Pesticide production wastewater treatment by Electro-Fenton using Taguchi experimental design

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ABSTRACT

In this study, the electro-Fenton (EF) method was applied to remove total organic carbon (TOC) from the pesticide production wastewater containing tricyclazole (TC). Statistical Taguchi method was used to optimize the treatment performance. Analysis of variance (ANOVA) indicated that the polynomial regression model fitted experimental data with $R^2$ of 0.969. The optimal conditions for eliminating 75.4% TOC and 93.7% TC were 0.2 mM of Fe$^{2+}$, 990 mg/L of Na$_2$SO$_4$, 180 min of reaction time at pH 3 with 2.22 mA/cm$^2$ of current density. The removal of TC present in the wastewater followed the first-order reaction kinetic model ($R^2 = 0.993$); while that was the second-order kinetic model in the case of the TOC removal ($R^2 = 0.903$). In addition, the experimental results and theory approaches (density functional theory and natural bond orbital calculations) also showed the C-N bond breaking and nitrate ions cleavage to ammonia. Acute toxicity of the pesticide wastewater after treatment (PWAT) on microcrustaceans showed that the treated wastewater still exhibited high toxicity against $D. magna$, with LC$_{50}$ values of 3.84%, 2.68%, 2.05%, and 1.78% at 24 h, 48 h, 72 h, and 96 h, respectively.

Key words: $D. magna$, electro-Fenton, pesticide, Taguchi method, Tricyclazole

HIGHLIGHTS

- Electro-Fenton (EF) was employed to remove TOC and tricyclazole from real pesticide wastewater.
- Taguchi approach (L27) had been developed on five factors of EF on TOC removal.
- ANOVA showed a well-fitted polynomial regression model with $R^2$ of 0.969.
- The nitrogen minerals reached 25.3 as explained by DFT/NBO calculations.
- Cost analysis, kinetic reaction of EF process and bioassay toxicological test also evaluated.

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INTRODUCTION
Pesticide residue contamination in water or wastewater poses a significant threat to environmental and human health (Liao et al. 2020). Once chronically exposed to the pesticide, humans might suffer from proliferative prostatic lesions, bone fractures, kidney dysfunction, hypertension, and even cancer (Duy et al. 2021). A lot of studies reported the presence of pesticides in groundwater, surface waters, effluents of wastewater treatment plants, and other drinking water sources (Liao et al. 2020; Saleh et al. 2020). Moreover, these contaminated pesticides are high concentration, high solubility, and hardly-biodegradable in water (Hoang & Holze 2021); therefore, the conventional processes; that is, adsorption, coagulation, biological methods, and so on, are not adequate for eliminating these pollutants in practice (Matsushita et al. 2018; Saleh et al. 2020; Duy et al. 2021). As a result, finding an efficient way to eliminate these pollutants in water or wastewater always has a high priority and urgency. Recent attention has been drawn to advanced oxidation processes (AOPs), including cold plasma (Sarangapani et al. 2016), activated persulfate (Rasoulifard et al. 2015), ozone (Jabesa & Ghosh 2021), photocatalysis (Kanan et al. 2020) or electron-beam process (Duy et al. 2021), and so on, which have successfully mitigated the pollutants present in synthetic pesticides; however, these AOPs exhibit practical limitations when used on an industrial scale. One of the most widely used AOPs for dealing with pesticide contamination is the homogeneous Fenton process (Li et al. 2009). Fenton is related to peroxide reactions (usually hydrogen peroxide – $\text{H}_2\text{O}_2$) with iron ions to form a series of active oxygen reactions that oxidize organic or inorganic compounds. The basic theory of the Fenton process was developed in late 1890 to oxidize tartaric acid (Ha & Thanh 2019). However, this method has drawbacks related to the wastage of oxidants (iron ions or $\text{H}_2\text{O}_2$) and the formation of excess sludge (Benatti et al. 2009). The new Fenton process based on electrolysis systems has been developed and called electro-Fenton (EF) to overcome the disadvantages of homogeneous Fenton (Zhong et al. 2013). In the EF process, $\text{H}_2\text{O}_2$ can be generated at the cathode when bubbling oxygen gas through the acidic solution, followed by reducing $\text{H}_2\text{O}_2$. The electrochemical generation of $\text{Fe}^{2+}$ ion occurs through the reaction of anodic material dissolution or cathodic reduction of $\text{Fe}^{3+}$ ions (Figure 1). In this process, pollutants are destroyed by the Fenton’s action reagent together with the combination of anode oxidation on the anode surface. The Fenton process and electrochemical are combined with increasing the degradability of organic compounds present in high-intensity wastes.

Although EF is based on the Fenton process, it is simple, produces less sludge, and does not require the addition of chemicals as a ‘clean reagent’. Therefore, EF has attracted a great deal of attention. It has been successfully applied to eliminating organic contamination from wastewaters like from dyeing and textiles (Gökkuş et al. 2018; Teymori et al. 2020), pharmaceuticals (Ganzenko et al. 2020), coke (Zhou et al. 2020), and pesticides (Da Pozzo et al. 2005; Dominguez et al. 2018; Hoang & Holze 2021). Even though EF can reduce the organic compounds in aqueous solutions, studies on removing pesticide contaminants from real production wastewater are still absent. Moreover, marginal information of pesticides’ decomposition mechanism using EF is available. To elucidate the decomposition mechanism of organic pollutants in the wastewater by this EF process, density functional theory (DFT), a well-known theory approach, has been applied to calculate and optimize the electronic and geometric structures by the interactions of outer shell orbitals of the molecules; that is, the highest occupied molecular orbital (HOMO) of the reducing molecules will interact with the lowest unoccupied molecular orbital (LUMO) of the oxidizing agents. Therefore, DFT has been used in many published papers to predict the decomposition
mechanism (Han et al. 2014; Duy et al. 2021). Nonetheless, little information is available about the toxic effects of raw and treated pesticide wastewater on aquatic microcrustaceans (Duy et al. 2021).

