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Abstract: The characteristics of active chlorine formation were studied during the electrolysis of water containing chloride ions (Cl\textsuperscript{−}). The screening experiments were performed using an undivided Ti/RuO\textsubscript{2} plate electrode under different pH, current density, chloride concentration, and flow rate (retention time of chloride) conditions. In addition, the influence of inorganic ions (SO\textsubscript{4}\textsuperscript{2−}, NO\textsubscript{3}−, HCO\textsubscript{3}−, and CO\textsubscript{3}\textsuperscript{2−}), and organic compounds (phenol, and dissolved organic carbon (DOC) solution) were also evaluated in this study. Response surface methodology (RSM) was used to evaluate the influence of four main factors (chloride concentration, current density, flow rate, and pH). The results showed that the contribution of flow rate, chloride concentration, pH, current density were 37.2%, 33.59%, 18.28%, 10.93%, respectively. Besides it also was used for the optimization of the parameter in the decomposition process fenobucarb. A mathematical model was established to predict and optimize the operational conditions for fenobucarb removal in the electrolysis NaCl process. The main transformation products (seven compound structures) were detected by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS).

Keywords: electrochemical; active chlorine; response surface methodology; fenobucarb; transformation products

1. Introduction

In recent decades, rapid economic growth, urbanization is the cause of increasingly serious water pollution, one of the major concerns around the world today is the level of water pollution by organic compounds arising from many human activities [1]. Agriculture, which accounts for 70% of the wastewater, most of which are pesticides, herbicides and fungicides play a major role in water pollution [2-5]. Therefore, treatment of organic compounds especially pesticides needs attention. However, there are many different sources of wastewater, their composition is extremely diverse, often containing a mixture of complex organic and inorganic compounds, the treatment becomes difficult and mainly depends on nature and concentration pollutant levels [6-8]. For the treatment of polluted wastewater by organic compounds, the biological oxidation method is the most cost-effective process, but this method does not appear to be effective in the presence of organic substances high toxicity [9]. In the chemical method, it has proved its effectiveness for decades, besides processing organic compounds, disinfecting water but also resisting reinfection for a certain period of time. But the main drawback of the chemical method is the unwanted reaction of the oxidizing agent with the substances in the water, the by-products formed can cause similar toxicity or even higher than the original compounds, on the other hand, the production and transport of O\textsubscript{3}, Cl\textsubscript{2} is very dangerous [9, 10]. In recent years, researchers have combined advanced oxidation methods with electrochemical technology to improve the efficiency of processing organic compounds in water environments [10, 11].
The electrochemical method can treat non-selective the organics by the direct and indirect way that based on the activity of free radicals and strong oxidants formed in the electrolysis process. The literature has shown that some main strong oxidants are produced as O₂, *OH, H₂O₂, HClO, OCl⁻, [12-14] by electrochemical and chemical reactions that present in equations (1), (2), (3), (4), (15), (16) in Table S1. The main advantage of the electrochemical technologies is their environmental compatibility because the main reagent, the electron, is a clean reagent. Other advantages include their versatility, high energy efficiency, amenability to automation, easy handling because of the simple equipment required and safety because of they operate under mild conditions [15].

In the electrochemical method, the ability to produce oxidants strong depends on the main factors such as electrode materials, electrolyte composition, current, pH, and temperature, in which electrode material is considered one of the most important factors [16-18]. Currently, the types of electrodes used in the electrolytic process are divided into two types: the active electrode and the inactive electrode. Boron-doped diamond electrode (BDD), PbO₂, SnO₂ [19] only play the role of exchanging electrons without chemical interactions with the oxidants generated. In contrast, active electrodes such as Pt-, IrO₂-, RuO₂- dimensionally stable anodes (DSAs) [19, 20] in addition to performing the electron exchange process have chemical interactions with oxidants. Because of the electrochemical activity of the two different electrodes, it is necessary to select suitable electrode materials in each specific case [21]. In this study, we use oxidizing agent chlorine for the treatment of organic compounds, so the use of active electrodes will be more effective such as Ti-RuO₂, Ti-IrO₂ [17, 22]. On the other hand, limiting the formation of some by-products such as ClO₂ and ClO₃ during electrolysis of chlorine [23] should be considered because they seriously affect human health [24-27], therefore Ti-RuO₂ electrodes were used for this study.

In this research, we aimed to: (1) investigate screening and using RSM to evaluate the effects of operational parameters on active chlorine formation in electrolysis,(2) apply the RSM to evaluate the interactions of four independent factors (i.e., Cl⁻, fenobucarb concentration, current density and flow rate (retention time)) and optimal conditions on the fenobucarb degradation process, and (3) postulate the probable degradation pathways of fenobucarb under the electrolysis chloride treatment by the liquid chromatography tandem-mass spectrometry (LC-MS/MS) methodology.

