Fast and environmental-friendly degradation of tert-butyl mercaptan from contaminated soil using bimetallic-modified Fenton process

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In this work, the fast remediation of tert-butyl mercaptan from the polluted soil via a bimetallic Fenton treatment that included Fe²⁺/Fe³⁺/Fe⁰/Cu²⁺ in the presence of gasoline was studied. The analysis of variance and the Pareto analysis resulting from the central composite design (CCD) showed that the H₂O₂, CuSO₄, Fe₃O₄ nanoparticles, nano zerovalent iron (nZVI), and gasoline initial concentrations as a secondary contaminant were influential factors on the removal efficiency of tert-butyl mercaptan (with an effectiveness of 2.09%, 13.38%, 1.92%, 2.01%, and 39.73% respectively). Moreover, the interaction of H₂O₂/nZVI, H₂O₂/nFeO₄, H₂O₂/CuSO₄, nZVI/nFeO₄, and nZVI/CuSO₄ had a positive effect on removal efficiency, while nFeO₄/CuSO₄ had a negative one. Surprisingly, the mixing of nZVI and nFeO₄ before adding them to the reactor did not affect the removal efficiency. The optimum conditions suggested for the maximum removal efficiency of tert-butyl mercaptan were the minimum levels of the initial gasoline concentration (2.5 %w/w), a maximum level of CuSO₄ (0.12 %w/w), and an optimum concentration of H₂O₂, nano-ZVI, and nano-FeO₄ (8.92 %w/w, 0.1194 %w/w and 0.0898 %w/w, respectively) in the studied intervals. This condition led to a 99.27% efficiency removal of tert-butyl mercaptan removal in 20 minutes without pH and temperature adjustments.

1. Introduction
Tert-butyl mercaptan is widely used for various purposes such as natural gas odorization, the rubber industry, etc. The release of this odorant hydrocarbon has significant public safety health and environmental concerns. Exposure to tert-butyl mercaptan could lead to skin and eye irritation, other allergic reactions, muscular paralysis, dizziness, nausea, and central nervous system depression [1,2]. Furthermore, the secondary environmental impact of tert-butyl mercaptan (repulsive odor), including social dissatisfaction and economic problems due to the loss of tourist revenue, signify the importance of the remediation of this organosulfur. Over the last decades, a modified Fenton treatment has been developed for the remediation of soil and groundwater contaminated by a wide variety of hydrocarbons such as persistent organic pollutants (POPs) [3], polychlorinated biphenyls (PCBs) [4], nonaqueous-phase liquids (NAPLs) [5], polycyclic aromatic hydrocarbons (PAHs) [6] and gasoline [7]. In some studies, the Fenton treatment has been modified using iron nanoparticles to improve its removal efficiency with lower environmental impact [8-10]. The main reactions of the Fenton treatment process, which are based on the formation and consumption of hydroxyl radicals [11], are represented as follows [12]:

H₂O₂+Fe²⁺→Fe³⁺+OH*+OH⁻   (1)
Fe³⁺+H₂O₂→Fe²⁺+HO₂⁻+H⁺   (2)
*OH+RH→*R+H₂O   (3)
*R+H₂O₂→ROH+*OH⁻   (4)
*OH+Fe³⁺→Fe⁰+OH⁻   (5)
*OH+H₂O₂→H₂O+*HO₂   (6)
*OH+*OH→H₂O₂   (7)

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The mercaptan can be attacked with a hydroxyl radical to form disulfide and sulfonic acid. The overall reaction of mercaptan with hydrogen peroxide is represented in reactions 16 and 17 [13].

\[ 2\text{RSH} + \text{H}_2\text{O}_2 \rightarrow \text{RSSR} + 2\text{H}_2\text{O} \]  \hspace{1cm} (16)

\[ \text{RSH} + 3\text{H}_2\text{O}_2 \rightarrow \text{SO}_3\text{H} + 3\text{H}_2\text{O} \]  \hspace{1cm} (17)

