Remediation of Spent Caustic in the Wastewater of Oil Refinery by Photo-Fenton Process

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Background & Aims of the Study: Currently, the advanced oxidation processes have received increasing attention for the treatment of industrial wastewater. In the present study, the photo-Fenton process was used for the remediation of the spent caustic in the wastewater of Kermanshah Oil Refining Company in Iran. The effluent comprising spent caustic is toxic dark brown with a high level of alkalinity.

Materials and Methods: Diluted wastewater covering the spent caustic from Kermanshah Oil refinery was used in this study in September 2018. In addition, the effects of operative factors, such as the initial concentrations of hydrogen peroxide ($\text{H}_2\text{O}_2$), ferrous ion, and initial chemical oxygen demand (COD), have been investigated. The response surface method and Box-Behnken design of experiments were employed to examine the effects of three independent variables on the response function to obtain the optimum conditions.

Results: Analysis of variance was performed to determine the significance of the effects of independent variables on the response function. Various amounts of variables were optimized for the removal of COD. At optimum conditions (i.e., an $\text{H}_2\text{O}_2$ concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l), the removal efficiency for COD was 91.5% after 60 min of reaction.

Conclusion: According to the obtained results, the suggested quadratic model demonstrated good correctness. The statistical analysis showed that the model was satisfactory to predict the performance of the process. The wastewater containing spent caustic cannot proficiently be degraded by ultraviolet radiation and hydrogen peroxide ($\text{H}_2\text{O}_2$) oxidation separately; however, the photo-Fenton method is verified to be operative and can considerably degrade this pollutant. One of the main disadvantages of this process in the treatment of spent caustic is that the optimum pH is near 3, and a considerable amount of acid is needed to neutralize and acidify the alkalinity of spent caustic.

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Background

Some companies, such as refineries and petrochemicals, are under more severe environmental rules to enhance monitoring and control their wastewater streams. One of the most difficult wastewater streams is created in
the process of extracting hydrogen sulfide, mercaptans, and organic acids from hydrocarbon streams. Often diluted caustic (NaOH) solutions are used in the oil refinery industries for the removal of acidic compounds and volatile (organic) sulfur combinations from gaseous streams and liquefied petroleum gas.

The use of caustic leads to the foundation of a waste product referred to as spent caustic (1). Spent caustic is a brown liquid with a sharp odor of sulfur compounds formed by washing sulfur compounds and other contaminants from light hydrocarbon compounds with a solution containing sodium hydroxide. This effluent has high salinity, high alkalinity, high sulfur content, and strong unpleasant odor that should be considered for disposal or purification (2-3).

Some approaches, including physical-chemical techniques or processes of customary oxidation, were used for the treatment of refinery wastewater. Although the oil itself can hold sulfur, the remediation technique is generally applied after the distillation of oil fraction, based on its contact with air, permitting the production of H₂S that is very resistant and corrosive (4).

In current decades, several studies have been carried out to develop a better technique for the remediation of spent caustic. Graaff et al. investigated the probability and benefits of a two-step procedure for the biological remediation of sulfide spent caustics in haloalkaline circumstances (5). There are three approaches to the remediation of industrial wastewater, including chemical physical and biological methods. However, they are non-destructive and only transfer contaminants from water to another phase and consequently making secondary pollution (6). Therefore, expensive processes, such as the post-treatment of solid-waste and production of the adsorbent supplies, are required in this regard (7).

The photo-Fenton oxidation is an upgrade of Fenton’s reagent with adding an irradiation source. According to the literature, it was reported that the degradation proficiency of the oxidation process enhanced under ultraviolet (UV) lighting, compared to that of the ordinary Fenton reaction. Therefore, the existence of UV illumination in the photo-Fenton method causes the photoreduction of ferric species into ferrous ion (8-9).

Some studies, such as a study carried out by Hsiungsheu et al., investigated the removal of more than 94% of chemical oxygen demand (COD) in wastewater using neutralization and Fenton system considerably reducing the COD and sulfide (10). In a study conducted by Rodriguez et al. on the treatment of caustic wastewater using the electro-Fenton process, 95% of COD was removed at a pH of 4, temperature of 40°C, and iron of 100 mg/l (11).

Abdullah et al. studied synthesized the treatment of spent caustic wastewater using the photo-Fenton oxidation process. They used the response surface method (RSM) for the experiment design of their study (12). Another study carried out by Chen et al., investigated the actual spent caustic wastewater remediation with the COD of 25000 by catalytic and typical wet air oxidation.

Many optimization approaches have been offered in industrial applications. In the traditional optimization approach, the one-factor-at-a-time manner method has many difficulties, such as being time-consuming, expensive, and unsuccessful at both the identification of the interactions among the parameters and prediction studies(13). The alternative to the classical technique is the utilization of statistical and mathematical experimental designs, such as Box-Behnken design (BBD), which was used in the present study.