2. Materials and methods

2.1. Materials

Sodium chloride (NaCl), sodium chlorite (NaClO₂), sodium chlorate (NaClO₃), sodium perchlorate (NaClO₄), sodium nitrate (NaNO₃), sodium sulfate (Na₂SO₄), sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄), phenol (C₆H₅OH), 2-(phenylethylhydrazono)propionic acid (C₇H₆N₃O₂), sodium acetate (C₃H₅NaO₃), DPD (N, N-diethyl-P-phenylenediamine, C₆H₄N₂), and fenobucarb (C₂₃H₂₄NO₃) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Meanwhile, phosphoric acid, methanol, and acetonitrile of high-performance liquid chromatography (HPLC) grade were obtained from Fisher Scientific (Waltham, MA, USA). Deionized water with resistance <18 MΩ was using for preparing sample and chemicals. DOC solution was made by a mixture from many compounds that solution properties were shown in Table S2, and it was filtered by 0.45µm cellulose filter before using.

2.2. Electrochemical equipment and procedure

Electrochemical system is shown in Fig.1 and Fig.S1. The undivided reactor cell and electrodes are produced by Adept Water Technology. The volume of the tank is 278 cm³, the parameters are as follows height 16.1cm, width 1.5cm, length 11.5cm. The current is supplied by the Voltage adjustable supplier (PS3020). Samples are pumped into the electrolysis cell by Master Flex pump (USA). The experiments are performed continuously by pumping the sample from the test solution container into the cell and the current is set up at 0.5-3.5A during sample electrolysis. Electrode Ti-
RuO$_2$ was provided by Adept Company. SEM (Scanning Electron Microscope) image and EDX spectrum (Energy-dispersive X-ray) of the electrode were shown in Fig.S2, Fig.S3 and Table S3.

Figure 1. The electrochemical system: 1- Electrolysis cell, 2- Electrode, 3- Adjustable DC power supply, 4- Peristaltic Pump, 5- Inlet reservoir, and 6: Outlet reservoir.

2.3. Analysis of the sample solutions

The concentration of active chlorine was measured using DPD (N, N-diethyl-p-phenylenediamine, C$_{10}$H$_{10}$N$_2$) method with U-2900 UV/VIS spectrophotometer 200V (Hitachi) at wavelength 515nm according to ISO 7393-2:2017. ClO$_3^-$, ClO$_4^-$ and Cl$^-$ were analyzed using ion chromatography (Metrohm) with Column Metrosep A Supp 5, 100x4mm 61006.510 and detector IC 819. The injection volume was 20µl and the eluent was Na$_2$CO$_3$: 3.2mM, and NaHCO$_3$: 1.0mM, the flow rate of pumped at 0.7ml min$^{-1}$ [28]. The H$_2$SO$_4$: 2M was used as a suppressor solution. Samples were filtered by membrane 0.45µm before measuring the ions by ion chromatography. The initial DOC concentration was determined by 254 TOC meter of Shimazu and calculated as total organic carbon (TOC) concentration.

The fenobucarb was detected at wavelength 215nm by HPLC-UV Thermo Scientific series 3300 HPLC system (Thermo Scientific Technologies, CA, USA) equipped with a G1311A Quart pump, a G1313A autosampler, a G1322A degasser, a G1316A column oven. Chromatographic separation was performed using a Supelco C18 reversed-phase analytical column (2.1 × 250 mm; 5 µm particle size; Supelco, Milford, CT, USA) maintained at 30°C. A binary mobile phase system, consisting of (A) methanol and (B) water deionized (70/30, v/v) was employed in iso-cratic pump mode with an injection volume of 20 µL.

The intermediates were identified by an LC/HRMS Q-Exactive Focus system (Thermo). The MS/MS parameters were optimized as follows: sheath gas flow rate: 35, aux gas flow rate: 15, sweep gas flow rate: 1, spray voltage (kV): 3.4, capillary temperature: 320 °C, S-lens RF level: 50, aux gas heater temperature: 350 °C, and CE: 18. The used mobile phase includes solvent (A) H$_2$O 0.1% Formic acid and solvent (B) CH$_3$CN, with the gradient being 0 min: 5%B, 0–27 min: 5–95%B, 27–28 min: 95%B, 28–28.5 min: 5%B, and 28.5–30 min: 5%B. The signals were normally recorded in two modes, such as positive and negative in 30 min.