Aside from selecting removal techniques, experimental design plays a key role in saving both time and money on wastewater treatment. Taguchi method, a kind of experimental design based on orthogonal arrays and signal to noise ratio (S/N) qualification (Rasoulifard et al. 2015; ÖZyonar 2018), has succeeded in improving, optimizing, and interpreting the factor effects in many treatment processes from wastewater of textile (Gökkus et al. 2018), pulp and paper mill (Gholami et al. 2017), oily (ÖZyonar 2018), etc. However, the research literature on applying the Taguchi approach for pesticide production wastewater using the EF method is still very limited.

In light of the fact that (i) very few studies to date have been carried out on EF to eliminate organic compounds in real pesticide production wastewater, (ii) interpreting the effect of variables of EF on the TOC removal efficiency with less experiment. In this study, Taguchi design was employed with five variables, such as initial pH, current density, reaction time, the concentration of Fe2+ ions, and amount of sodium sulfate (Na2SO4). Besides, the decomposition mechanism based on kinetic studies and DFT calculations, the toxicity of treated wastewater on Daphnia magna, and the operating cost of this EF treatment were executed.

**MATERIALS AND METHODS**

**Wastewater characteristics**

The wastewater was taken from Ha Long agrochemical production facility located in Long An province, Viet Nam. The effluent characteristics are as follows: initial pH of 6.6–7.2, TOC of 1,236–1,358 mg/L, tricyclazole (TC) of 23.7–25.1 mg/L, total nitrogen (TN) 240–272 mg/L, NH4+–N of 3.5–5.3, NO3–N of 12.6–18.2, and no detection of NO2–N.

**Experimental apparatus**

The bipolar batch reactor used for the treatment was made of Plexiglas with the dimensions 160 cm × 300 mm, totalling a volume of 4 L of effluent per treatment (Figure 2). The active area and each electrode’s distances were 899.68 cm² (150 × 146 × 2 mm) and 10 mm with two iron electrodes as the cathode (Fe: 99.25% - CT2) and carbon plated iron anode connected.
in parallel. Only the outer electrodes were connected to the self-build digital DC power supply (30 V and 5 A) whose poles automatically switched every 30 seconds.

**Design of experiment procedures**

Taguchi approach with five controllable factors was considered, i.e., Fe$^{2+}$ concentration, sodium sulfate concentration, current density, pH, and reaction time. Three levels of these factors were selected for the experimental design with 27 experiments (Table 1). The design used MINITAB software and the significant evaluation was based on ANOVA and S/N ratio. To optimize the levels of the independent factors, pH (3–4), current density (1.11–3.33 mA/cm$^2$), Fe$^{2+}$ concentration (0.05–1 mM), Na$_2$SO$_4$ (330–990 mg/L) and reaction time (60–180 min) were evaluated based on our previous investigations (Ha 2016, 2019).

**Procedures and analysis**

In each run, 3.0 L of the wastewater, altered to the desired pH value using H$_2$SO$_4$ (0.2 M), was placed into the electrolytic cell. The FeSO$_4$ and Na$_2$SO$_4$ concentrations were mixed in the wastewater to the needed values. While the air flowrate was fixed at 3 L/min (Zhou et al. 2013), the current densities were applied based on the designed value within the range of reaction time. After 30 min settling at the end of each run, 25 mL of the treated samples were collected, filtered, raised the to desired pH value using NaOH, and determining total organic carbon (TOC), total nitrogen (TN) using TOC Vcph/cpn

| Table 1 | Factors and their level used for the design of experiments by the Taguchi method |
|-----------------|-----------------|-----------------|-----------------|
| Independent factors | Level 1 | Level 2 | Level 3 |
| pH | 3.0 | 3.5 | 4.0 |
| Current density (mA/cm$^2$) | 1.11 | 2.22 | 3.33 |
| FeSO$_4$ (mM) | 0.05 | 0.2 | 1 |
| Na$_2$SO$_4$ (g/L) | 330 | 660 | 990 |
| Reaction time (min) | 60 | 120 | 180 |
instrument (Shimadzu, Japan) and TC (LC-MS/MS, 4,000 QTRAP, Applied Biosystems, USA) according to our previous study (Duy et al. 2021). Other parameters such as ammonium (NH₄⁻N), nitrate (NO₃⁻N), and nitrite (NO₂⁻N) concentrations were by the standard method (APHA 2005). Furthermore, to avoid electrode passivation, the electrodes were washed thoroughly with water and dipped in HCl solution (10% v/v) for at least 15 min at the end of each run. All analyses were conducted in duplicate for reproducibility of data, and all of the data in the results was the average value. Energy consumed per unit volume (E) during the EF process could be determined by Equation (1) (Pieus & Pooppana 2021):

\[
E \text{(kWh/m}^3\text{)} = \frac{U \times I \times t}{60V} \tag{1}
\]

while the concentration of iron generated in the solution or electrode consumption was expressed by Equation (2) below:

\[
C \text{(gFe/m}^3\text{)} = \frac{I \times t \times M}{Z \times F \times V} \times 60 \tag{2}
\]

Herein: F is the Faraday’s constant (96485 Columb/mol), M is the molecular weight of iron (56 g/mol), Z is the number of electron transfer (assumed here \(Z_{Fe} = 2\)), I is electric current (A), U is voltage (V), t is electrolysis time (min), and V is treated volume (L).

