Efficient Rapid Deodorization of Mercaptan-Contaminated Soil by Sono-Fenton Process: Response Surface Modeling and Optimization

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The entry of mercaptans into the environment as the odor pollutants has always been an environmental concern. In this research, a sonochemical oxidation (sono-Fenton) method was used for rapid deodorization of tert-butyl mercaptan (TBM) contaminated soil. The design of the experiments was conducted by central composite design method and the effect of four different factors was investigated on the treatment efficiency. The complete treatment of the soil was achieved at 1 g l⁻¹ concentration of hydrogen peroxide, the iron sulfate/soil weight ratio of 0.004, the sonication power of 100 W, and the pollution charge of 25000 ppm. Pareto analysis showed that the factor of H₂O₂ concentration with an effect of 43% and sonication power with 26% effect has the greatest effect on the efficiency of mercaptan removal. Based on the experimental results, increasing the hydrogen peroxide concentration and sonication power through increasing hydroxyl oxidation radicals result in enhancing the removal efficiency. Further, increasing the pollution load decreases the treatment efficiency although the intensity and heat generated by the oxidation reaction are increased. The fitted quadratic model with correlation coefficient of 98% can accurately predict the removal efficiency. The results of this study showed that the ultrasound waves as an auxiliary agent can reinforce the penetration of Fenton initiators in clay soils and improve purification efficiency.

Keywords: Soil deodorization, Tert-butyl mercaptan (TBM), Advanced oxidation, Fenton, Ultrasound energy

INTRODUCTION

The entry of mercaptans (sulphur containing compounds) into the environment as an odor pollutant has always been considered as one of the environmental concerns. In some parts of Iran, there are places such as huge oil and gas complexes, as well as in the national gas pipeline and on the outskirts of the cities, the release of mercaptans has led to emergency situations and the concern and discomfort of the people, along with the creation of intense smell and pollution of soil and air. In addition, this type of contamination leads to a decline in the development of industries and agriculture due to the nasty odor caused.

Inhalation of very low amounts of these substances leads to severe headache, nausea, and fatigue and muscle weakness. This batch of materials at high concentrations results in serious problems for the lungs and anesthesia. Workers exposed to 500 ppm concentration of mercaptan, for one hour, have reported some problems such as neck pain [1]. It should be noted that the human sensitivity to detect unpleasant smells is very high, and the threshold of detection and the maximum tolerable amount of odor differ almost several thousand times. In the case of mercaptans, this difference is about 750,000 times [2].

Mercaptans are considered as volatile organic compounds containing sulfur. There are several methods for evaporating organic compounds, especially sulfur compounds, which can be classified in physical methods such as dilution and absorption, chemical methods such as non-thermal oxidation and chemical absorption, thermal degradation methods such as combustion, bioremediation methods like bio-filtration and phytoremediation and soil stabilization methods including crystallization and...
cementation. Among the methods stated, chemical oxidation methods are more appropriate options for removal of mercaptans from the soil with a harsh and nasty smell, due to the high removal speed of contamination and the ability to use in the site of contamination. The Fenton method is one of these methods, originally invented by Henry John Fenton in 1890. The oxidant agent in this method is a solution of hydrogen peroxide and iron bivalent ion based on the theory of increasing the rate of oxidation of tartaric acid by this solution [3]. Hydrogen peroxide is a weak acid which can oxidize organic compounds, including aromatic compounds. However, it is impossible to use for high levels of contamination due to the low reaction rate at the usual concentrations of this substance. Therefore, the salt of intermediate metals such as iron is added to increase the rate of hydrogen peroxide decomposition. This reaction produces hydroxyl radical as the second most powerful oxidant after Fluorine. Further, this radical has a high potential for oxidation of organic contaminants such as polycyclic aromatic hydrocarbons [4-5].

The classic Fenton method or the modified one has been used for the oxidation of hydrocarbons such as polyphenols [6], ethyl benzene [7], perchloroethylene [8], polycyclic aromatic hydrocarbons [9], gasoline [10], diesel fuel [11] and fuel oil [12] in soil conditions. There is a wide range of soil decontamination efficiency for the Fenton method that can be related to multiple factors. Factors such as the type of pollutant and its chemical characteristics, soil structure, organic compounds in the soil, acidity, temperature, reaction time and the amount of reactant can be effective in the process of soil treatment and its efficacy [4].