2.4. Response surface methodology (RSM)

The RSM was used as a useful tool to evaluate the influence of factors on the objective function [29]. For the active chlorine formation, four factors were selected for the study: chloride concentration, flow rate, current, and pH. Besides, the RSM also used to optimize the parameter of variables the removal of fenobucarb in water. The central composite circumscribed (CCC) was used in this study. MODDE 12.1 trial software supports the design experimental, statistical analysis, and optimization.
Technically, the electrolytic efficiency of chloride depends on their retention time in the electrolytic device, and the current density on the electrode. However, in order to facilitate the process of changing parameters and design experimental in this study we converted into flow rate and current values respectively shown in Table 1.

<table>
<thead>
<tr>
<th>Flow rate (L/minute)</th>
<th>Retention time (s)</th>
<th>Current (A)</th>
<th>Current density(mA.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>167</td>
<td>0.2</td>
<td>3.64</td>
</tr>
<tr>
<td>0.2</td>
<td>83</td>
<td>0.5</td>
<td>9.11</td>
</tr>
<tr>
<td>0.3</td>
<td>56</td>
<td>1.0</td>
<td>18.22</td>
</tr>
<tr>
<td>0.4</td>
<td>42</td>
<td>1.5</td>
<td>27.33</td>
</tr>
<tr>
<td>0.5</td>
<td>33</td>
<td>2.0</td>
<td>36.44</td>
</tr>
<tr>
<td>0.6</td>
<td>28</td>
<td>2.5</td>
<td>45.55</td>
</tr>
<tr>
<td>0.8</td>
<td>21</td>
<td>3.0</td>
<td>54.66</td>
</tr>
<tr>
<td>1.0</td>
<td>17</td>
<td>3.5</td>
<td>63.77</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Mass balance

As we know that chloride is transformed into active chlorine, chlorate, and perchlorate by an electrochemical and chemical reaction in sodium chloride electrolysis. The mass balance process was studied to assess the loss of chloride due to the formation of Cl\(_2\) gas in the electrolysis process. So the chloride concentration in the input, output solution were determined, besides chlorate, and perchlorate were also measured in the output solution (converted into chloride content). Total chloride content before and after electrolysis was compared. The result (Fig.2) shown that the total amount of chloride, active chlorine, chloride and chlorate in outlet solution (0.176mM) close to chloride inlet solution (0.178mM). This indicated that during electrolysis of chloride little loss is due to partial evaporation of Cl\(_2\).

3.2. Effect of initial chloride concentration, pH, flow rate, and current density

The formation ways of active chlorine, chloride, chlorate, and perchlorate results from electrochemical and chemicals reactions in electrolysis system were shown equations from (1) to (17) Table S1. The results experiments on adept electrochemical technology shown active chlorine formation (HOCl, OCl\(^-\)) is depended on flow rate, current density, pH solution, and initial chloride concentration. From Fig.3a, it is easy to see that when the flow rate is increased from 0.1L/min to 1.0L/min, the amount of chlorine formed decreases from 2.73 to 0.07ppm, respectively. Because
when the flow rate increases, the retention time of chloride in the electrolytic system decreases (Table 1) so the oxidation efficiency of the chloride at the anode electrode decreases.

Fig. 3b indicated that the effects of chloride concentration and current density come to active chlorine formation. At certain current density values, when increasing the concentration of chloride inlet solution from 10 to 100 ppm, the amount of active chlorine increases accordingly, typically at current density 36.44 mA cm\(^{-2}\) (0.5 A), the amount of active chlorine formed increased from 6.41 to 17.64 ppm.

The influence of current density on the ability of chlorine formation is very clear, at chloride 10 ppm inlet solution, when the current density increases from 3.64 to 36.44 mA cm\(^{-2}\), the amount of active chlorine increases from 0.33 to 6.42 ppm, respectively. The same variability results at other chloride content in inlet solutions.

This result is explained by the change in the amount of electricity q (current density), the conductivity of the solution (chloride concentration) which is shown in Fick's, Faraday law, and the Nerst equation [30].
The results of the investigation on the effect of pH on the ability to form active chloride are shown in Fig.4. Clearly, that increasing the initial pH from six to eight by PEHP, HCO$_3^-$ then the ability to form active chloride decreases, notably range pH=7-8. The cause of the decrease in active chlorine when pH increases the ability to produce ClO$_2^-$ and ClO$_3^-$ increases from active chloride [31, 32] is indicated in equations (5), (6), (8), (17) (Table S1). In addition, when the pH reduces from 7 to 6, the active chlorine production increased slowly, due to the equilibrium (18), (19) (Table S1) the shift direction towards the left. This means reducing the formation of active chlorine from chlorine generated during electrolysis.
Figure 4. Effect of pH to formation active chlorine pH of inlet solution is adjusted by PEHP(a), and HCO₃(b).