**Acute toxicity assay**

The pesticide wastewater after treatment (PWAT) with the optimal treatment condition for TOC was selected to test the toxicity to *Daphnia magna*. The PWAT has average values as pH of 3.94, TOC of 319.5 mg/L, TC of 1.54 mg/L, TN of 139.3 mg/L, NH₄⁺N of 23.7 and NO₃⁻N of 56.3. The acute test was performed according to the OECD guideline 202 (OECD 2004). *D. magna* live stocks were cultured in glass containers at a density of 1 individual/10 mL of ISO medium (Römer et al. 2013). The test organisms were fed daily with a mixture of *Scenedesmus* sp. and *Chlorella* sp. The culture medium was renewed every three days and maintained at 25 ± 1 °C under a 12:12 h light-dark cycle.

For each test sample, a serial dilution of 0.1%, 0.25%, 0.5%, 1.0%, 2.0%, and 5.0% of PWAT plus the blank control was used. All test concentrations were prepared in triplicate and spiked with 40 mL of ISO medium in 50 mL glass beakers. Ten neonates (<24 h old) were added to each beaker. The test was run for 96 h at a stable pH and temperature of 7.5 and 25 ± 1 °C, respectively. The mortality of tested neonates was checked at 24 h, 48 h, 72 h, and 96 h. The median lethal concentrations (LC₅₀) at 24 h, 48 h, 72 h, and 96 h were calculated using Probit analysis.

**Calculation methods**

The optimal calculation of TC’s geometric and electronic structure and its intermediates is done based on the density functional theory (DFT) on the basis set of B3LYP/6-311++g(d, p). Both structure optimization and natural bond orbital (NBO) calculation were performed by Gaussian software (Han et al. 2014; Duy et al. 2021). Calculations were conducted in aqueous solvents with a Polarizable continuum model (PCM).

**RESULTS AND DISCUSSION**

**Evaluation of Taguchi approach**

The data of 27 experiments for pesticide removal are presented in Table 2. The output signal–noise (S/N) ratio from the Taguchi analysis would be estimated to be ‘the larger, the better’ for every test run to identify the distinguishing characteristics between control or signal factors to maximize the pesticide removal process. S/N ratio is the ratio of signal power to the noise power, which determines the desired signal level to background noise level; the higher the S/N ratio, the higher molarity of sufficient information than noisy false data.

**Variation of signal to noise**

The importance of the independent factors such as pH, current density, Fe²⁺ concentration, sodium sulfate, and reaction time on TOC removal are described in Figure 3 and Table S1 in Supplementary Material.

Figure 3 illustrates the steepest inclination of the pH line, indicating an enormously significant influence on removing pesticides. Following are reaction time, amount of Na₂SO₄, Fe²⁺ concentration, and current density. It can be seen that pH,
reaction time, and sodium sulfate are more critical because they had first, second, and third influence on pesticide mineralization compared to Fe²⁺ concentration and current density, whose line tended to have little relative to the horizontal. The response with the highest S/N ratio always performs the optimum results. Therefore, the best combination of factors to obtain the maximum value for S/N ratio and consequently pesticide removal efficiency of EF process was pH level 1 (pH 3), current density level 2 (2.22 mA/cm²), Fe²⁺ concentration level 2 (0.2 mM), sodium sulfate level 3 (990 mg/L), and reaction time level 3 (180 min). The predicted combination experiment was evaluated by confirmed experiments.

**Effect of pH**

pH plays a critical role in the EF process, pH not only could maintain the Fe²⁺ ion (Perng & Ha 2014) but also increased the *OH redox potential according to the Nernst equation (Nguyen et al. 2021):

\[ E^0 = E_{\text{HO}^*/\text{H}_2\text{O}_2}^0 - 0.059\text{pH} \]  

(3)

In other words, the redox potential of *OH slightly decreased from 2.62 to 2.56 with the increase in the pH 3–4. The results correspond to the reduction in S/N ratio from 33.21 to 27.60 at the reducing pH from 3 to 4 as in Figure 3; another possible

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**Table 2 | Experimental and predicted results of the TOC removal efficiency**

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>Current density (mA/cm²)</th>
<th>Fe²⁺ concentration (mM)</th>
<th>Sodium sulfate (mg/L)</th>
<th>Reaction time (min)</th>
<th>TOC removal (%)</th>
<th>Experiment</th>
<th>Predicted</th>
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explanation for these results could be that with increasing pH value the decrease in H$_2$O$_2$ formation was according to the following Equations (4)—(6), leading to the decline in ·OH generated and subsequently low production of oxidants during the EF. These reducing trends with the variation in pH during the EF process were in good agreement with those reported in previous studies (Guenfoud et al. 2014; Teymori et al. 2020). Hence, this pH value (3) is selected for optimal experiments.