In some studies, application of ultrasonic waves as one of the methods for eliminating soil contamination has been highlighted. Although Alfred Leonis (1927) discovered the principle of using ultrasonic waves to perform some reactions, the application of these waves was developed after the production of cheap ultrasonic emission devices in the 1980s [13]. Despite the various applications of ultrasonic waves, their environmental function has been considered for decontamination since the 1990s [14]. The reasons for using ultrasonic waves are that they have been effective in eliminating hydrocarbon contamination with no secondary pollutants production and no need to use chemical substances. The elimination efficiency reported for ultrasonic wave emission has been less than 90%, and the cost of such removal are sometimes beyond the expectations.

To the best of our knowledge, treatment methods such as aerobic biodegradation [15], H2O2/KMnO4/NaClO oxidation system [16] and sonication [17] were applied to remove TBM from the soil. Disadvantages such as prolonged cleaning time (for biodegradation method), high chemical consumption (for oxidation method) and high price with low removal efficiency (for sonication method) have prompted efforts to improve the TBM remediation process. Therefore, this study is suggested to combine different methods in order to minimize the use of chemicals, and eliminate the pollution using ultrasound waves with lower cost. The combination of Fenton and sonication methods is described as the sono-Fenton method for the removal of pollutants such as alachlor herbicide [18], dyes [19], diazinon [20], nitrophenol [7], hexachlorobenzene [21], naphthalene [22] and bisphenol A [23].

The present study aimed to use the sono-Fenton method to treat soil contaminated with TBM and evaluate the effect of operational variables on the removal rate. Fenton method is one of the non-thermal oxidation methods. It is predicted that the use of ultrasound waves will accelerate and improve the oxidation process and eliminate the unpleasant smell.

**MATERIALS AND METHODS**

**Materials**

The soil used in experiments was collected from the Asalouyeh area in Bushehr province from the construction site of the mercaptan production unit and artificially contaminated to achieve the desired pollution levels. In addition, iron peroxide (purity 35%), iron sulfate heptahydrate (99.98% purity), tert-butyl mercaptan (98% purity) and ethyl alcohol (96% purity) were all prepared from Merck and deionized water from Kasra were used to conduct TBM removal experiments by sono-Fenton method.

**Procedure**

All experiments were conducted in a glass reactor with a capacity of 200 ml. In order to prevent possible
contamination effect, all laboratory equipment were sterilized. For doing so, all were washed with distilled water and then placed in an oven at 120 °C for 6 h. Further, the soil was placed in a temperature of 120 °C for 24 h to minimize the effect of potential microorganisms.

At the stage of the contamination removal, the iron sulfate powder was added to 20 g contaminated soil and mixed with a mixer manually. Then, 30 ml of hydrogen peroxide was injected into the reactor and the slurry mixture was immediately exposed to ultrasonic waves for 6 min by a Bandelin-Sonopuls probe. After the desired time, with the addition of ethyl alcohol to the slurry, the sono-Fenton reaction was stopped and the two-stage filtration was performed with a syringe filter and centrifuge.

Gas chromatography was used to obtain the concentration of TBM in the soil sample. The chromatograph (Agilent 7890) was equipped with a FID detector and a HP-Plot Q column. The inlet, oven, and detector temperatures of the device were 280 °C, 60 °C and 300 °C, respectively. Helium was used as a carrier gas, and dry air and hydrogen were also used as the detector. In order to calculate the efficiency of TBM removal, the Eq. (1) was used:

\[
\text{Removal efficiency (\%) } = \frac{C_1 - C_2}{C_1} \times 100
\]  

where \( C_1 \) represents the initial concentration and \( C_2 \) indicates the final concentration of TBM.

### Data Analysis

In order to determine the factors affecting the removal of mercaptan from soil, the central composite design based on the response surface methodology was implemented. The present study focuses on the effect of four factors, the \( \text{H}_2\text{O}_2 \) initial concentration, the \( \text{FeSO}_4/\text{soil weight ratio} \), the ultrasound waves power and the pollution loading. The details of the factors examined are presented in Table 1.