3.3. Effect of inorganic salts as SO₄²⁻, NO₃⁻, CO₃²⁻, HCO₃⁻

Other inorganic ions also affect the formation of active chlorine and chlorate, but to a less extent than sulfate (Fig. S4). The order of decreasing effect is: SO₄²⁻ > NO₃⁻ > CO₃²⁻ > HCO₃⁻.

Sulfate has a marked effect on the production of active chlorine and chlorate (Fig. S5, Fig.S6). As the concentration of sulfate increase from 5 to 50 ppm, the formation of active chlorine and chlorate decreases. At a concentration of SO₄²⁻ (5ppm) the amount of active chlorine, chlorate generated only 48.00%, 20.22% and 52.79%, 22.27% compared to the absence of SO₄²⁻ ion at different current density 9.11mA.cm⁻² (0.5A), 45.55mA.cm⁻² (2.5A). We investigated the influence of SO₄²⁻ at further concentration, still, match result. The effect of sulfate is probably due to the formation of peroxodisulphate [14, 33], however, there are not many kinds of literature demonstrate clearly reaction mechanic of persulfate and active chlorine. The accepted two pathway are the formation of sulfate radical from sulfate electrolysis that reacts to chlorine radical in equation (28) [34] and competitive electrochemical reaction between sulfate and chloride. However, the reaction of sulfate and chlorine radical is studied clearly in electrochemical processes.

\[
\begin{align*}
\text{Cl}^\bullet + \text{S}_{2}\text{O}_8^2^- & \rightarrow \text{products} \quad (27) \\
\text{Cl}^\bullet + \text{S}_{2}\text{O}_8^2^- & \rightarrow \text{products} \quad (28) \\
\text{HOCl} + \text{S}_{2}\text{O}_8^2^- & \rightarrow \text{Cl}^\bullet + \text{HSO}_5^- + \text{SO}_4^- \quad (29) \\
\text{HOCl} + \text{SO}_4^- & \rightarrow \text{Cl}^- + \text{HSO}_5^- \quad (30)
\end{align*}
\]

The interference by ion (NO₃⁻) is due to the formation of reduced species that subsequently reacts with hypochlorite [13, 14, 35].

\[
\begin{align*}
\text{NO}_3^- + \text{H}_2\text{O} + 2e & \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (31) \\
\text{NO}_3^- + 6\text{H}_2\text{O} + 2e & \rightarrow \text{NH}_3 + 9\text{OH}^- \quad (32) \\
\text{NO}_3^- + \text{OCl}^- & \rightarrow \text{NO}_2^- + \text{Cl}^- \quad (33) \\
2\text{NH}_3 + 2\text{OCl}^- & \rightarrow \text{N}_2 + 2\text{HCl} + 2\text{H}_2\text{O} + 2e \quad (34) \\
\text{NH}_3 + 4\text{OCl}^- & \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+ + 4\text{Cl}^- \quad (35)
\end{align*}
\]

Besides, active chlorine reducing ions are mainly due to the changing pH in the presence of HCO₃⁻, CO₃²⁻ ions. The solution containing HCO₃⁻ 25ppm has a pH value 6.5. The solution containing CO₃²⁻ 25ppm has pH value 10.3 so the effect of ions CO₃²⁻ stronger than HCO₃⁻.
3.4. Effect of organic compounds as phenol, DOC solution

The electrochemical oxidation of phenol in presence of sodium chloride as electrolyte is investigated in many kinds of literature recently [36, 37]. Phenol could be degradation by direction and indirect oxidation by electrochemical [38]. In presence of chloride as an electrolyte, the small fraction of phenol was oxidized direct electrolysis, while complete degradation of phenol was achieved by indirect electrochemical oxidation. Many investigators have noted the formation of the polymeric film is produced on anode surface in during direct oxidation that causes electrochemical degradation rate of phenol is slow. The phenol was indirect electrochemical oxidation by active chlorine, hypochlorous, hypochlorite ion and \( \cdot \text{OH} \) when using chloride as electrolyte [39, 40]. In this study, the formation of active chlorine, chlorate, perchlorate is investigated with simultaneity presence of chloride and phenol in electrolysis. Fig.S7 show that the formation of active chlorine is affected by the phenol concentration and electrolytic current, active chlorine decrease when phenol concentration increases from 5ppm to 100ppm at each current value. The cause of active chlorine decrease due to oxidation of phenol by special chlorous as shown in the previous literature [40, 41]. Beside, phenol is also oxidized directly at the surface of the electrode, so when increasing phenol concentration content in the inlet solution leads to the competition of phenol with chloride ion. The effect of phenol on the chlorate formation is shown in Fig.S8, which is similar to active chlorine. This is perfectly acceptable, due to the most of the chlorate generated during electrolysis from activated chlorine (5), (6), (7) Table S1, so that the amount of active chlorine decreases, resulting in reduced chlorate.