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
H_2O_2 + H^+ & \rightarrow H_3O_2^+ \\
H_2O_2 + 2H^+ + 2e^- & \rightarrow 2H_2O
\end{align*}
\]

Effect of reaction time
Figure 3 and Table S1 revealed a significant increase in the S/N ratio of reaction time from 60 (29.00) to 180 min (31.78). When the reaction time increases, the S/N of the TOC removal increases, which means a positive influence of the reaction time on pesticide removal. This result is consistent with the theory: The reaction time exhibited a positive effect on the degradation of organic compounds in the EF process. With the increase in the reaction time, the disturbing process robust, the reaction occurs rapidly, and organic substances are exposed to strong oxidizing substances. This pattern of results is consistent with the study of Zhang et al. (2006), who stated that the decomposition of 5,000 mg/L of COD from landfill leachate to around 2,500 mg/L only within 30 min and obtained 1,000 mg/L at around 75 min. Based on the result, the reaction time was varied from 30 to 180 min for EF optimum experiments.

Effect of Fe$^{2+}$ concentration
The amount of catalyst plays an essential role in the EF processes; Equation (7) highlights the role of the catalyst for the generation of ·OH in the presence of an adequate amount of H$_2$O$_2$.

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- 
\]

The effect of the Fe$^{2+}$ concentration on the degradation of the pesticides was investigated by conducting experiments with 0.05, 0.2 and 1 mM concentration of Fe$^{2+}$. Figure 3 indicated that the increase of Fe$^{2+}$ concentration from 0.05 to 0.2 mM led to an increase in the S/N ratio (from 30.41 to 31.23) and then decreased to 29.7 at 1 mM. The variation in the S/N ratio could be explained: as an increase in Fe$^{2+}$ concentration (from 0.05 to 0.2 mM) the ·OH generation through Equation (3) were
accelerated, leading to an increase in TOC treatment removal. In contrast, with the increase in the Fe$^{2+}$ concentrations from 0.2 to 1 mM, TOC decreased due to the reaction between Fe$^{2+}$ ions with intermediates, decreasing the TOC removal efficiency (Yazdanbakhsh et al. 2015).

Effect of sodium sulfate
Electrolytes can affect the removal efficiency during the EF process; as electrolyte concentration increases, the ion and electron in a solution will be more flexible or reduce the resistance of the solution, which gives the Fe$^{2+}$ a greater chance for reacting with H$_2$O$_2$. However, in this experiment, the change of sodium sulfate (Na$_2$SO$_4$) from 330 to 990 mg/L lead to a slight increase in S/N ratio corresponding to 29.74 to 31.39, respectively (Figure 3 and Table S1), suggesting that the increase of TOC removal efficiency was mainly due to the lower pH of wastewater during the EF process, which makes the ion or electron flexible enough to conduct Fenton reaction (Equation (7)). The increase in Na$_2$SO$_4$ is only a minor contribution to EF treatment in some cases (Malakootian & Moridi 2017). Another reason for the trend could be reported by Ghoneim et al. (2011), who stated that SO$_4$ could consume the generated *OH as Equation (8), reducing the TOC removal efficiency. A Na$_2$SO$_4$ concentration of 0.2 mM may be a suitable alternative for optimum EF experiments.

\[ \text{SO}_4^{2-} + *\text{OH} \rightarrow \text{SO}_4^{*} + \text{OH}^- \quad (8) \]

Effect of current density
As described in Figure 3 and Table S1, the least significant TOC removal efficiency was current density. The S/N of the current density slightly increase from 30.39 to 30.53 as the current density varied from 1.11 to 3.33 mA/cm$^2$. This slight increase may be related to the suitable amount of *OH produced by the Fenton reaction (Equation (7)), where H$_2$O$_2$ is generated in situ by reducing O$_2$ on the cathode (Equation (4)). The more negligible effect of current density on EF treatment could also be found in some previous studies (Robles et al. 2017). Moreover, the lower current density could save energy and safety for the worker; therefore, the current density of 2.22 mA/cm$^2$ could be chosen in this case for the optimum EF experiment.

Model fitting and analysis
The significance of each factor was analyzed by using Analysis of Variance (ANOVA), which was given in Table 3. As described in the table, the F value and p-value of the quadratic regression model were 36.74 and 0.000, respectively, indicating the model to be significant with linear and interactions on TOC removal at their confidence level 90%.

Table 3 | ANOVA for polynomial regression model obtained for effective removal of TOC