Over time, the modified Fenton treatment has been favored to obtain more efficient hydrocarbon removal [6,12,14,15]. In this method, hydrogen peroxide in a catalyzed system [16-18] with goethite [19], stabilizers and chelating agents [20,21], or magnetite [22-24] were used to remove some of the hydrocarbons. Moreover, various factors such as the pollutant aging and its physicochemical properties, organic matter of soil, reactant dosage, pH, soil texture, reaction time, and type of catalyst and stabilizers could affect the soil remediation efficiency [3,25]. There are a few studies concerning the remediation of tert-butyl mercaptan [26] via the Fenton modified process. Moreover, the removal of tert-butyl mercaptan from soil by a combination of a modified Fenton method with K\text{MnO}_4 and Na\text{ClO} [27], sonication process [28], sono-Fenton process [29], and aerobic biodegradation [30] have been studied. These remediation processes investigate effective factors such as the initial oxidant concentration, iron ion concentration, sonication power, pollution load, etc. But so far, no one has investigated the impact of a bimetallic system such as copper/iron. Recently, nano-scale catalysts with enhanced reactivity have been widely applied to remediate contaminated soil [31-34]. Nanoparticles can pass through the porous media and remain suspended in aquifer systems due to their size. They have the potential capacity to be used for soil remediation. Magnetite nanoparticles (nFe\text{O}_2) have an inverse spinel structure with an FCC (face-centered cubic) unit cell. They contain both trivalent and divalent iron ions, where Fe\text{III} occupies both the tetrahedral and octahedral sites while Fe\text{II} occupies only the octahedral sites [22]. The use of nFe\text{O}_2 is a good alternative because it can be separated and reused to solve the recovery problem of the nanoparticles, as well as reducing remediation costs. Zero-valent iron (ZVI) is another catalyst which has been applied for a Fenton-like reaction. Recently, nano-scale zerovalent iron (nZVI) has been widely used to remediate contaminated soil and water [35-38]. Transition metals such as Ni(II) or Cu(II) and Co(II) can form complexes on the surface of solid iron in an aqueous Fenton system which can increase the reactivity of the iron nano-particles by producing reactive oxidants [39,40]. This modification leads to the formation of Fe ions that can be used for the oxidative removal of the pollutant. Since the electron affinity of Cu (1.235 eV) is greater than Ni (1.156 eV) [41,42], CuSO\text{4} is selected as an additive. Several studies used the Cu ion or bimetallic system in the Fenton treatment [43], but none of them used three types of iron ions, namely Fe\text{II}, Fe\text{III}, and Fe\text{0}. The Fe-Cu bimetallic oxides, supported an aluminum-containing MCM-41 using 0.049 mol/L of H\text{2}O\text{2}in Fenton system, 47% TOC reduction was achieved (pH=4, T=60 °C) [44]. Also, functional kaolin-supported bimetallic Fe/Ni nanoparticles (K-Fe/Ni) were applied for the removal of Direct Black G (DBG) [45]. In other work, a CuFe/SBA-15 bimetallic catalyst was utilized for the Fenton degradation of N, N-diethyl-p-phenylation diamine (DPD) with 83% destruction within 120 min [46]. Gong et al. used aerobic degradation of 4-chlorophenol (4-CP) over bimetal modified nZVI (Bi/Fe\text{0}) due to the generation of a reactive oxygen species. In this method, the bismuth covering on the Fe\text{0} surface was under a zero-valent state [47]. Due to the social and environmental consequences of tert-butyl mercaptan and the little research concerning its remediation, this work aims to study the tert-butyl mercaptan oxidation yields in polluted soil via a modified Fenton process using bimetallic nano-particles of magnetite. In this work, the mass fraction of CuSO\text{4}, Fe\text{3}O\text{4} nanoparticles, and nZVI to the soil as well as the initial concentration of H\text{2}O\text{2} with their positive, negative, and opposing effects were investigated. Central composite design (CCD) that was based on response surface methodology (RSM) was implemented to design the experiments. It led to the minimizing of the number of the experiments compared to the “one-factor-at-a-time” statistical approach [48] and analyzing of the effects of the factors and their interactions [49], mathematical modeling, and predict the optimal experimental condition [50-54]. To the best of our knowledge, enhanced remediation of tert-butyl mercaptan from polluted soil by use of CuSO\text{4}, Fe\text{3}O\text{4} nanoparticles, and nZVI in the Fenton treatment process has not been reported so far.

2. Materials and methods

2.1. Contaminated soil

Tabriz is located in Iran’s East Azerbaijan province. It is a historical and tourist city with a population of more than 1.5 million. Tert-butyl mercaptan has been widely used for natural gas odorization in Tabriz. The characteristics of the sample soil collected from the industrial zone of this city are presented in Table 1. This soil was sampled from a 1-meter depth.
2.2. Chemical reactants and reactor

The reactants used for the tests and GC calibration were hydrogen peroxide (35% w/v) and tert-butyl mercaptan [55] (98% w/v), which were reagent grade from the Merck Company (Germany). Some of the physical and chemical properties of tert-butyl mercaptan are shown in Table 2. CuSO₄ (anhydrous, powder, ≥99.99% trace metals basis) and Fe₂O₃ nano powder (50-100 nm particle size, 97% trace metals basis and average surface area >60 m²/g) were supplied by Sigma- Aldrich. The nZVI (average particles size of 50 nm, an average surface area of 20-25 m²/g, a narrow particle size distribution of 20-100 nm and a high content of iron in the range of 80-90 %wt) was purchased from NANO IRON (Czech Republic). The deionized water was produced with a Pars Azma deionizer. All parts of the reactor were washed with distilled water and sterilized at 110 °C for 50 min in order to eliminate all undesirable contaminants and microbial activity (the optimal temperature for microbial activity is 35 °C [56]). This sterilizing process was repeated five times. All experiments were performed in the batch reactor, which was made from 100 ml cylindrical glass (Figure 1). The polluted soil was agitated with a 20 rpm agitation system. The first and final concentration of the tert-butyl mercaptan in the soil system was monitored from five points around the reactor. These five points were averaged and recorded as the final result.