The initial concentration of TOC is a strong effect to the formation of active chlorine in sodium chloride electrolysis (Fig.5). Formation of active chlorine is decreased when increasing the concentration of DOC, the results are quite reasonable, because DOC contains carboxylic acid groups, phenolic groups, dissolved organic carbon and inorganic ions such as \( \text{SO}_4^{2-} \), \( \text{PO}_4^{3-} \), \( \text{NO}_3^{-} \), these are the factors that reduce active chlorine [42].

![Figure 5. Effect of DOC to the formation of active chlorine in solution.](image)

3.5. Modeling

The response surface methodology (RSM) was used to evaluate the effect of four factors (chloride concentration, flow rate, current density, and initial pH) on form active chlorine. Independent variables were investigated at five levels and real value into coded shown in Table 2.
The active chlorine content depends on different parameters of the four independent variables shown in Table S4. The results were used for statistical analysis and determined regression equation by MODDE 12.1 trial software. The regression coefficient corresponding to the coding variable of the polynomial quadratic equation is shown in Table S5, and the P-value was used to evaluating the significance of the regression coefficients. Table S6 show that the coefficient representing the linear interaction of the four independent variables, the second order interaction of the variables X1, X2, and between the two variables X1 and X4 on the formation active chlorine were statistically significant (P-value<0.05 at level confident 95%) [43]. However, the significance of the linear regression coefficients are greater than regression coefficients interaction.

The regression equation obtained after removal of the coefficients insignificant (P-value>0.05) and adjusted the values of the coefficients of significance (Table S6).

\[ Y_1 = 6.713 + 3.717X_1 - 3.079X_2 + 1.882X_3 - 2.190X_4 + 0.591X_1^2 + 0.961X_2^2 - 0.959X_1X_4 \]

However, the individual P-value is insufficient to evaluate the statistical significance of the predictors and develop the model. Therefore, the analysis of variance (ANOVA) at level 95% confidence was applied, and the results are represented in Table S7. The ANOVA indicate statistical significance of the model is expressed by the coefficient of determination (R^2), the coefficient of determination adjustment (R^2_adj), P-value (lack of fit), and Fisher test (F-test). The values R^2, R^2_adj of the model are 0.915; 0.889 close to one, and F calculated for the second order regression equation is 1.594 (<F(0.95, 17, 6) = 3,874) show that the model is consistent with good data. In addition, the lack of fit also calculated to evaluate between model and experiment. The P-value (lack of fit) is 0.293 (>0.05) indicating that the building model has very well.

The three-dimensional response surface represents the interaction of the two factors to the formation of active chlorine shown in Fig.S9, and the percent factor contribution is shown Fig.6.

From Table S6, and Fig.6, Fig.S9 show that the chloride concentration and current are proportional to the active chlorine formation, whereas pH value of inlet solution and flow rate are inversely proportional to active chlorine formation. The influence of factors have been explained in section 3.2

Analysis results by statistical algorithms show that the percentage contributes to the chlorine content of flow rate, chloride, pH, and current density are 37.20%, 33.59%, 18.28%, 10.93%,

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Variable</th>
<th>Coded variable and Indipendent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>Chloride concentration (ppm)</td>
<td>-α -1 0 +1 +α</td>
</tr>
<tr>
<td>X2</td>
<td>Flow rate (L/min)</td>
<td>0.1 0.2 0.3 0.4 0.5</td>
</tr>
<tr>
<td>X3</td>
<td>Current density (mA.cm^{-2})</td>
<td>9.11 18.22 27.33 36.44 45.55</td>
</tr>
<tr>
<td>X4</td>
<td>pH</td>
<td>5 6 7 8 9</td>
</tr>
</tbody>
</table>

**Table 2. Parameter and level independent variables**
respectively. Show that the two main factors affecting the ability of active chlorine formation are flow rate and chloride concentration.