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Coef</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>12</td>
<td>386</td>
<td>3,120.40</td>
<td>260.034</td>
<td>36.74</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>X$_1$ – pH</td>
<td>1</td>
<td>–120.5</td>
<td>48.26</td>
<td>48.265</td>
<td>6.82</td>
<td>0.021</td>
</tr>
<tr>
<td>X$_2$ – Current density</td>
<td>1</td>
<td>–120.8</td>
<td>30.19</td>
<td>30.194</td>
<td>4.27</td>
<td>0.058</td>
</tr>
<tr>
<td>X$_3$ – Fe$^{2+}$</td>
<td>1</td>
<td>–143.9</td>
<td>28.26</td>
<td>28.257</td>
<td>3.99</td>
<td>0.066</td>
</tr>
<tr>
<td>X$_4$ – Na$_2$SO$_4$</td>
<td>1</td>
<td>0.0548</td>
<td>84.67</td>
<td>84.668</td>
<td>11.96</td>
<td>0.004</td>
</tr>
<tr>
<td>X$_5$ – Reaction time</td>
<td>1</td>
<td>0.1930</td>
<td>27.59</td>
<td>27.589</td>
<td>3.90</td>
<td>0.068</td>
</tr>
<tr>
<td>X$_1$ X$_2$</td>
<td>1</td>
<td>36.8</td>
<td>33.32</td>
<td>33.320</td>
<td>4.71</td>
<td>0.048</td>
</tr>
<tr>
<td>X$_1$ X$_3$</td>
<td>1</td>
<td>46.9</td>
<td>28.57</td>
<td>28.567</td>
<td>4.04</td>
<td>0.064</td>
</tr>
<tr>
<td>X$_1$ X$_4$</td>
<td>1</td>
<td>–0.0293</td>
<td>9.28</td>
<td>9.275</td>
<td>1.31</td>
<td>0.272</td>
</tr>
<tr>
<td>X$_2$ X$_4$</td>
<td>1</td>
<td>–0.00148</td>
<td>0.87</td>
<td>0.868</td>
<td>0.12</td>
<td>0.731</td>
</tr>
<tr>
<td>X$_2$ X$_5$</td>
<td>1</td>
<td>–0.0065</td>
<td>2.10</td>
<td>2.100</td>
<td>0.30</td>
<td>0.595</td>
</tr>
<tr>
<td>X$_3$ X$_5$</td>
<td>1</td>
<td>–0.0041</td>
<td>0.19</td>
<td>0.194</td>
<td>0.03</td>
<td>0.871</td>
</tr>
<tr>
<td>X$_4$ X$_5$</td>
<td>1</td>
<td>0.000023</td>
<td>2.42</td>
<td>2.421</td>
<td>0.34</td>
<td>0.568</td>
</tr>
<tr>
<td>Error</td>
<td>14</td>
<td></td>
<td>99.09</td>
<td>7.078</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td></td>
<td>3,219.49</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Based on the statistical analysis, the polynomial equation of these factors on TOC removal efficiency could be described as Equation (9):

\[
\text{TOC removal} (\%) = \frac{386}{C_0^{120}} X_1 - \frac{120}{C_0^{8}} X_2 - \frac{143.9}{C_0^{9}} X_3 + \frac{0.0548}{C_0^{143}} X_4 + \frac{0.1930}{C_0^{9}} X_5 + \frac{56.8}{C_0^{46.9}} X_1 X_2 - \frac{0.0293}{C_0^{0.0548}} X_1 X_5 - \frac{0.00148}{C_0^{0.0063}} X_2 X_4 - 0.0063 X_2 X_5 - 0.0041 X_3 X_5 + 0.000025 X_4 X_5
\] (9)

The coefficient of determination (R²) and adjusted coefficient of determination (R² adj) were found to be 0.9692 and 0.9428 for TOC removal efficiency. This implied that the prediction of experimental data was quite satisfactory. The correctness of the proposed model was also confirmed by the normal probability plot of residuals in Figure 4. There proved no unusual observations or no unusual structure patterns.

Figure 5 revealed the predicted TOC removal capacity according to the regression model on these influence factors. The figure indicated that the TOC removal increased with the increase in reaction time and Na₂SO₄. In contrast, the TOC removal decreased to a rise in pH and Fe²⁺ concentration and varied with current density. As seen in Figure 5, the TOC removal could greater than 70% occurred for conditions of pH = 3; current density of 1.11 to 2.50 mA/cm², Fe²⁺ concentration ≥0.1 mM, reaction time from 90 to 180 min, and Na₂SO₄ from 660 to 990 mg/L.

According to the S/N ratio and predicted regression model, the optimal operation treatment using EF to TOC removal efficiency could be selected as 1st level of pH value (5), 2nd level of current density (2.22 mA/cm²), 2nd level of Fe²⁺ concentration (0.2 mM), 3rd level of sodium sulfate (990 mg/L) and 3rd level of reaction time (180 min). The serial confirmation experiments of the four factors with these values on various reaction times (30–180 min) were also conducted. The results of the confirmation experiments in Figure 6 and Table S2 proved to be consistent with predicted optimal results with the highest TOC removal efficiency around 75.37% and very narrow error variation (1.75–3.48%). The obtained results again demonstrated the excellent accuracy of the proposed model or Taguchi approach. The set of confirmation experiments could also be used to evaluate the kinetic of TC and the mineralization process.

**Reaction kinetic model and proposal decomposition mechanism**

**Kinetic model of TOC removal**

The TOC removal, as mentioned above, was a key parameter for the evaluation of the EF processes’ performance. After the optimized experimental conditions of the EF processes had been achieved, we further studied the kinetics of the TOC removal, as shown in Figure 6.
removal under such conditions to give a better understanding of the relationship between TOC concentrations and reaction times. Because the TOC is rather a complicated parameter that includes concentrations of many different organic pollutants, it is very hard for the TOC removal to be extremely fitted with a specific kinetic reaction model. Some authors also studied the kinetics of the TOC removal as in textile or municipal wastewater by several models (Rosal et al. 2009; Lopez-Lopez et al. 2015). In this work, the TOC removal by the EF process under optimal conditions (pH 3, Fe$^{2+}$ concentration 0.2 mM, current density 2.22 mA/cm$^2$, sodium sulfate 990 mg/L) showed suitably well with a second-order kinetic model with $R^2 = 0.903$ as indicated and other kinetics such as first or third-order apparently not fitted with the experimental data (Figure S1 and Table S3). Accordingly, the half-life time ($t_{1/2}$) of the TOC removal was 72.4 minutes and the rate constant was $1.065 \times 10^{-5}$ L/(mg. min) with the initial TOC concentration of about 1,297 mg/L.