In the current study, the synthetic wastewater containing spent caustic was treated by the photo-Fenton process. The present study examined the effect of different variables, such as the concentrations of H₂O₂, concentration of ferrous, and initial COD, on the efficiency of
COD removal using BBD.

**Materials & Methods**

**Materials**

The investigated wastewater was the effluent of the spent caustic from Kermanshah Oil Refining Company in Iran after dilution in distilled water with the succeeding properties (Table 1). The features of the spent caustic were not similar at different time points, and the amounts of parameters were not entirely constant. The spent caustic confirmation is greatly variable depending on the procedure condition. The FeSO₄.7H₂O and H₂O₂ solution (30% w/w) were supplied from Merck Company. Supplied manganese oxide (MnO₂) (≥99%) was provided by Sigma-Aldrich Company. In addition, distilled water was utilized in all the experiments.

**Photo reactor and experiments**

The COD content was originated from both inorganic and organic compounds (such as sulfides) in the spent caustic. The COD of the samples was determined by the HACH’s COD method utilizing a COD reactor and measured through the standard closed reflux and Colorimetric method [14]. The absorbance of the samples for the COD test was estimated using a spectrophotometer (Agilent 5443) at 600 nm. The pH was adjusted by NaOH or hydrochloric acid (0.1 M) and measured by pH Meter PT-10P (Sartorius Instrument, Germany).

All the experiments were conducted in a one-liter glass photoreactor. The system was equipped with a sampling system (Figure 1). A 15W Philips (UV-C) mercury lamp vertically placed at the center of the reactor was utilized as the source of light. The reactor was equipped with a water jacket with an external flow controlled through a thermostat for the adjustment and maintenance of the temperature at 25°C. The solution was mixed with a stirrer for preventing the precipitation of iron ions in the reactor and keeping the solution homogeneous.

The amount of 1000 ml of diluted wastewater was utilized in each experiment. The concentration of hydrogen peroxide, ferrous ions, and initial COD were the intended parameters, and it was aimed to decrease the percentage of COD removal. The reaction time was reported as 60 min in all the experiments. The percentage of COD removal was calculated using the following equation:

$$\text{Removal of COD}(%) = \left( \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \right) \times 100 \quad \text{Equation (1)}$$

### Table 1) Approximate properties of the studied wastewater (after dilution)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide</td>
<td>260 mg/l</td>
</tr>
<tr>
<td>NaOH</td>
<td>1200 mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>900 mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>13.0</td>
</tr>
<tr>
<td>Color</td>
<td>Dark brown</td>
</tr>
</tbody>
</table>

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**Figure 1)** Utilized schematic diagram of reactor in laboratory scale: 1) cooling water jacket; 2) magnetic stirrer bar; 3) ultraviolet lamp; 4) glass reactor; 5) magnetic stirrers; 6) input wastewater; 7) output wastewater; 8) cooling water input; 9) cooling water output; 10) electric connection
where $COD_0$ and $COD_t$ are considered the values of COD at the initial and $t$ times, respectively. The amount of $H_2O_2$ remaining in the samples, interfering with the COD test, was removed using MnO$_2$ powder. The samples were filtered for the separation of MnO$_2$ powders [15].

**Experimental design and statistical analysis**

The experimental design was utilized for the optimization of the percentage of COD removal in a scientific way. The impacts of hydrogen peroxide concentration ($X_{HP}$), ferrous concentration ($X_F$), and initial COD ($X_{COD}$) on the removal of COD were examined in order to optimize the procedure $X_{HP}X_FX_{COD}$. Table 2 tabulates the input variables ($X_{HP}$, $X_F$, and $X_{COD}$), along with the associated dimensions and values. The empirical results of the percentage of COD removal are shown in Table 3.

Among all the RSMs, experimental BBD needs a smaller number of experiments (i.e., a total of 15 experiments for three variables) [16]. Based on the design of the experiments, the following model was presented for the response variable ($COD$ Removal, %), as a polynomial equation of the independent variables:

$$\text{Res.} = b_0 + \sum b_iX_i + \sum\sum b_{ij}X_iX_j + \sum b_{ii}X_i^2 + \varepsilon \quad \text{Equation (2)}$$

where $b_0$ is a constant number; $\varepsilon$ is the remainder of the equation, $b_{ij}$ is a linear interaction between the input variables of $X_i$ and $X_j$ ($i = 1, 2$ and $j = 1, 2, 3j = 1, 2, 3$); $b_i$ is the slope of the variable; $b_{ii}$ is the second order of the input variable $X_i$ ($i = 1, 2, 3$).

