</td>
<td>41</td>
<td>18</td>
<td>0.13</td>
</tr>
<tr>
<td>( \text{Co}^{2+} )</td>
<td>34</td>
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<td>0.17</td>
</tr>
<tr>
<td>( \text{Fe}^{2+}/\text{Ag}^+ )</td>
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<td>6</td>
<td>0.11</td>
</tr>
<tr>
<td>( \text{Fe}^{2+}/\text{Co}^{2+} )</td>
<td>79</td>
<td>9</td>
<td>0.12</td>
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<tr>
<td>( \text{Ag}^+\text{Co}^{2+} )</td>
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<td>4</td>
<td>0.09</td>
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<tr>
<td>( \text{Fe}^{2+}/\text{Ag}^+/\text{Co}^{2+} )</td>
<td>70</td>
<td>8</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* \( \text{H}_2\text{O}_2 \) concentration was 100 mg L \(^{-1} \) at pH 3 and 25 °C; the concentration of each transition metal was 10 mg L \(^{-1} \).*
3.4. Effect of Fenton’s reagent concentration

Table 3 shows the values for diazinon degradation and TOC removal and the ratios of TOC removal/diazinon degradation at different Fe(II) concentrations, H₂O₂ concentrations and temperatures. Diazinon degradation by the ultrasound/H₂O₂ process (no Fe(II) addition) was only 26% with 5% TOC removal, which could be explained by the insufficient formation of *OH radicals for diazinon degradation. However, diazinon degradation significantly increased when Fe(II) was added to the solution. When the Fe(II) concentration became greater than 10 mg L⁻¹ with 150 mg L⁻¹ H₂O₂, diazinon degradation was higher than 86%. It is understood that increasing amounts of Fe(II) enable the formation of *OH radicals [10]. However, exceeding a specific iron-salt dose decreased the treatment efficiency, which would be expected if *OH molecules were being reduced by excessive amounts of Fe(II) [25–27]. Hence, diazinon degradation and TOC removal were both lower in the presence of 30 mg L⁻¹ Fe(II) compared with 20 mg L⁻¹ Fe(II). The ratios of TOC removal/diazinon degradation shown in Table 2 were between 0.15 and 0.30, and the ratio obtained when no Fe(II) addition was slightly greater than those observed when Fe(II) was at 10 and 15 mg L⁻¹. This finding indicates that the major degradation pathway of diazinon by the ultrasound/H₂O₂ process (without Fe(II)) was ultrasonic thermal cleavage. As Fe(II) was added, the formation of *OH increased and allowed for more diazinon degradation. However, if this *OH increase does not result in the total destruction of the diazinon, then TOC removal remains as a consequence of thermal cleavage inside of cavitation bubbles [10], and the ratio of TOC removal/diazinon degradation decreases.

Increasing the H₂O₂ concentration in the sono-Fenton process is useful for increasing the degradation efficiency of organic compounds [28]. In each case, Table 3 shows that the degradation of diazinon was higher than 85% at 10 mg L⁻¹ Fe(II) at four different H₂O₂ concentrations and that the diazinon degradation efficiency increased with increasing H₂O₂ concentrations. More effective diazinon degradation was observed at 150 mg L⁻¹ H₂O₂. However, the differences in diazinon degradation and mineralization that were obtained when the H₂O₂ concentration was between 100 mg L⁻¹ and 150 mg L⁻¹ were insignificant. More addition of H₂O₂ led to the more formation of *OH and resulted in the oxidation of the organic compounds [29]. However, additional doses of H₂O₂ in the solution phase could capture the *OH radicals and quench the reactions between *OH and organic compounds [30]. Consequently, the degradation efficiency of diazinon decreased when 200 mg L⁻¹ of H₂O₂ was added to the solution. Although H₂O₂ is generally used as an oxidant and disinfectant in water and wastewater treatment processes, the detergent characteristics of H₂O₂ inactivate the microorganisms during biological processes [9]. Hence, based on the comparable results obtained for 100 and 150 mg L⁻¹ H₂O₂, as shown in Table 3, if a higher treatment efficiency is the priority for diazinon degradation by the sono-Fenton process, then combining 150 mg L⁻¹ H₂O₂ with 20 mg L⁻¹ Fe(II) provides better experimental conditions. Otherwise, if operational costs and the detergent characteristics of H₂O₂ are important factors, the addition of decreased amounts (such as 100 mg L⁻¹ H₂O₂ with 10 mg L⁻¹ Fe(II)) is preferred.

3.5. Effect of temperature

Generally, higher reaction temperatures produce more cavitation bubbles for degrading organic pollutants [9]. However, extremely high temperatures could lead to Fe(II) unstable and self-decomposition of H₂O₂, which would reduce the reaction rates or degradation efficiencies of organic compounds [31]. The increase in temperature also results in the faster cushioning of cavitation bubbles compared with low temperatures. Thus, increasing the temperature could decrease the degradation efficiencies of organic pollutants [32]. As shown in Table 3, the degradation of diazinon at the five temperatures varied from 96 to 98%, which indicated that the effect of temperature on diazinon degradation was insignificant. However, the results of diazinon mineralization differed from the accompanying degradation results, in which the TOC removal slightly increased from 26% (15 °C) to 30% (25 °C) then generally decreased to 16% (55 °C). These results indicated that the faster cushioning of cavitation bubbles at higher reaction temperatures inhibited the complete diazinon mineralization and resulted in decreasing TOC removal. In addition, the results obtained for TOC removal/diazinon degradation were comparable to those obtained for TOC removal, for which the optimal ratio of TOC removal/ diazinon degradation occurred at 25 °C.