Table 2. Physical and chemical properties of tert-butyl mercaptan [55].

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th>Hill Formula</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar Mass: 90.1872 g/mol</td>
<td>C₄H₉S</td>
<td>(CH₃)₂CSH</td>
</tr>
<tr>
<td>Boiling point: 63.7-64.2 °C</td>
<td>Colorless liquid, Stable and Flammable</td>
<td></td>
</tr>
<tr>
<td>Relative density (water = 1): 0.80</td>
<td>Solubility:</td>
<td></td>
</tr>
<tr>
<td>Vapor density: 3.1 (Air = 1)</td>
<td>- Very soluble in alcohol, ether and liquid hydrogen sulfide</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure: 181 mm Hg @ 25 °C (Extrapolated)</td>
<td>- Slightly soluble in water (2.0×10⁻³ mg/L @ 25 °C (estimated))</td>
<td></td>
</tr>
<tr>
<td>Dissociation Constant: pKa = 11.22 @ 25 °C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3. Material analyzing

Amorphous and crystalline iron and manganese oxyhydroxides were analyzed by citrate-bicarbonate-dithionite extractions [57]. For determining the organic carbon content, the sample soil was analyzed by combustion at 900 °C with the evolved CO₂ trapped in KOH and measured by the back titration of the unreacted OH⁻ [58]. The amount of the contaminant (tert-butyl mercaptan) in the polluted soil in parts per million by weight (ppm) were analyzed by a gas chromatograph (Agilent 7890) that was equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD) and an HP-Plot Q column. The fuel and carrier gas was H₂ (99.999%), the support gas was zero-grade dry air, and the make-up gas was He (99.999%) that were obtained from the Sabalan Company. The temperature program began at 105 °C for 2 min, ramped at 12 °C/min to 240 °C, and was held at 240 °C for 4 min with the column head gauge pressure of 3.9 psi. The injection port and detector temperatures were at 170 and 270 °C, respectively [27].

2.4. Procedure

A constant amount of soil (20 gr) was contaminated with gasoline, and tert-butyl mercaptan was added to the batch reactor. Next, the initial concentration of tert-butyl mercaptan was measured. Then, 5-level amounts of Fe₂O₃ nanoparticles (97% trace metal), nZVI (range of 80-90 %wt.), and CuSO₄ (99.99% trace metal) were added to the soil respectively. The polluted soil was oxidized with 20 ml of H₂O₂ and agitated for progress oxidation (20 min) with no temperature and pH adjustments. All experiments were conducted at the initial temperature of 24 °C and an initial pH of 6.6. Limited time interval resulted in a minimum influence of biodegradation, due to the slower reaction of the biodegradation process compared with chemical oxidation [30]. The removal efficiency of mercaptan contamination (%R) as a function of time is given by Eq. 18.
Removal efficiency($\%$) = \( \frac{C_1 - C_2}{C_1} \times 100 \) \hspace{1cm} (18)

Where $C_1$ and $C_2$ are the initial tert-buty mercaptan concentration (ppm) and its concentration after reaction time (ppm), respectively.

2.5. Design of experiments

In this study, a central composite design (CCD) based on the response surface method (RSM) was used to obtain the appropriate effects of the main factors and their interaction, which led to a mathematical model for the prediction of the remediation behavior. This method is an efficient way of determining the optimized condition [59]. The five factors under study included the initial concentrations of $H_2O_2$ (\%w/v), $Fe_3O_4$ nanoparticles to soil ratio (\%w/w), $nZVI$ to soil ratio (\%w/w), CuSO$_4$ to soil ratio (\%w/w), and initial concentration of gasoline contaminant (\%w/w). Their levels were determined by pre-experiment, safety, and legal considerations. The concentration ranges and levels of reactants are shown in Table 3.

### Table 3. Experimental factors and their ranges and levels

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Symbol</th>
<th>Factor Code</th>
<th>Ranges and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>$nZVI$ to soil ratio (%w/w)</td>
<td>$nZVI:S_o$</td>
<td>$X_1$</td>
<td>0.04 0.06 0.08 0.10 0.12</td>
</tr>
<tr>
<td>Initial $H_2O_2$ concentration (%w/v)</td>
<td>$H_2O_2_o$</td>
<td>$X_2$</td>
<td>1 3 5 7 9</td>
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<tr>
<td>CuSO$_4$ to soil ratio (%w/w)</td>
<td>CuSO$_4$:S$_o$</td>
<td>$X_3$</td>
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<tr>
<td>Initial gasoline to soil ratio (%w/w)</td>
<td>(I.C.S)$_o$</td>
<td>$X_4$</td>
<td>2.5 5 7.5 10 12.5</td>
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<tr>
<td>$Fe_3O_4$ to soil ratio (%w/w)</td>
<td>$Fe_3O_4$:S$_o$</td>
<td>$X_5$</td>
<td>0.03 0.05 0.07 0.09 0.11</td>
</tr>
</tbody>
</table>

Table 4. The 5-factors 5-level CCD matrix with the observed and the predicted responses.