3.6. Application to removal fenobucarb in surface water

Based on the screening experiments, we found that four main factors affecting the fenobucarb removal efficiency were chloride concentration ($X'_1$), current density ($X'_2$), flow rate ($X'_3$) and initial fenobucarb ($X'_4$). For optimum fenobucarb removal efficiency, the RSM was used with the experimental design of central composite circumscribed (CCC) four independent variables at five levels which indicate Table 3. The number of experiment design were 31 (16 base experiments, 8-star experiments (distance star: 2), and 7 central experiments) [29, 44].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Variable</th>
<th>Coded variable and Indipendent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X'_1$</td>
<td>Chloride concentration (ppm)</td>
<td>-α</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>$X'_2$</td>
<td>Current density (mA.cm$^{-2}$)</td>
<td>27.33</td>
</tr>
<tr>
<td>$X'_3$</td>
<td>Flow rate (L/min)</td>
<td>0.1</td>
</tr>
<tr>
<td>$X'_4$</td>
<td>Fenobucarb concentration (ppm)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The fenobucarb removal efficiency depends on different parameters of the four independent variables were shown in Table S8, and used for statistical analysis and regression equation. The regression coefficient corresponding to the coding variable of the polynomial quadratic equation is shown in Table 4. The $P$-value was used to evaluate the significance of the regression coefficients.

<table>
<thead>
<tr>
<th>Y2</th>
<th>Coeff. SC</th>
<th>Std. Err.</th>
<th>p</th>
<th>Conf. int(±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b'_0$</td>
<td>45.4714</td>
<td>1.9002</td>
<td>5.92352x10$^{-14}$</td>
<td>4.0282</td>
</tr>
<tr>
<td>$b'_1$</td>
<td>4.6788</td>
<td>1.0262</td>
<td>0.000321708</td>
<td>2.1755</td>
</tr>
<tr>
<td>$b'_2$</td>
<td>2.2779</td>
<td>1.0262</td>
<td>0.0412374</td>
<td>2.1755</td>
</tr>
<tr>
<td>$b'_3$</td>
<td>-9.0738</td>
<td>1.0262</td>
<td>1.47924x10$^{-7}$</td>
<td>2.1755</td>
</tr>
<tr>
<td>$b'_4$</td>
<td>-2.4796</td>
<td>1.0262</td>
<td>0.0279997</td>
<td>2.1755</td>
</tr>
<tr>
<td>$b'_{11}$</td>
<td>-5.6294</td>
<td>0.9401</td>
<td>1.89544x10$^{-6}$</td>
<td>1.9930</td>
</tr>
<tr>
<td>$b'_{22}$</td>
<td>-2.2832</td>
<td>0.9401</td>
<td>0.027321</td>
<td>1.9930</td>
</tr>
<tr>
<td>$b'_{33}$</td>
<td>-4.3269</td>
<td>0.9401</td>
<td>0.000294319</td>
<td>1.9930</td>
</tr>
<tr>
<td>$b'_{44}$</td>
<td>-0.7832</td>
<td>0.9401</td>
<td>0.41709</td>
<td>1.9930</td>
</tr>
<tr>
<td>$b'_{12}$</td>
<td>-0.1544</td>
<td>1.2569</td>
<td>0.903778</td>
<td>2.6644</td>
</tr>
<tr>
<td>$b'_{13}$</td>
<td>-0.4981</td>
<td>1.2569</td>
<td>0.697102</td>
<td>2.6644</td>
</tr>
<tr>
<td>$b'_{14}$</td>
<td>0.0494</td>
<td>1.2569</td>
<td>0.96915</td>
<td>2.6644</td>
</tr>
<tr>
<td>$b'_{23}$</td>
<td>-1.5206</td>
<td>1.2569</td>
<td>0.243906</td>
<td>2.6644</td>
</tr>
<tr>
<td>$b'_{24}$</td>
<td>-0.8681</td>
<td>1.2569</td>
<td>0.499648</td>
<td>2.6644</td>
</tr>
<tr>
<td>$b'_{34}$</td>
<td>1.5006</td>
<td>1.2569</td>
<td>0.249901</td>
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</tbody>
</table>

$N = 31$  \[ R^2 = 0.913 \]  $Q^2 = 0.570$  \[ Cond. no. = 4.686 \]  $DF = 16$  \[ R^2\text{ adj.} = 0.836 \]  $RSD = 5.027$

Notes: DF = degree of freedom; RSD = relative standard deviation; Std. Err. = standard error; Conf. int(±) = confidence interval; $p$ = probability.

The result shows that four independent variables (chloride concentration, current intensity, flow rate, and fenobucarb concentration) have an effect on the removal efficiency fenobucarb ($P$-value<0.05). In addition, the second order interaction of chloride concentration, current density, and flow rate were statistically significant ($P$-value<0.05) [44]. The regression equation obtained after
removal of the coefficients insignificant (P-value > 0.05) and adjusted the values of the coefficients of significance (Table S9).

\[ Y = 44.672 + 4.679X'_{1} + 2.278X'_{2} - 9.074X'_{3} - 2.480X'_{4} - 5.546X'_{1}^2 - 2.200X'_{2}^2 - 4.244X'_{3}^2 \]

Analysis of variance was used to evaluate the predicted regression equation with the experiment. The results obtained in Table 5 show that the coefficient of determination \( R^2 \) and the coefficient of determination adjusted \( R^2 \text{adj} \) of the removal efficiency fenobucarb is 0.89, 0.86 (>0.80) respectively. The predictive power of the model is relatively good. However, the \( R^2, R^2 \text{adj} \) values do not fully reflect the suitability of the model. Therefore, the lack of fit assessment and the use of the Fisher standard model is essential.