3.6. Possible degradation by-products and pathway for diazinon

In this study, the possible degradation by-products of diazinon were identified using the GC/MS, and the diazinon degradation pathways were proposed based on suggestions from the literature [3,6,8,33,34]. The experimental results indicated that four by-products, diethyl phosphate, 2-isopropyl-6-methyl-4-pyrimidinol (IMP), diazoxon and hydroxydiazin, were observed during degradation of diazinon (Fig. 2a). The proposed degradation pathway for diazinon is shown in Fig. 2b. It was understood that the formation of diazoxon, which resulted from the substitution of sulphur with oxygen (on the P=S bond through oxidation) [33], occurred first. Then, IMP was produced from the hydrolysis of diazoxon, which involved cleavage of the P=O bond on the pyrimidine group [36]. As the diazinon was degraded, an important pathway basing on the attack of *OH on the O=P=O functional group dividing the diazinon into two by-products, which resulted in the formation of diethyl phosphate and IMP [8]. The third pathway identified was hydroxylation, where the *OH group became attached to the isopropyl functional group in diazinon and produced hydroxydiazinon. Based on further hydrolysis, it was possible to divide hydroxydiazinon into diethyl phosphate and IMP.

Table 3

<table>
<thead>
<tr>
<th>Factors</th>
<th>Diazinon degradation (%)</th>
<th>TOC removal (%)</th>
<th>TOC removal/Diazinon degradation</th>
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<tr>
<td>Fe(II) concentration (mg L⁻¹)</td>
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<td>97</td>
<td>19</td>
<td>0.20</td>
</tr>
<tr>
<td>55</td>
<td>97</td>
<td>15.6</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a H₂O₂ concentration was 150 mg L⁻¹ at 25 °C.
b Fe(II) concentration was 10 mg L⁻¹ at 25 °C.
c Fe(II) and H₂O₂ concentrations were 20 and 150 mg L⁻¹, respectively.
Even the sono-Fenton process can effectively degrade diazinon, TOC removal only reached approximately 30%, which indicated that 70% of the carbon content remaining in the solution phase. This un-mineralized carbon content could increase or decrease toxicity. Hence, in addition to the degradation efficiencies, further investigations were carried out regarding the determination of toxicity changes based on cell viability measurements. Fig. 3 shows the cell-viability results that were obtained from untreated diazinon (item I), treated wastewater after 60 min reaction with ultrasound (item II), ultrasound/Fe$^{2+}$ (item III), ultrasound/H$_2$O$_2$ (item IV), Fenton (item V) and sono-Fenton process (item VI), as well as in the blank (Reverse Osmosis water, in which cell viability was defined as 100%, item VII). Before degradation, the cell viability of the untreated diazinon was 49%. As the diazinon was treated, the cell viability increased to 54–84%, which indicated that the toxicity of diazinon was slightly reduced by ultrasonic treatment alone, ultrasound/Fe$^{2+}$ and ultrasound/H$_2$O$_2$ processes, moderately reduced in the treatments using the Fenton process, and was completely removed in the sono-Fenton process.

3.7 Toxicity profiles

Fig. 2. (a) GC/MS spectra of diazinon and its degradation by-products; (b) proposed degradation pathway for diazinon under sono-Fenton treatment.

Fig. 3. Cell viability profiles for (I) untreated diazinon, wastewater after 60 min of treatment by (II) ultrasound, (III) ultrasound/Fe$^{2+}$, (IV) ultrasound/H$_2$O$_2$, (V) the Fenton process, and (VI) the sono-Fenton process and (VII) the blank (RO water).
and significantly reduced in the treatments using the sono-Fenton process. Fig. 4 depicts the satisfactory relationships between diazinon degradation and cell viability and shows a liner relationship between TOC removal and cell viability. An increase in cell viability obviously resulted from diazinon degradation and the removal of TOC. In addition, the R² value of diazinon degradation and cell viability was greater than that of TOC removal, which indicated that diazinon degradation could be the primary reaction involved in reducing toxicity. Additionally, by reducing diazinon toxicity via the sono-Fenton process, this wastewater could be further treated using biological methods.

4. Conclusions

This study examined the effectiveness of different sonochemical processes, namely, a combination of ultrasound with three transition metals and two oxidants, for diazinon degradation. The addition of Ag⁺ and Co²⁺ negatively affected diazinon degradation and mineralization. The contributions of H₂O₂, SO₄²⁻ and H₂O₂/SO₄²⁻ to the degradation of diazinon in the sonolysis systems were comparable. However, H₂O₂ appeared to be the better oxidant. The maximum diazinon degradation efficiency, which was achieved by combining ultrasound with the Fenton process, was 98% with the mineralization of 30%. In addition, the toxicity of treated diazinon significantly decreased based on a remarkable increase in cell viability. The effect of increasing temperature was insignificant. Four intermediates were observed during diazinon degradation, and hydrolysis and •OH radical oxidation were the major reaction mechanisms that resulted in the breakdown of the diazinon structure. There was a strong relationship between diazinon degradation and toxicity reduction, which indicated that the diazinon degradation was a key step in toxicity reduction.

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References