<table>
<thead>
<tr>
<th>Standard order</th>
<th>Run order</th>
<th>Block</th>
<th>Coded values</th>
<th>Removal efficiency (%)</th>
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<td>14</td>
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<td>16</td>
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<td>24</td>
<td>3</td>
<td>2</td>
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</tr>
</tbody>
</table>

A blocking technique was used for investigating the reactant addition mode. In mode 1, $nZVI$ and $Fe_3O_4$ were mixed together and then added to the contaminated soil. In mode 2, $nZVI$ and $Fe_3O_4$ were poured into the reactor separately. Moreover, a randomization technique was used to guard against unknown and uncontrolled factors as lurking
nuisance factors. The coded variables resulting from Eq. 19 were used for statistical calculations for simplicity in the experimental design as follows:

\[ x_i = \frac{X_i - X_c}{\delta X} \]  

(19)

where \( x_i \), \( \delta X \), \( X_i \), and \( X_c \) are the coded value of the independent variables, the step change, the actual values of the independent variables, and the actual values of the independent variables at the center point, respectively.

3. Results and discussion

3.1. CCD method

The design of the experiment via CCD in the 5-factor 5-level matrix is summarized in Table 4. In this study, 33 experiments were performed: 16 cubic points, 7 replicates at the center point in cubes and axial (\( \alpha = 0 \)), and 10 axial points (\( \alpha = \pm 2 \)). Blocks 1 and 2 represent the experiments which were conducted in nZVI and nFeO4 addition mode 1 and 2, respectively.

For the prediction of the response, a quadratic polynomial response was used as Eq. 20:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \]  

(20)

Where, \( Y \), \( x_i \) and \( x_{ij} \) are the response variable, coded independent variables, coded interaction term and random error accounting for the differences between observed and predicted results, respectively. \( \beta_0 \), \( \beta_i \), \( \beta_{ij} \) and \( \varepsilon \) are intercepting term, linear, quadratic and interaction effects in the prediction model, respectively. \( i \) and \( j \) represent the index numbers for the patterns, in which \( i \neq j \) must be observed for the interaction term.\( k \) denotes the number of input variables [60,61]. According to the results of the experiments and those of Eq. 20, to predict the response concerning the main factors and their interactions, an experimental mathematical model was obtained in coded values (Eq. 21).

\[ Y = 74.4903 + 0.8031 x_1 + 0.8176 x_2 + 2.0704 x_3 - 3.5674 x_4 + 0.7833 x_5 - 0.8881 x_1 x_2 - 0.7007 x_1 x_3 - 0.0631 x_1 x_4 + 0.4593 x_4 x_4 - 1.0388 x_2 x_4 + 0.9814 x_2 x_3 + 1.3794 x_3 x_3 + 0.2189 x_1 x_4 + 1.4496 x_1 x_5 + 0.9975 x_2 x_5 + 0.4070 x_3 x_5 + 0.692 x_4 x_5 - 5 x_1 x_2 x_3 x_4 x_5 - 1.8655 x_1 x_2 x_3 x_5 - 0.3725 x_1 x_3 x_5 \]  

(21)

3.2. Analysis of variance (ANOVA)

Based on the results from Table 4, the analysis of variance (ANOVA) is summarized in Table 5. Because the significance level (\( \alpha \)) is 0.05 for a certain degree of freedom (DF), if the \( P \)-value for each factor is smaller than 0.05, it is recognized as an effective factor [62-64].

According to Table 5, the iron catalysts addition mode (catalysts mixing before/after addition to soil) is not an effective factor in the studied interval because the \( P \)-value is greater than 0.05 for the blocks (\( P \)-value=0.103). Also, the \( P \)-value of the lack-of-fit (0.617) indicates that variations in the data around the mathematical model (Eq. 21) are not significant relative to the pure error and adequately fits the data with the high correlation coefficient (\( R^2=0.9851 \)) [65; 66]. Moreover, the \( P \)-values show that the linear, square and interactions are significant on the variation in the removal efficiency of tert-butyl mercaptan (\( P \)-values<0.05). Table 6 shows the \( P \) and \( t \) values for the estimated regression coefficients. This table indicates that the five main factors and the interactions effect of \( \text{H}_2\text{O}_2/\text{nZVI}, \text{H}_2\text{O}_2/\text{nFeO}_4, \text{H}_2\text{O}_2/\text{CuSO}_4, \text{nZVI/CuSO}_4, \text{nZVI/nFeO}_4, \) and \( \text{CuSO}_4/\text{nFeO}_4 \) are significant in the model.