Lack of fit the model is to evaluate the significance of the empirical data and the predictive value of the model. If statistical testing was significant (P-value <0.05), the model’s prediction was not appropriate. Table 5 shows that the P-value (lack of fit) is 0.201 (>0.05) indicating the fit between the predicted and experimental results. The calculated F value of the model is 1.99 (<F (0.95, 17, 6) = 3.94) which also demonstrates that the regression model yields results consistent with empirical values.

Table 5. The result of ANOVA

<table>
<thead>
<tr>
<th>Y2</th>
<th>DF</th>
<th>SS</th>
<th>MS (variance)</th>
<th>F</th>
<th>p</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>31</td>
<td>43453.9</td>
<td>1401.74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constant</td>
<td>1</td>
<td>38824.6</td>
<td>38824.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total corrected</td>
<td>30</td>
<td>4629.33</td>
<td>154.311</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>7</td>
<td>4117.91</td>
<td>588.273</td>
<td>26.4564</td>
<td>0.000</td>
<td>24.2543</td>
</tr>
<tr>
<td>Residual</td>
<td>23</td>
<td>511.418</td>
<td>22.2356</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>17</td>
<td>434.489</td>
<td>25.582</td>
<td>1.99339</td>
<td>0.201</td>
<td>5.05551</td>
</tr>
<tr>
<td>Pure error</td>
<td>6</td>
<td>76.9287</td>
<td>12.8215</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: SS = sum of squares; MS = mean square; F = Fisher calculate; SD = standard deviation.

The combined effect of two elements on the fenobucarb removal efficiency was shown through the 3D response face in Fig.7a and Fig.S10. The results show that four factors of chloride concentration, flow rate, current density, and fenobucarb concentration all affect the removal efficiency in the water. In particular two factors, flow rate and fenobucarb concentration are inversely proportional to the decomposition efficiency of fenobucarb. As the flow rate increases leading to a decrease in the retention time of cell components, it results in reduced active chlorine formation, the degree of decomposition of fenobucarb by oxidation directly on the electrode surface or by active chlorine decreases. The current density and concentration of chloride proportional to this fenobucarb removal efficiency are related to active chlorine formation, perfectly consistent with the research results in Section 3.2, 3.5.

The influence of each factor is shown in Fig.7b, the most contribute effect is fenobucarb, besides the influence of flow rate and chloride concentration are almost equal. The study results section 3.5 indicate that the chloride is high contribute influence on the active chlorine formation in the electrolysis process, however in the decomposition process only 6.48%. Since contributes to current density is 39.58%, therefore, it shows that in addition to decomposition by oxidizing agents, fenobucarb was direct oxidation on electrodes plays an important role. The results showed that it was completely consistent with previous studies [45-47].
One of the main purposes of this study was to find the optimal conditions for the treatment of fenobucarb by advantage oxidation method using the active chlorine radicals. MODDE 12.1 trial software was used to optimal conditions. Optimum conditions were shown in Table 6. Moreover, the attained optimal conditions were tested in another experimental run to validate the responses. The result demonstrated that 55.14% of fenobucarb in solution was removed within 10 min. This confirmed the model reliability and accuracy because this removal efficiency lies 54.57% and 57.44% (the 95% confidence interval). Therefore, the modeling result can serve to estimate the removal efficiency of fenobucarb with a high level of accuracy.

### Table 6. Optimal experiment conditions

<table>
<thead>
<tr>
<th>Chloride concentration (ppm)</th>
<th>Current density (mA.cm(^{-2}))</th>
<th>Flow rate (L/min)</th>
<th>Fenobucarb concentration (ppm)</th>
<th>% Removal efficiency fenobucarb</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.05</td>
<td>54.65</td>
<td>0.177</td>
<td>1.0</td>
<td>Predicted 57.44, Experiment 55.14</td>
</tr>
</tbody>
</table>