**Reaction kinetic model of TC**

The reaction kinetics of TC degradation were conducted individually with an initial concentration of 24.4 mg/L under the optimized experimental conditions and are presented in Table 4 and Figure S2. TC degradation reaction followed first-order

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**Figure 5** | Contour plots for TOC removal efficiency with (a) Fe$^{2+}$ and pH (current density 1.11 mA/cm$^2$, Na$_2$SO$_4$ 990 mg/L; reaction time 120 min); (b) Fe$^{2+}$ and reaction time (current density 1.11 mA/cm$^2$, Na$_2$SO$_4$ 990 mg/L; pH 3); (c) reaction time and current density (pH 3; Na$_2$SO$_4$ 990 mg/L, Fe$^{2+}$ 0.2 mM); (d) pH and current density (Fe$^{2+}$ 0.2 mM; Na$_2$SO$_4$ 990 mg/L, reaction time 120 min).
reaction kinetics with the squared correlation coefficient $R^2 = 0.9929$. Similar results were also obtained by Duy et al. (2021), who reported second and third orders were not fitted as the first-order reaction for removal of TC from aqueous solution using the electron beam technique. The decomposition mechanism of TC could be calculated using theoretical calculation.

### Table 4 | Reaction kinetic model parameters for the decompose of TC

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>Regression equation</th>
<th>$R^2$</th>
<th>Rate constant</th>
<th>$t_{1/2}$ (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$y = 0.0161x + 0.01876$</td>
<td>0.9929</td>
<td>$1.61 \times 10^{-2} \left( \frac{1}{\text{min}} \right)$</td>
<td>43.05</td>
</tr>
<tr>
<td>2</td>
<td>$y = 0.003678x - 0.05805$</td>
<td>0.8744</td>
<td>$3.68 \times 10^{-3} \left( \frac{L}{\text{mg} \cdot \text{min}} \right)$</td>
<td>11.14</td>
</tr>
<tr>
<td>3</td>
<td>$y = 0.002526x - 0.09718$</td>
<td>0.7250</td>
<td>$1.26 \times 10^{-3} \left( \frac{L^2}{\text{mg}^2 \cdot \text{min}} \right)$</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Proposed mechanism for the oxidation of TC by the attacking of $^\bullet$OH radical

The redox reaction between the two substances essentially transfers electrons from the reducing agent to the oxidizing agent. Chemically quantum, this electron of the reducing substance is located in the outermost orbital of the molecule, also known as HOMO; the empty orbital of the oxidizer that accepts the electrons of the reducing agent, also known as LUMO, has an energy level close to the HOMO orbital. Thus, if it is possible to determine the position of the element or the bond that mainly contributes to these two molecular HOMO and LUMO orbitals, it is possible to determine the position of the reaction occurring on the molecule (Han et al. 2014). However, the HOMO and LUMO orbitals of a molecule, as defined by the molecular orbital theory, are molecular orbitals distributed throughout the molecule (especially molecules with conjugated pi bonds). Therefore, in calculating the reactive location of a molecule, it is often based on the theory of localized molecular orbital. And the calculation based on the NBO is one of the most used calculations.

As shown earlier in Equation (7), the most powerful oxidizing agent formed under this reaction medium $^\bullet$OH. Thus, the TC, in this case, acts as a reducing agent. To determine the reactive centers of TC and its intermediates under attack by $^\bullet$OH,
quantum calculations based on density functional theory (DFT) were used to optimize their structures in water solvent and then followed by NBO computations. The highest occupied NBO orbitals of TC and its intermediates have been calculated and listed in Table S4. It indicated that the highest occupied NBO orbital is located at the bonding between C5-C6 (Figure 7) since position C5 has been bound to the methyl group, so the OH group reacts to the C6 position. Similarly, the active position of the TC1 molecule is at the S9 (lone-pair), so ‘OH will attack this location, and one of the two bonds S9-C8a and S9-C9a can be broken. The TC2 molecule has an active position located at S15 so that element S can be oxidized to a higher oxidation number; specifically, the -S-OH bond will be converted to -SH = O. For the TC3 molecule, localized bonding orbital C1-C2 will act as a reducing center and ‘OH will attack C1 because C2 is attached to the -OH group. Using similar calculations and inference, we proposed significant pathways for the oxidation of TC, as illustrated in Figure 7.

Further oxidation of TC8 and TC9 also occurred under the same mechanism. Under such reaction medium (low pH, high ‘OH), the molecules TC8 and TC9 were mineralized to minerals such as CO2, H2O, NH4+, and NO3/, etc. These results agree with the previous study of Zhong et al. (2013). They described NO3/ as one of the essential products of the electrooxidation process. The mineralization of this pollutant using EF to NH4+ and NO3/ could be discussed in the next section.

Figure 7 | Proposed pathways for the oxidation of TC under attack of hydroxyl radical.
**Mineralization process**

To determine if the EF could eliminate the pesticide to final nitrogen ion products, the formation of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$ ions, and total nitrogen (TN) at optimized experimental conditions (pH 3, $\text{Fe}^{2+}$ concentration 0.2 mM, current density 2.22 mA/cm$^2$, sodium sulfate 990 mg/L) were explored with varied reaction time (60, 120 and 180 min). The mineralization of nitrogen (mineral N) represents a decomposing pesticide in wastewater to a combination of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ calculated by Equation (10) (Da Pozzo et al. 2005).