![Table 5](image)

<table>
<thead>
<tr>
<th>Terms removal of tert-butyl mercaptan</th>
<th>Coefficient</th>
<th>t-Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
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<td>( \beta_0 )</td>
<td>74.9903</td>
<td>203.471</td>
<td>0.000</td>
</tr>
<tr>
<td>( \beta_1 )</td>
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<td>4.009</td>
<td>0.002</td>
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<td>( \beta_2 )</td>
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<td>( \beta_{11} )</td>
<td>-0.8881</td>
<td>-4.975</td>
<td>0.000</td>
</tr>
<tr>
<td>( \beta_{12} )</td>
<td>-0.7007</td>
<td>-3.925</td>
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</tr>
<tr>
<td>( \beta_{13} )</td>
<td>0.0631</td>
<td>0.353</td>
<td>0.731</td>
</tr>
<tr>
<td>( \beta_{14} )</td>
<td>0.4593</td>
<td>2.573</td>
<td>0.026</td>
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<tr>
<td>( \beta_{15} )</td>
<td>-1.0388</td>
<td>-5.820</td>
<td>0.000</td>
</tr>
<tr>
<td>( \beta_{12} )</td>
<td>0.9814</td>
<td>4.000</td>
<td>0.002</td>
</tr>
<tr>
<td>( \beta_{13} )</td>
<td>1.3794</td>
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<td>( \beta_{14} )</td>
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<td>5.897</td>
<td>0.000</td>
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<tr>
<td>( \beta_{23} )</td>
<td>0.9975</td>
<td>4.066</td>
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</tr>
<tr>
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<td>1.659</td>
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</tr>
<tr>
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<td>2.823</td>
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<tr>
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<tr>
<td>( \beta_{35} )</td>
<td>-1.8655</td>
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<td>( \beta_{45} )</td>
<td>-0.3725</td>
<td>-1.518</td>
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</table>

The Pareto analysis resulting from Eq. 22 demonstrates the comparison between the influence of the main factors and the interactions [67].
Adding Cu(II) to induce better conditions for the supply of Fe(II) from nZVI (reaction 25), leads to a better remediation yield.

\[
\text{Cu}^{2+} + \text{Fe}^{0}(s) \rightarrow \text{CuO} + \text{Fe}^{2+}(s)
\]  

Figure 3. (a) The effect of nZVI to soil ratio (%w/w), (b) The effect of CuSO\(_4\) to soil ratio (%w/w), (c) The effect of initial tert-butyl mercaptan to soil ratio (%w/w) (d) The effect of Fe\(_2\)O\(_4\) to soil ratio (%w/w) and (e) The effect of initial H\(_2\)O\(_2\) concentration (%w/v) on tert-butyl mercaptan removal efficiency. T\(_\text{f}\)=24 °C, pH\(_0\)=6.6, Time=20 min.

As the CuSO\(_4\) participates in the reactions, the Cu\(^{2+}\) enhances the nZVI reactivity, but the SO\(_4^{2-}\) can block the reactive sites of Fe\(^{0}\) by the formation of inner-sphere complex-forming ligands [6,8] (reaction 24) that consume Fe\(^{2+}\) and Fe\(^{3+}\) and can reduce the removal efficiency. Therefore, CuSO\(_4\) participation leads to two opposite results because of Cu\(^{2+}\) and SO\(_4^{2-}\). As illustrated in Figure 3(b), increasing CuSO\(_4\) concentration increases the removal efficiency. Therefore, the positive effect of Cu\(^{2+}\) from reaction 25 and H\(_2\)O\(_2\)-CuSO\(_4\) has a higher removal efficiency when compared with that of reaction 26.

\[
\text{Fe}^{2+} + \text{Fe}^{3+} + \text{SO}_4^{2-} + 12\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{(OH)}_4 + 3\text{SO}_4 + 12\text{H}^+
\]  

When the initial gasoline concentration increases, the pollutant is more exposed to the oxidizing agent due to the solubility of mercaptan to gasoline. On the other hand, some possible zones of accumulated contaminant are created, which hinders the contact between the target organic pollutants, and this led to less accessibility for oxidation remediation. Furthermore, some of the oxidation agent molecules attack to degrade the gasoline. These two phenomena will lead to two competing results. As demonstrated in Figure 3(c), when the initial gasoline concentration increases, the removal efficiency falls, but its slope decreases. As demonstrated in Figure 3(d), the tert-butyl mercaptan removal efficiency increases as the Fe\(_2\)O\(_4\) nanoparticles are raised up to a certain level (about 0.09 %w/w) in constant amounts of the other main parameters ([H\(_2\)O\(_2\)]\(_0\)=5% %w/v, (nZVI:S)\(_0\)=0.08 %w/w, (CuSO\(_4\):S)\(_0\)=0.08 %w/w, (IC:S)\(_0\)=7.5 %w/w). But the removal efficiency falls with the further addition of nFe\(_2\)O\(_4\) due to the side and propagation reactions (Eqs. 5, 8 and 13). Figure 3(e)