Using the experimental results obtained, a quadratic mathematical model derived using MINITAB16 software was presented to predict the efficiency of contamination removal. This mathematical model is based on the following equation:

\[
R = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad i \neq j
\]  

where \( \beta_0 \) represents the constant term, the \( \beta_i \) are the coefficients of the linear terms, the \( \beta_{ij} \) are the coefficients of the interaction terms, and the \( \varepsilon \) is the error term.
Table 3. The Four-factor Five-level CCD Matrix in Uncoded Units with the Observed and Predicted Response

<table>
<thead>
<tr>
<th>EXP NO.</th>
<th>Experiment conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[H\textsubscript{2}O\textsubscript{2}]o</td>
<td>(Fe:S)o</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.0025</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>0.0025</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.0025</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0.0055</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>0.0025</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>0.0070</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>11</td>
<td>7</td>
<td>0.0055</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>0.0055</td>
</tr>
<tr>
<td>14</td>
<td>7</td>
<td>0.0055</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>0.0025</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>0.0040</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>19</td>
<td>3</td>
<td>0.0025</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>21</td>
<td>9</td>
<td>0.0040</td>
</tr>
<tr>
<td>22</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>23</td>
<td>3</td>
<td>0.0055</td>
</tr>
<tr>
<td>24</td>
<td>3</td>
<td>0.0055</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>26</td>
<td>5</td>
<td>0.0010</td>
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<tr>
<td>27</td>
<td>5</td>
<td>0.0040</td>
</tr>
<tr>
<td>28</td>
<td>3</td>
<td>0.0025</td>
</tr>
<tr>
<td>29</td>
<td>3</td>
<td>0.0055</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
<td>0.0055</td>
</tr>
<tr>
<td>31</td>
<td>7</td>
<td>0.0025</td>
</tr>
</tbody>
</table>
In the above equation, \( R \) represents the percentage of contamination removal efficiency, \( x_i \) and \( x_j \) are the encoded values of the factors, \( x_i x_j \) is the coded value of the interactions, \( \varepsilon \) is the error between the observed and predicted value, \( i \) and \( j \) represent index numbers with the condition that \( i < j \) must be observed for interaction term, and \( \beta \) indicates constant of the second-order model. In addition, in order to compare the effect of main factors and their interactions, Pareto analysis was used, which is calculated according to Eq. (3):

\[
P_i = \left( \sum \beta_i^2 \right) \times 100 \quad i \neq 0
\]  

In Eq. (3), the parameter \( P_i \) is a criterion of the relative percentage of the factors and the interaction between them.

**RESULTS AND DISCUSSION**

**Soil Sample Analysis**

Soil samples were analyzed to determine the characteristic of the soil. Table 2 indicates the results of the analyses.

**Experimental and Predicted Results of TBM Removal Efficiency**

According to the experimental results listed in Table 3, the highest percentage of mercaptan removal was found to be 98% in the conditions of the \( \text{H}_2\text{O}_2 \) concentration 9% (w/v), the \( \text{FeSO}_4/\text{soil} \) weight ratio 0.004, the wave power 60 W, and the pollution loading of 75,000 ppm. This removal efficiency, regarding relatively short wave duration (6 min), indicates that this method is capable of rapidly eliminating mercaptan contamination. In Fig. 1, the experimental results are compared with the predicted values using the quadratic model. The values of model coefficients are given in Table 4.

The results of ANOVA are reported in Table 5. A significance level of \( \alpha = 0.05 \) is considered for analyzing the experiment results. P-values indicate that the linear effects and interactions are highly significant (P-Value ≤ 0.05) during the variation in mercaptan removal efficiency. P-value of lack-of-fit (0.117) indicates that variations in the data around the suggested model are not significant relative to the pure error. Moreover, \( R^2 \) indicates that the quadratic polynomial model can describe 98.23% of variability in removal efficiency.

Pareto analysis was used to compare the effect of main factors and their interactions. The results are illustrated in Fig. 2. Among the main factors and their interactions, two factors of \( \text{H}_2\text{O}_2 \) initial concentration and ultrasound waves power are more effective than other factors and interactions. This statistical analysis shows the important role of Fenton's chemical reaction to ultrasound waves in removing mercaptan from the soil, however, it is not possible to ignore the effect of ultrasonic waves and their facilitating role on the peroxide diffusion.