Analysis of variance (ANOVA) was utilized to investigate the significance of each variable (i.e., operating parameter) in the polynomial equation (Equation 2) [17]. In ANOVA, a $p$-value of 0.05 was considered statistically significant. The $p$-values of less than 0.0500 determine the importance of model terms. The $p$-values greater than 0.10, demonstrate that the model terms are not important.

The statistical significance of the second-order models was defined by F-value. When the estimated F-value is higher than the F-value in Table 4, the $p$-value will be much less
indicating the importance of the statistical model. The estimated F-value is obtained by dividing the mean squares of regression (including linear, square, and interaction) by the mean squares of the residual as follows (18):

\[ F = \frac{MS_{Reg}}{MS_{Res}} \]

Equation (3)

The regression degree of freedom \((DF_{Reg})\) is the number of terms minus one. In addition, the residual degree of freedom \((DF_{Res})\) is the total degree of freedom minus the regression degree of freedom [18]. The design of the experiments was comprised of 15 tests (i.e., 13 tests and 2 replicates at the central point). Table 3 tabulates the percentages of COD removal. All the experiments were randomly conducted for the minimization of the experimental errors.

Results

Design of experiments and analysis of the response variance

Optimal conditions were determined in order to maximize the removal of COD using the photo-Fenton process. In the current study, the impacts of three independent variables (i.e., \(H_2O_2\) concentration, \(Fe^{2+}\) concentration, and initial COD) on the percentage of COD removal \((COD_{rem}%)\) were studied using BBD to obtain desirable conditions. The quadratic relationship was obtained using the least squares method for the determination of the response in terms of the three independent variables as follows:

\[ COD\ Rem = 76.9 - 0.0375X_{COD} + 0.162X_{Fe^{2+}} + 0.0482X_{H_2O_2} - 0.000006X_{COD}^2 - 0.000452X_{Fe^{2+}}^2 - 0.000044X_{H_2O_2}^2 - 0.000142X_{Fe^{2+}}X_{COD} + 0.000042X_{COD}X_{H_2O_2} + 0.000002X_{Fe^{2+}}X_{H_2O_2} \]

Equation (4)

Figure 2 illustrates the predicted values of the quadratic model for the percentage of COD removal, compared to the observed values. The calculated values for the percentage of COD removal were obtained using Equation 4.

Table 4 tabulates the findings of ANOVA for the evaluation of the COD removal model.
between the variables has a p-value of more than 0.05 indicating that the interaction of variables is non-significant. Moreover, the significance of the lack of fit is more than 0.05, indicating the model’s mismatch.

**Effects of operating variables**

Figures 3-5 depict the effects of hydrogen peroxide (200, 400, and 600 mg/l), Fe$^{2+}$ (50, 100, and 150 mg/l), and initial COD (300, 600, and 900 mg/l) concentrations on the removal of COD in spent caustic wastewater. The aforementioned figures illustrated the contour plots of COD removal based on these variables using Equation 4. The contour plots of the COD removal according to hydrogen peroxide, ferrous, and initial COD concentrations are depicted in Figure 3. In addition, the maximum percentage of COD removal was obtained in low values of COD and practically high values of hydrogen peroxide. In the photo-Fenton method, the efficiency of COD removal enhanced with an increase in H$_2$O$_2$ concentration.

Various amounts of Fe$^{2+}$ (range: 50-150 mg/l) were used to reach the optimal concentration. As illustrated in Figure 4, it is...
Figure 4) Contour plots of chemical oxygen demand (COD) removal in terms of ferrous and initial COD concentrations ($pH = 3$, $T = 25°C$, and $t = 60$ min)

Figure 5) Contour plots of chemical oxygen demand removal versus ferrous and hydrogen peroxide concentrations ($pH = 3$, $T = 25°C$, and $t = 60$ min)

clear that in the photo-Fenton process, the removal efficiency of COD increased with an increase in the dosage of ferrous ions based on the following equations (20):

\[ \text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \text{OH}^+ + \text{OH}^- \quad \text{Equation (5)} \]

\[ \text{Fe}^{+2} + \text{OH}^+ \rightarrow \text{OH}^- + \text{Fe}^{+3} \quad \text{Equation (6)} \]

In the photo-Fenton process, the creation of hydroxyl radicals and removal of COD increased with an increase in the concentration of Fe$^{2+}$ ions from 50 to 100 mg/l. Based on figures 3-5, the increase in the catalyst dosage was partly helpful. However, the catalyst should not be added without any limitations. High amounts of catalyst negatively affected the removal of COD, since the scavenging results might happen (Equations 7-9).

\[ \text{OH}^+ + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} \quad \text{Equation (7)} \]
\[ H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+} \quad \text{(Equation 8)} \]

\[ FeOOH^{2+} \rightarrow HO_2^+ + Fe^{2+} \quad \text{(Equation 9)} \]

At the high catalyst amounts, the additional catalyst would consume the produced hydroxyl radical. Higher catalyst quantities would clearly upsurge the treatment cost. Furthermore, the extreme catalyst dosage would result in the production of the high amounts of sludge, which would increase the requirement for the subsequent treatment of sludge.