Figure 3(b) shows that the addition of CuSO\(_4\) to the reaction increased the removal efficiency. With respect to reaction 24, the Fe(II) generated by the oxidation of the nZVI surface with H\(_2\)O\(_2\) is limited and is not enough to fully consume the H\(_2\)O\(_2\). Due to this phenomenon, hydroxyl radicals generated in the catalytic system (reaction 1) is low, and a cation needs to be added to enhance the reactivity of nZVI in the Fenton system by producing more •OH.

\[
\text{H}_2\text{O}_2 + \text{Fe}^{0}(s) \rightarrow 2\text{H}_2\text{O} + \text{Fe}^{2+}(s)
\]  

3.3. Effects of the main factors and interactions

The effects of the operational parameters on the removal efficiency of the tert-butyl mercaptan by the modified Fenton treatment are shown in Figure 3. As demonstrated in Figure 3(a), the removal efficiency of the tert-butyl mercaptan from polluted soil increases as the nZVI to soil ratio increases in constant amounts of the other main parameters ([H\(_2\)O\(_2\)]\(_0\)=5% %w/v, (CuSO\(_4\):S)\(_0\)=0.08 %w/w, (IC:S)\(_0\)=7.5 %w/w, (nFe\(_2\)O\(_4\):S)\(_0\)=0.07 %w/w). This figure shows that increasing the nZVI up to a certain level leads to higher tert-butyl mercaptan removal efficiency. But the removal efficiency decreases with any further addition of nZVI due to the side and propagation reactions (Eqs. 5, 8 and 13).

\[
P_i = \left( \frac{\beta_i}{\sum \beta_i} \right) \times 100 \quad i \neq 0
\]  

The Pareto graph analysis represents the percentage effect of each factor on the response (Figure 2). In order to obtain a simpler empirical model and a better fit for the removal efficiency, the insignificant terms can be removed from Eq. 19, which then represents the final model in coded form (Eq. 23).

\[
Y=74.4903+0.8031\times x_1+0.7833\times x_5-0.8881\times x_1^2-0.7007\times x_5^2+0.4593\times x_2^2-
1.0388\times x_3^2+0.9814\times x_1\times x_3+1.3794\times x_5\times x_3+1.4496\times x_1
x_5+0.9975\times x_3\times x_5+0.6925\times x_2\times x_5-1.8655\times x_1 x_5
\]  

Fig. 2. Pareto graphical analysis of the main factors and interactions.
illustrates the effect of the initial H$_2$O$_2$ concentration on tert-butyl mercaptan removal efficiency (\%R). This figure shows that the removal efficiency increases with the initial hydrogen peroxide concentration up to a certain level (about 7 \%w/v). Further increasing of H$_2$O$_2$ concentration leads to a decrease in tert-butyl mercaptan degradation efficiency. According to reactions 6, 7 and 15 [67; 69; 70] this result is due to a series of propagation reactions and scavenging that produce less reactive radicals such as hydroperoxide radicals and hydroxyl ions (‘OOH and OH’). According to Table 6 and the mathematical model (Eq. 21), the interaction between the initial H$_2$O$_2$ concentration and nZVI to soil ratio is an effective factor on the removal efficiency. Fe$^{2+}$ is an alternative to enable more extensive and greater contaminant oxidation. As represented in Figure 4, increasing the hydrogen peroxide concentration or nZVI to a certain level could increase the removal efficiency due to *OH radicals generation [67,71-73]. A higher concentration of H$_2$O$_2$ or nZVI decreases the removal efficiency due to a series of side and propagation reactions like Equations 5, 6, 7, 8 and 15 [67,69,70].

\[
\text{Fe}^{2+} + \text{Fe}^{2+} \rightarrow 3\text{Fe}^{3+}
\]  

\[(27)\]

Figure 5 illustrates that nZVI and nFe$_3$O$_4$ have an effective interaction which increases tert-butyl mercaptan removal efficiency. In a low concentration of nZVI, the removal efficiency falls due to the side reaction, which is illustrated before. This result is similar to nFe$_3$O$_4$. But when nZVI and nFe$_3$O$_4$ are used in the reaction, the Fe$_3$O$_4$ nanoparticles would restrain the formation of a passivated layer on the nZVI surface [74]. As a result, the nFe$_3$O$_4$ made a medium to promote the electron transfer between the nZVI and tert-butyl mercaptan. Because of the electron transfer from Fe$^0$ to magnetite Fe(III) (Eq. (27)) and the *OH formation in Fe$_3$/iron oxide suspensions, the Fe$_3$O$_4$/Fe$^0$ possessed a higher activity than the pure Fe$_3$O$_4$ or Fe$^0$.