Mineralized N (%) = $100\% \times \frac{\text{Final (NO}_3^-\text{-N + NH}_4^+\text{-N)} - \text{Initial (NO}_3^-\text{-N + NH}_4^+\text{-N)}}{\text{Initial TN}} \quad (10)$

As obtained in the analysis results, $\text{NO}_2^-\text{-N}$ ions were undetected while the evolution of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ concentrations occurred and are presented in Figure 8. As seen in this figure, after 180 min, $\text{NO}_3^-\text{-N}$ is accumulated to a larger extent by EF up to 56.3 mg/l related to 16.0% of initial N content and lower final $\text{NH}_4^+\text{-N}$ concentrations of 23.7 (7.5% initial N). Figure 8 also indicated a gradual increase in the percentage of mineralized N from 10 to 23.5%, corresponding to 56.6 to 75.4% TOC removal (Figure 6 and Table S5). These results once again indicated the mineralization of refractory organic compounds by EF treatment. Table 5 below summarizes the removal efficiencies for pesticide using electro-Fenton reported in recent studies. In addition to EF systems similar to those used herein, other approaches using expensive materials have been studied, such as Boron-doped diamond -BDD (Dominguez et al. 2018), $\text{TiO}_2/\text{IrO}_2/\text{Ta}_2\text{O}_5$ (Xu et al. 2016), TiO$_2$/SnO$_2$ – Sb/PbO$_2$ (Zhong et al. 2013), etc. Specifically, only this research discussed real wastewater contaminated in high concentrations as well as mixtures of pesticides (around 20 pesticides – data not shown). In a shorter time, this study achieved consistent results compared with other reference studies. The pesticide removal efficiency is high (>93% for tricyclazole). This value is consistent with the study of Zhong et al. (2013) and Xu et al. (2016), with about TC treatment efficiency 79.4% (20 min) and 93.4% (150 min), respectively. However, these studies use too expensive materials, which are not suitable for practical application. Besides, a few studies were conducted with other pesticides such as Diuron, glycolphosphate (Rosa Barbosa et al. 2018), Chlotoluron, Carbophuran, Bentazone (Abdessalem et al. 2008), and Lindane (Dominguez et al. 2018). It seems to have the same TOC removal efficiency but longer reaction time (over 240 min). Based on the economic and processing efficiency of this method with carbon plate/stainless steel electrode, this technique can be used for biological pretreatment in real application.

**Daphnia magna survival**

The toxicity of the PWAT on *D. magna* was investigated. The survival of *D. magna* in the controls without pesticide wastewater was 100%. According to OECD guidelines, this high control survival meets the requirement for the toxicity test (OECD

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**Figure 8** | Products of degradation of pesticide in wastewater at optimal conditions ($\text{Fe}^{2+}$ concentration of 0.2 mM, current density of 2.22 mA/cm$^2$, Na$_2$SO$_4$ of 990 mg/L, pH 3).
The LC values of the PWAT against the microcrustacean *D. magna* at different time intervals are listed in Table 6. The results demonstrated that the PWAT generated high toxic effects on *D. magna*, with LC50 values of 3.84%, 2.68%, 2.05%, and 1.78% at 24 h, 48 h, 72 h, and 96 h, respectively. These toxicity effects on *D. magna* are lower than the untreated pesticide wastewater (Duy et al. 2021). However, the PWAT still generates toxic effects on *D. magna*. Probably, the treated pesticide wastewater contained unknown or other toxic compounds that contributed to toxic effects on *D. magna*. Further study on the chemical composition and toxic effects of this treated wastewater on other aquatic organisms is recommended, and the method could require more treatment steps to reach the standard for release to the environment.

**Operation cost analysis of the EF treatment**

One of the greatest contributions to EF cost is energy consumption, which significantly increases by current density or reaction time (Ha & Thanh 2019). The variation of energy consumption (kWh/m³) on current density and reaction time are tabulated in Table S5. The evolution of the table confirmed that with a longer treatment time and higher current density, more electrical energy was consumed per m³. According to Table S5, at optimal condition (Fe2⁺ concentration 0.2 mM, current density 2.22 mA/cm², sodium sulfate 990 mg/L, pH = 3 and reaction time) electrical energy consumed could be found

### Table 5 | Comparision of EF treatment for the elimination of pesticide compounds in water and wastewater

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Matrix</th>
<th>Electro-Fenton reactor/electrodes</th>
<th>Current density (mA/cm²)</th>
<th>Reaction time (min)</th>
<th>Fe⁴⁺ (mM)</th>
<th>Na₂SO₄ (mM)</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricyclazole</td>
<td>Aqueous solution (85 mg/L TC)</td>
<td>Reactor (200 mL), TiO₂/TrO₂/Ti₂O₂ - Carbon black PTFE/graphite membrane Combine: Aerator</td>
<td>1</td>
<td>20</td>
<td>1.0</td>
<td>0.05</td>
<td>TC 79%</td>
<td>Xu et al. (2016)</td>
</tr>
<tr>
<td>Tricyclazole</td>
<td>Aqueous solution (100 mg/L TC)</td>
<td>Reactor (200 mL), TiO₂/SnO₂ – Sb/ PbO₂ Stainless steel</td>
<td>25</td>
<td>150</td>
<td>-</td>
<td>0.05</td>
<td>TC 93.4% COD 69.5%</td>
<td>Zhong et al. (2013)</td>
</tr>
<tr>
<td>Diuron, Glycophosphate</td>
<td>Aqueous solution (0.1 mM Diuron, 0.13 mM Glycophosphate)</td>
<td>Continuous reactor Ti/Ru₀.₃₆Ti₀.₆₄O₂ DSA plate Carbon felt</td>
<td>0.45</td>
<td>180</td>
<td>1.0</td>
<td>0.05</td>
<td>Diuron 8% Gly 94% TOC 34%</td>
<td>Rosa Barbosa et al. (2018)</td>
</tr>
<tr>
<td>Chlortoluron, Carbofuran, Bentazone</td>
<td>Aqueous solution 0.05 mM for each one.</td>
<td>Reactor (500 mL), Carbon felt piece and grid</td>
<td>480</td>
<td>0.1</td>
<td>50</td>
<td>Chlortoluron 98% Carbofuran 94% Bentazone 92%</td>
<td>Abdessalem et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>Lindane</td>
<td>Aqueous solution (10 mg/L Lindane)</td>
<td>Reactor (230 mL), BDD Carbon felt</td>
<td>240</td>
<td>0.05</td>
<td>50</td>
<td>TOC 80%</td>
<td>Dominguez et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>Tricyclazole</td>
<td>Real wastewater (24.4 mg/L TC)</td>
<td>Reactor (3,000 mL), Carbon plate Stainless steel</td>
<td>2.22</td>
<td>180</td>
<td>0.2</td>
<td>7</td>
<td>TC 93.7% TOC 75.4%</td>
<td>This study</td>
</tr>
</tbody>
</table>