**Investigating the Effects of Main Factors**

The influence of each factor was analyzed using mean values. The effect of increasing the concentration of \( \text{H}_2\text{O}_2 \) on the efficiency of decontamination is shown in Fig. 3. An increase in the \( \text{H}_2\text{O}_2 \) concentration leads to an increase in the TBM removal efficiency. In Fenton initiator reactions, the hydroxyl ion produced is a strong oxidizer. The reaction of Fenton as the initiator of the hydroxyl radical chain is as follows:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^-
\]  

The hydroxyl radical has a high potential for oxidation of organic pollutants. Further, the occurrence of propagation reactions usually leads to the production of superoxide ions (\( \text{O}_2^- \)), hydro peroxide ions (\( \text{HO}_2^- \)) and organic radicals (\( \cdot \text{R} \)). When \( \text{H}_2\text{O}_2 \) is extensively present, more radicals are produced than the conventional reaction of Fenton. In addition to the reactions occurring between the oxidant and the existing organic matter, as the reactions of the Fenton system, the radical reactions occur due to the presence of additional \( \text{H}_2\text{O}_2 \). Therefore, there are more radicals to react with contaminants. In almost all cases, the intermediates produced in these reactions are more biodegradable in comparison to the primary compounds.

The effect of the weight ratio of \( \text{FeSO}_4/\text{soil} \) on the mercaptan removal efficiency is shown in Fig. 4. The efficiency of decontamination increases with increasing the \( \text{FeSO}_4/\text{soil} \) ratio up to the optimum value of 0.0055. Iron
Fig. 1. Surface plots for TBM removal efficiency versus H₂O₂ initial concentration and (a) FeSO₄/soil weight ratio, (b) ultrasound waves power, and (c) pollution loading (black points represent the experimental results).
Table 4. The Coefficient of Full Quadratic Model for Sono-Fenton Removal of Mercaptan

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>t-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$</td>
<td>90.1629</td>
<td>258.854</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>3.9129</td>
<td>20.801</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1.2971</td>
<td>6.895</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>3.0446</td>
<td>16.185</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>-1.3771</td>
<td>-7.321</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_{11}$</td>
<td>0.3717</td>
<td>2.157</td>
<td>0.047</td>
</tr>
<tr>
<td>$\beta_{22}$</td>
<td>-1.2083</td>
<td>-7.011</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_{33}$</td>
<td>-0.7383</td>
<td>-4.284</td>
<td>0.001</td>
</tr>
<tr>
<td>$\beta_{44}$</td>
<td>0.7792</td>
<td>4.521</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>-0.6469</td>
<td>-2.808</td>
<td>0.013</td>
</tr>
<tr>
<td>$\beta_{13}$</td>
<td>-1.5231</td>
<td>-6.611</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_{14}$</td>
<td>0.5694</td>
<td>2.471</td>
<td>0.025</td>
</tr>
<tr>
<td>$\beta_{23}$</td>
<td>1.3531</td>
<td>5.873</td>
<td>0.000</td>
</tr>
<tr>
<td>$\beta_{24}$</td>
<td>-0.1144</td>
<td>-0.496</td>
<td>0.626</td>
</tr>
<tr>
<td>$\beta_{34}$</td>
<td>0.1344</td>
<td>0.583</td>
<td>0.568</td>
</tr>
</tbody>
</table>

Fig. 2. Pareto analysis for main effects and interactions.
bivalent ion appears in the reaction of Fenton as a catalyst, leading to the formation of hydroxyl radicals. Furthermore, an increase in the amount of FeSO₄ beyond the optimum amount results in initiating undesirable side reactions and terminating the chain (reactions 5 and 6), which leads to the reduction of hydroperoxide radicals and formation of iron trivalent ion, and eventually decrease in the oxidation power.

\[ \text{HO}_2^- + \text{Fe}^{2+} \rightarrow \text{O}_2 + \text{H}^+ + \text{Fe}^{3+} \]  \hspace{1cm} (5)

\[ \text{HO}_2^- + \text{Fe}^{3+} \rightarrow \text{HO}_2^- + \text{Fe}^{5+} \]  \hspace{1cm} (6)

Figure 5 represents the effect of increasing the wave power. As shown, an increase in wave power in the range of 20-100 W results in enhancing the removal efficiency. According to the theory of cavitation, compression and