### 3.7. By-products of fenobucarb’s degradation
Figure 8. fenobucarb decreases with time.

According to the HPLC-UV data (Fig. 8), the initial fenobucarb concentrations decreased over the electrolysis reaction time under experimental conditions. This means that the fenobucarb compound was decomposed and transformed into the different compounds, including metabolites of fenobucarb [48]. However, the formed metabolites of fenobucarb are strongly dependent on the experimental conditions, such as Cl\textsuperscript{−} concentration, current intensity, and flow rate. The structure of formed fenobucarb metabolites is accuracy determined by the combination of ultra-high-performance liquid chromatography coupled with high-resolution (UPLC-HRMS) spectrometry (Q-Orbitrap) for response to mass errors of less than 5 ppm. Moreover, in order to detect and identify the compound of metabolites, the Compound Discoverer 2.1 (Thermo) program to detect the metabolite and recognize two identified fragments were applied. The degradation pathways of fenobucarb under experimental conditions optimal can be summarized in Fig. 9, including four possible pathways.

Generally, the structures of the metabolites are unknown. Therefore, it is necessary to analysis the metabolite compounds in both positive and negative modes. At a neutral solution pH, two major identified metabolites were derived from the hydrolysis of fenobucarb. They were 2-(sec-butyl) phenol (2) (m/z = 151.11095; Fig.S11) and methylcarbamic acid (3) (m/z = 76.03203; Fig.S12). In addition, the compound (3) was decomposed to methylamine and carbon dioxide (Pathway 1, Fig.9). In essential, in aqueous solution, the carbamate compounds (i.e., fenobucarb) often react hydrolysis to produce certain phenolic and carbamic compounds [49].
However, under the presence of free radicals (Cl$^*$ and $^*\text{OH}$), compound (2) will consecutively react hydroxylation; as a result, one new –OH group appear in its benzene ring. Under the effect of Cl$^*$ and $^*\text{OH}$, the bond between O and H (in the –OH group) was easily breakdown. Sequentially, the electron transfer between O and the benzene ring resulted in (1) double bonds between O and aromatic ring and (2) the formation of free radicals at the para position. The $^*\text{OH}$ radical in solution attacked the para position of the benzene ring to form a new –OH group (Pathway 2, Fig.9). This group was dehydrated to form the dione compound 2-(sec-butyl) cyclohexane-2,5-diene-1,4 –dione ($m/z = 165.08373$; Fig.S13).

For Pathway 3, the formed (4) compound 2-(prop-1-en-2-yl) phenyl methylcarbamate, ($m/z = 192.09464$; Fig.S14) resulted in the de-alkylation and dehydration reactions of fenobucarb. The reactions were described as follows (1) the free Cl$^*$ radicals in the solution attacked the alkyl group of fenobucarb to form a free organic radical, (2) the free $^*\text{OH}$ radicals in the solution attacked the free-formed organic radical to form an alcoholic compound, and (3) the alcoholic was dehydrated to form an alkene compound. Lastly, some unknow compounds of degradation of fenobucarb included (6) ($m/z = 102.97379$) and (7) monochloride compound ($m/z = 82.95235$). This is because of their small molecular weights and insufficient identification fragmentations.

4. Conclusions

From this work, the following conclusions can be drawn:

- Factors influencing active chlorine formation have been shown, with four main factors: chloride content, electric current, flow rate (retention time of Cl$^-$ ion), and initial pH. In addition, the influence of inorganic ions were studied, in which the influence of inorganic ions decreases in order SO$_4^{2-}$ > NO$_3^-$ > CO$_3^{2-}$ > HCO$_3^-$. And the influence of organic compounds such as phenol and DOC is also considered.
The percentage of the four main factors contribution were indicated by RSM. In which the influence of the factors arranged in descending direction is flow rate > chloride concentration > pH > current density.

RSM is used to assess the interaction of 4 independent variables in the process of eliminating fenobucarb. The results showed that the highest fenobucarb removal ability under optimal chloride conditions 40.05ppm; current density 54.65 mA.cm$^{-2}$; flow rate 0.177 L/min(retention time 94.4s); fenobucarb 1.0ppm.

Seven metabolites were detected by LC-MS/MS in combination with Compound Discoverer 2.1. The decomposition of Fenobucarb occurs in four pathway: hydrolysis of fenobucarb, oxidation by Cl$^-$, HO free radicals, and direct oxidation of fenobucarb that can occur on the electrode surface.

The toxicity of metabolic products in the process of decomposing fenobucarb by advanced oxidation methods, with free radicals generated during electrolysis of chloride, need to be evaluated.

**Author Contributions:** All authors have equivalent contributions to this study.

**Funding:** This research was financially supported by National Foundation for Science and Technology Development (NAFOSTED) (the grant number: 104.06-2013.54).

**Acknowledgment:** The authors would like to thank National Foundation for Science and Technology Development for financial support.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**