2004). The LC values of the PWAT against the microcrustacean *D. magna* at different time intervals are listed in Table 6. The results demonstrated that the PWAT generated high toxic effects on *D. magna*, with LC₅₀ values of 3.84%, 2.68%, 2.05%, and 1.78% at 24 h, 48 h, 72 h, and 96 h, respectively. These toxicity effects on *D. magna* are lower than the untreated pesticide wastewater (Duy et al. 2021). However, the PWAT still generates toxic effects on *D. magna*. Probably, the treated pesticide wastewater contained unknown or other toxic compounds that contributed to toxic effects on *D. magna*. Further study on the chemical composition and toxic effects of this treated wastewater on other aquatic organisms is recommended, and the method could require more treatment steps to reach the standard for release to the environment.

**Table 6 | Lethal concentration (LC₅₀) of the PWAT sample on Daphnia magna**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Time (h)</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWAT (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LC10</td>
<td></td>
<td>1.92</td>
<td>1.28</td>
<td>0.92</td>
<td>0.65</td>
</tr>
<tr>
<td>LC50</td>
<td></td>
<td>3.84</td>
<td>2.68</td>
<td>2.05</td>
<td>1.78</td>
</tr>
<tr>
<td>LC90</td>
<td></td>
<td>4.18</td>
<td>2.89</td>
<td>2.32</td>
<td>1.96</td>
</tr>
</tbody>
</table>
30.2 kWh/m³ of real pesticide wastewater. Moreover, one of the factors that affect treatment cost most is sludge elimination. According to the environmental companies in Vietnam, the cost of dried sludge treatment assumed is $150/m³. The electrode material loss and adding chemical costs is also significantly involved in treatment costs. Besides these mentioned costs, the treatment price during EF process could include labor, maintenance and other fixed costs. However, energy, electrode material and sludge treatment costs are taken into account as major cost items in the calculation of the operating cost. Therefore, the operating cost using EF can be calculated by following Equation (11).

\[
\text{Cost} = \text{electrical price} \times \text{energy consumption (E)} + \text{electrode price} \times \text{loss electrode material (C)} + \text{chemicals amount} \times \text{prices} + \text{sludge treatment cost} \times \text{sludge formation}
\]  

(11)

Given the Vietnamese market in May 2021, the electrical energy price is 0.06 US$/kWh, H₂SO₄ price 0.25 US$/kg, FeSO₄ price 0.17 US$/kg, Na₂SO₄ price 0.35 US$/kg, and electrode anode price 0.33 US$/kg (iron). Table S6 summarizes the costs associated with the optimal treatment conditions. As shown in this table, the operating cost of the treated real wastewater by EF under the optimum conditions was 3.04 $/m³. The majority of the TC (93.7%) and TOC (75.4%) were removed under these conditions. This cost was much cheaper than 20.91 $/m³ in the study of Gaied et al. (2019); they were using EF for treating domestic wastewater or 10.68 $/m³ for landfill leachate samples (Pieus & Pooppana 2021).

**CONCLUSION**

The Electro-Fenton (EF) process using stainless steel and carbon fiber as electrodes showed good efficiency in treating a pesticide production effluent containing tricyclazole (TC). The Taguchi approach with L27 arrays had indicated that all five factors such as pH, reaction time, current density, Na₂SO₄, and FeSO₄ concentration presented statistical significance in the treatment with \( R^2_{adj} = 0.943 \). At the optimization conditions (Fe²⁺ concentration 0.2 mM, current density 2.22 mA/cm², Na₂SO₄ 990 mg/L, pH = 3) around 92% of TC and 75.4% of TOC were eliminated with operation cost of 3.04 $/m³. The first-order kinetic was apparently suitable for the decomposition of TC with \( R^2 \) approximately 0.993, but the TOC removal followed the second-order kinetic model (\( R^2 = 0.903 \)). Mineralization is intensified during the process, producing more NO₃⁻ and NH₄⁺ ions, further explaining the mechanism by theory calculations such as DFT and NBO. The PWAT still exhibited high toxicity against D. magna. Probably, unknown toxic compounds from the PWAT contributed to the toxic effects that need further investigation. Therefore, the EF can be applied to the remediation of wastewaters containing pesticides prior to the biological treatment.

**ACKNOWLEDGEMENTS**

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


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