### Table 5. Details of ANOVA for Mercaptan Removal from Soil by Sono-Fenton Process

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>MS</th>
<th>F value</th>
<th>P value</th>
</tr>
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<tr>
<td>Regression</td>
<td>14</td>
<td>836.417</td>
<td>59.744</td>
<td>63.46</td>
<td>0.001</td>
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<tr>
<td>Linear</td>
<td>4</td>
<td>696.162</td>
<td>174.04</td>
<td>184.86</td>
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<tr>
<td>[H₂O₂]₀</td>
<td>1</td>
<td>367.462</td>
<td>367.462</td>
<td>390.31</td>
<td>0.000</td>
</tr>
<tr>
<td>[Fe:S]₀</td>
<td>1</td>
<td>48.479</td>
<td>48.479</td>
<td>51.49</td>
<td>0.001</td>
</tr>
<tr>
<td>W</td>
<td>1</td>
<td>222.468</td>
<td>222.468</td>
<td>236.3</td>
<td>0.000</td>
</tr>
<tr>
<td>[Me]₀</td>
<td>1</td>
<td>57.753</td>
<td>57.753</td>
<td>61.34</td>
<td>0.001</td>
</tr>
<tr>
<td>Square</td>
<td>4</td>
<td>61.461</td>
<td>15.365</td>
<td>16.32</td>
<td>0.001</td>
</tr>
<tr>
<td>[H₂O₂]₀ *[H₂O₂]₀</td>
<td>1</td>
<td>7.06</td>
<td>4.221</td>
<td>4.48</td>
<td>0.050</td>
</tr>
<tr>
<td>[Fe:S]₀ *[Fe:S]₀</td>
<td>1</td>
<td>28.657</td>
<td>29.146</td>
<td>30.96</td>
<td>0.001</td>
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<tr>
<td>W*W</td>
<td>1</td>
<td>17.698</td>
<td>15.065</td>
<td>16</td>
<td>0.001</td>
</tr>
<tr>
<td>[Me]₀ *[Me]₀</td>
<td>1</td>
<td>8.046</td>
<td>8.046</td>
<td>8.55</td>
<td>0.010</td>
</tr>
<tr>
<td>Interaction</td>
<td>6</td>
<td>78.794</td>
<td>13.132</td>
<td>13.95</td>
<td>0.000</td>
</tr>
<tr>
<td>[H₂O₂]₀ *[Fe:S]₀</td>
<td>1</td>
<td>6.695</td>
<td>6.695</td>
<td>7.11</td>
<td>0.017</td>
</tr>
<tr>
<td>[H₂O₂]₀ *W</td>
<td>1</td>
<td>37.119</td>
<td>37.119</td>
<td>39.43</td>
<td>0.000</td>
</tr>
<tr>
<td>[H₂O₂]₀ *[Me]₀</td>
<td>1</td>
<td>5.187</td>
<td>5.187</td>
<td>5.51</td>
<td>0.032</td>
</tr>
<tr>
<td>[Fe:S]₀ *W</td>
<td>1</td>
<td>29.295</td>
<td>29.295</td>
<td>31.12</td>
<td>0.001</td>
</tr>
<tr>
<td>[Fe:S]₀ *[Me]₀</td>
<td>1</td>
<td>0.209</td>
<td>0.209</td>
<td>0.22</td>
<td>0.644</td>
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<tr>
<td>W*[Me]₀</td>
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<td>0.289</td>
<td>0.289</td>
<td>0.31</td>
<td>0.587</td>
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<tr>
<td>Residual error</td>
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<td>15.063</td>
<td>0.941</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>10</td>
<td>12.336</td>
<td>1.234</td>
<td>2.71</td>
<td>0.117</td>
</tr>
<tr>
<td>Pure error</td>
<td>6</td>
<td>2.727</td>
<td>0.455</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>30</td>
<td>851.48</td>
<td>R² = 98.23%</td>
<td>R²(adj) = 96.68%</td>
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</tr>
</tbody>
</table>

Fig. 3. Effect of H$_2$O$_2$ concentration on mercaptan removal from the soil.

Fig. 4. Effect of FeSO$_4$/soil weight ratio on mercaptan removal from the soil.