\[\text{Fe}^0 + 2\text{Fe}^{2+} \rightarrow 3\text{Fe}^{3+}\]

\[
(27)
\]

Figure 6 and Table 6 show that the H$_2$O$_2$ and nFe$_3$O$_4$ interaction has a positive role on removal efficiency. As shown in reactions 2, 9 and 12, Fe$^{3+}$ is an alternative to enable fast and could promote a reaction by reactive radical generation for contaminant oxidation. In these reactions, Fe$^{3+}$ is consumed while Fe$^{2+}$ is generated. From the reactions 1 and 2, which, *OH is generated from H$_2$O$_2$/Fe$^{2+}$ while *OH$_2$ is generated from H$_2$O$_2$/Fe$^{3+}$. Therefore, Fe$^{2+}$ generation leads to higher tert-butyl mercaptan removal efficiency due to higher reactivity of OH compared with *OH$_2$. Figure 6 demonstrates that with low H$_2$O$_2$ concentration, an increase in nFe$_3$O$_4$ in the studied interval decreases the removal efficiency. This phenomenon is due to the side reaction that results from the excess Fe$^{2+}$ that is not fully consumed by the H$_2$O$_2$. As the H$_2$O$_2$ concentration is raised up to a certain level, the tert-butyl mercaptan removal efficiency increases and the Fe$^{2+}$ is fully used for the oxidation reaction.

\[
\%R = \frac{\text{Initial concentration} - \text{Removal concentration}}{\text{Initial concentration}} \times 100
\]

\[
(5)
\]
shown in reactions 28 and 29, the Cu$^{2+}$ can promote a reaction by reactive radical generation (*OH and *HO$_2$) for contaminant oxidation. This figure and Equation 23 shows that Cu$^{2+}$ affect, as a catalyst, are more than nFe$_2$O$_3$ and nZVI in the presence of H$_2$O$_2$ (H$_2$O$_2$/CuSO$_4$ > H$_2$O$_2$/nZVI > H$_2$O$_2$/nFe$_3$O$_4$).

$$\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \text{HO}_2^+ + \text{H}^+ \quad (28)$$

$$\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{OH}^+ + \text{OH}^- \quad (29)$$

Figure 7 demonstrates that when the H$_2$O$_2$ concentration was raised to a certain level, there was an increase in tert-butyl mercaptan removal efficiency. The maximum tert-butyl mercaptan removal efficiency was achieved in the maximum initial Cu$^{2+}$ concentration in the studied interval.

As shown in Figure 8 and Table 6, the interaction between nZVI and CuSO$_4$ plays a positive role in the tert-butyl mercaptan remediation process. The oxidation-reduction mechanism which can be suggested for Cu$^{2+}$ and nZVI interaction is justified by the difference in Cu$^{2+}$/Cu$^0$ and Fe$^{2+}$/Fe$^0$ standard potentials. A comparison between the standard redox potential of Cu$^{2+}$/Cu$^0$ and Fe$^{2+}$/Fe$^0$ indicate that Cu(II) can be reduced to Cu$^0$ because of electron transfer from the nZVI surface and oxidized iron ($E_{\text{Cu}^{2+}/\text{Cu}^0}(\text{aq})=+0.34 \text{ V} > E_{\text{Fe}^{2+}/\text{Fe}^0}(\text{aq})=-0.44 \text{ V at } 298 \text{ K})$ [75]. Therefore, Cu(II) leads to the release of Fe$^{2+}$ (reaction 25) from the nZVI surface, which is essential for the reaction with H$_2$O$_2$ to produce a higher content of *OH to enhance the removal efficiency.

Table 6 illustrates the effect of the CuSO$_4$ and nFe$_3$O$_4$ interaction on removal efficiency. Surprisingly, Figure 9 shows that the CuSO$_4$ concentration increases the tert-butyl mercaptan removal efficiency in the presence of the minimum nFe$_3$O$_4$ concentration while the maximum nFe$_3$O$_4$ level in the studied intervals decreased it. These phenomena could be a result of Cu(II) reduction [76,77] and Fe(II) oxidized to Fe(III) (reactions 30 and 31 [78,79]). In reaction 30, Fe(II) was consumed, and Fe(III) was produced.