At a pH of higher than 3, the main fraction of Fe (II) was precipitated as Fe(OH)\(_3\), fading the reaction between H\(_2\)O\(_2\) and Fe\(^{2+}\). In addition, in alkaline conditions, the removal of COD reduced because the H\(_2\)O\(_2\) degrades faster into H\(_2\)O and O\(_2\). Consequently, in the present study, according to the preliminary experiment, pH was fixed at 3 in all the tests and was not optimized.

**Optimization of operating conditions**

As illustrated in figures 3-5, it is obvious that the percentage of COD removal can be high in some conditions. The values of various variables were achieved using Design-Expert software (version 7.0.0) for the maximization of the percentage of COD removal. Table 5 tabulates the aforementioned optimal values, with the percentage of COD removal. As shown in Table 5, the maximum rate of COD removal was achieved under several conditions, including hydrogen peroxide concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l. Under the aforementioned conditions, the maximum rates of COD removal were reported as 95.25% and 91.5% by the model (Equation 4) and experiments with three replications, respectively.

**Discussion**

As previously mentioned, this study examined the effects of hydrogen peroxide and Fe\(^{2+}\) concentrations and initial COD values on the percentage of COD removal from spent caustic wastewater. Figures 3-5 illustrate the contour plots of the percentage of COD removal and aforementioned variables. In addition, the figures were plotted using Equation 4.

Figure 3 depicts a contour plot of the percentage of COD removal regarding H\(_2\)O\(_2\) concentration and initial COD. Accordingly, it was observed that the highest percentage of COD removal was achieved when utilizing the mean values for both variables (i.e., H\(_2\)O\(_2\) and Fe\(^{2+}\) concentration).

In the photo-Fenton process, an extreme increase in the concentration of Fe (II) reduced the efficiency of COD removal because the production rate of primary hydroxyl radicals is very high at high concentrations of Fe\(^{2+}\), mostly due to H\(_2\)O\(_2\) decomposition (see Equation 10). Consequently, numerous hydroxyl radicals are consumed by side reactions before being utilized for the removal of COD (20–21).

\[ H_2O_2 + h\nu \rightarrow 2^*OH \quad \text{(Equation 10)} \]

Furthermore, the brown turbidity of the solution can result from the high concentration of the ferrous ion. As a result, the absorption of UV light, which is essential for photolysis, is delayed leading to the recombination of OH\(^{-}\) radicals (Equation 11). This finding has been also reported in multiple other studies (22–23).

\[ Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {^*OH} \quad \text{(Equation 11)} \]

The impact of Fe\(^{2+}\) on the removal of COD...
is similar to the effect of H$_2$O$_2$ concentration (24). A study carried out by Nueza et al. investigated the treatment of caustic wastewater by the electrochemical process, and 93% of COD was removed (25). In a study conducted by Hawari et al. on the treatment of caustic wastewater, 98% and 99% were reported as COD and sulfide removal at a pH of 1.5, respectively (26). The benefits of the photo-Fenton process were less sludge formation, fewer chemicals, and time obligation but at the cost of consumed power. The power consumption can be reduced by employing sunlight instead of artificial UV light to a larger amount.

**Conclusion**

In the present study, the spent caustic in the wastewater of Kermanshah Oil Refining Company was treated using the photo-Fenton process. The Box-Behnken system was applied for designing the experiments. In addition, the current study examined the effect of H$_2$O$_2$, Fe$^{2+}$, and initial COD on the percentage of COD removal. After conducting the tests, the findings were analyzed using ANOVA. The obtained results showed that some operating parameters were significant and effective in the removal of COD.

A quadratic model was presented to analyze the impacts of variables on the percentage of COD removal. At optimum conditions (i.e., hydrogen peroxide concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l) and after 60 min of reaction, the removal efficiency for COD was reported as 91.5%. The photo-Fenton process was powerful in the removal of COD. One of the main disadvantages of this process in the treatment of spent caustic is that the optimum pH is near 3, which is not optimized. Furthermore, a considerable amount of acid is required to neutralize and acidify the alkalinity of spent caustic.

**Footnotes**

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**Conflict of Interest**

The authors declare that they have no conflict of interest concerning the publication of the study.

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