Fig. 5. Effect of ultrasound waves power on mercaptan removal from the soil.
expansion cycles are produced during the ultrasound waves emission which exert positive and negative pressures respectively on a liquid. Accordingly, micro bubbles are created and an environment with high temperature and high pressure is formed by bursting bubbles, which provides the conditions for the destruction of pollutants. In a situation where the wave power increases, the power of the bubble increases in the slurry phase. In addition, by increasing the energy absorption by the bubble, the pressure and temperature of the bubble increase and according to the reactions 7-13, more increase takes place in the possibility of formation of hydroxyl radical. Further, more turbulence in the slurry phase retains the concentration gradient between the soil and slurry phases, which helps transfer the TBM from soil particles to the slurry phase.

$$\text{H}_2\text{O} + \rightarrow \cdot\text{OH} + \cdot\text{H}$$  \hspace{1cm} (7)

$$\text{O}_2 + \rightarrow 2\cdot\text{O}$$  \hspace{1cm} (8)

$$\cdot\text{OH} + \cdot\text{O} \rightarrow \cdot\text{OOH}$$  \hspace{1cm} (9)

$$\cdot\text{O} + \text{H}_2\text{O} \rightarrow 2\cdot\text{OH}$$  \hspace{1cm} (10)

$$\cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{OOH}$$  \hspace{1cm} (11)

$$\text{Pollutants} + \cdot\text{OH} + \rightarrow \text{Degradation products}$$  \hspace{1cm} (12)

$$\text{Pollutants} + \cdot\text{OOH} + \rightarrow \text{Degradation products}$$  \hspace{1cm} (13)

Figure 6 displays the influence of increasing the amount of TBM contaminant on its removal efficiency. As shown, an increase in the initial concentration of pollutants reduces the efficiency of the decomposition; however, the slope of these changes has a decreasing trend. The formation of hydroxyl radicals is not responsive to the higher amount of this pollution in conditions where the amounts of H$_2$O$_2$ and FeSO$_4$ are constant. However, based on the experiments, there is a strong reaction between the mercaptan and the oxidizing agents by increasing pollution load from a certain limit; so that reaction products in the gas phase escape with high pressure from the reaction vessel. The resulting heat causes the mercaptan to be released as a volatile material more rapidly and the decreasing trend of removal efficiency is limited. In this situation, the removal process also follows the thermal purge mechanism, in addition to the sonochemical mechanism.

Finally, the optimization study indicated that the complete treatment was obtained in the H$_2$O$_2$ concentration of 1 g l$^{-1}$, the iron sulfate/soil weight ratio of 0.004, the wave power of 100 W, and the TBM load of 25000 ppm, which is consistent with the results of complementary experiments. The TBM removal efficiency is increased in this work compared with previous works using H$_2$O$_2$/KMnO$_4$/NaClO system with a removal percentage of 95.7\% [16] and using ultrasound with a removal percentage of 82.8\% [17]. Based on the results, the sono-Fenton method can be useful as a suitable strategy for removing mercaptan volatile contaminants.
Regarding the results of the present study, the sono-Fenton method has a high ability to eliminate soil contamination with high adhesion. In addition, this method can be effective on the pollutant in the short term, which is a significant advantage in eliminating mercaptan contamination with a nasty smell and harmful environmental and health effects.

**CONCLUSIONS**

In the present study, a sonochemical oxidation method was used for rapid deodorizing from TBM-contaminated soil. An optimum condition for complete removal of contamination was obtained in the H$_2$O$_2$ concentration of 1 g l$^{-1}$, the FeSO$_4$/soil weight ratio of 0.004, the ultrasound wave power of 100 W, and the TBM load of 25000 ppm. The suggested model was in a good agreement (R$^2$ = 98%) with experiments. The Pareto analysis indicated that initial concentration of H$_2$O$_2$ is the most influential parameter (43%) in the studied process. The present study showed that the sono-Fenton method has a high ability to eliminate soil contamination with high adhesion. The use of ultrasound waves along with Fenton reagents will improve the oxidation process to eliminate the unpleasant smell.

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**REFERENCES**

[12] Tsai, T. T.; Kao, C. M.; Surampalli, R. Y.; Liang, S. H., Treatment of fuel-oil contaminated soils by biodegradable surfactant washing followed by fenton-