As a result, reactions 1, 2, 9 and 12 showed that the Fe(III) reactions compared with the Fe(II) ones generated less reactive species, which led to lower tert-butyl mercaptan removal efficiency [80,81]. In reaction 1 with Fe(II), *OH was produced, while *HO$_2$ and O$_2$ were produced by the reaction of Fe(III) (reactions 2, 9 and 12), which were lower reduction potential compared with *OH [82]. In reaction 31, Cu(II) was reproduced, and *HO$_2$ was consumed in reactions 8, 9, 10, 11, 14 and 15. Moreover, SO$^{2-}$ consumed Fe$^{2+}$ and Fe$^{3+}$ due to reaction 26 and could reduce the removal efficiency.

$$\text{Cu(II)}_{\text{aq}} + \text{Fe(II)}_{\text{aq}} \leftrightarrow \text{Cu(I)}_{\text{aq}} + \text{Fe(III)}_{\text{aq}} \quad (30)$$

$$\text{Cu(I)}_{\text{aq}} + \text{O}_2 \leftrightarrow \text{Cu(II)}_{\text{aq}} + \text{*HO}_2 \quad (31)$$

The results of the experiments showed that the presence of Cu(II) had two opposite effects on removal efficiency. On the one hand, the positive role of the interaction of Cu$^{2+}$/nZVI and Cu$^{2+}$/H$_2$O$_2$ increased the removal efficiency, and on the other hand, the negative role of the Cu/nFe$_3$O$_4$ interaction caused it to fall. As presented in Figure 9, increasing the CuSO$_4$ concentration in the presence of the minimum concentration of nFe$_3$O$_4$ could raise the removal efficiency due to Fe$^{2+}$ generation that resulted from the CuSO$_4$/nZVI interaction. But the high concentration of CuSO$_4$ with the maximum nFe$_3$O$_4$ drops the removal efficiency due to Fe$^{2+}$ consumption resulting from the CuSO$_4$/nFe$_3$O$_4$ interaction. The results of the experiments showed that the presence of Cu(II) had two opposite effects on removal efficiency. On the one hand, the positive role of the interaction of Cu$^{2+}$/nZVI and Cu$^{2+}$/H$_2$O$_2$ increased the removal efficiency, and on the other hand, the negative role of the Cu/nFe$_3$O$_4$ interaction caused it to fall. As presented in Figure 9, increasing the CuSO$_4$ concentration in the presence of the minimum concentration of nFe$_3$O$_4$ could raise the removal efficiency due to Fe$^{2+}$ generation that resulted from the CuSO$_4$/nZVI interaction. But the high concentration of CuSO$_4$ with the maximum nFe$_3$O$_4$ drops the removal efficiency due to Fe$^{2+}$ consumption resulting from the CuSO$_4$/nFe$_3$O$_4$ interaction.
3.4. Determination of optimal condition for tert-butyl mercaptan removal efficiency

The prediction models showed that the maximum removal efficiency was 99.06% for CCD at the optimum condition in the studied intervals. The optimum condition which is listed in Table 7 suggests that the concentration of H$_2$O$_2$, nZVI, and nFe$_3$O$_4$ must be at a certain level in the presence of the maximum CuSO$_4$ and minimum initial gasoline concentration in the studied intervals. A verification experiment was conducted to verify the resulting optimized condition. The result showed that the maximum removal efficiency of tert-butyl mercaptan from the polluted soil was 99.27% according to the optimum condition. This efficiency was more than some methods like sonication and the modified Fenton process for tert-butyl mercaptan remediation from polluted soil [28].

In the results of this study, the maximum tert-butyl mercaptan removal efficiency (99.27%) was greater than those of the modified Fenton process (94.14%) [26], the combination of the Fenton with KMnO$_4$ and NaClO (95.71%) [27], and the sonication process (82.83%) [28] in the limited time interval. The nearly complete remediation of tert-butyl mercaptan was reported using the sono-Fenton process with the contaminant load of 25000 ppm [29], but it consumed much more energy for sonication compared with the bimetallic modified Fenton process in the present work.

4. Conclusions

Tert-butyl mercaptan is an organosulfur material and its remediation from soil is important to study. The modeling and optimization of tert-butyl mercaptan removal efficiency from polluted soil using a bimetallic-nano-modified Fenton process have not been studied before. Pareto analysis and ANOVA indicated that all investigated factors were effective in removal efficiency. Moreover, the interaction of H$_2$O$_2$/nZVI, H$_2$O$_2$/nFe$_3$O$_4$, H$_2$O$_2$/CuSO$_4$, nZVI/nFe$_3$O$_4$, and nZVI/CuSO$_4$ have a positive effect on the removal efficiency, while nFe$_3$O$_4$/CuSO$_4$ has a negative effect. The maximum tert-butyl mercaptan removal efficiency was achieved with the lower levels of initial gasoline concentration, the optimum concentration of H$_2$O$_2$, nFe$_3$O$_4$, nZVI, and the highest concentration of CuSO$_4$ in the studied interval. Surprisingly, iron catalysts addition mode (catalysts mixing before/after addition to soil) was not an effective factor in the studied interval. The method investigated in this study could be used for increasing the removal efficiency of similar organosulfur because of the positive interaction between the reactants.

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