Treatment of Iraqi Petroleum Refinery Wastewater by Advanced Oxidation Processes

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Abstract. Iraq is facing a major environmental crisis due to oil-spills which polluted the Tigris River and caused many problems in the environment depending on the volume of the oil spilled. Therefore these problems need emergency solutions and one of the solutions is treatment using Advanced Oxidation Processes (AOPs). In this research the degradation of acidic aqueous solutions of the synthetic diesel oil water emulsion has been studied by advanced oxidation processes (AOPs) using Fenton reagent (Fe²⁺/H₂O₂). The effect of different process parameters, such as pH, oxidant's dose (FeSO₄/H₂O₂) and the reaction times on the removal of diesel oil were investigated in terms of chemical oxygen demand (COD). At an optimum concentration optimum of [H₂O₂] = 11×10⁻² M; [Fe²⁺] = 7.4×10⁻³ M, pH=3.5 and reaction time 60 min reduced COD 65% of diesel oil at [Diesel Oil] = 1300 ± 23 mg O₂/ L. The real oily wastewater was collected from Baghdad south gas power plant-2 and its composition is unknown. The treatment of this wastewater by Fenton oxidations under optimal conditions were removed 86% of the initial COD and 97 % of total petroleum hydrocarbons TPH of the oily wastewater.

Keywords. Treatment, Diesel Oil, Advanced Oxidation Processes and Fenton Reagent

1. Introduction
Iraq is facing a huge environmental problem following the most recent destructing of the export pipeline in the north, as massive black brown oily spots floating in the surface of the Tigris River as shown in Figure (1) [1]. Also, In Iraq there is a significant incident of spilling fuel from storage tanks due to corrosion or structural failure, resulting in pollution of surface or underground water and soil. In addition to the petroleum refining activities uses large scale quantities of water and generate enormous volumes of an industrial effluent containing hydrocarbons. Approximately 300 liters of water is being consumed in the production of one barrel of crude oil [2, 3].
Figure 1. The oily spots in the Tigris River after the destruction of the oil pipelines north of Iraq in 2013. (Al-Najar and Lando, 2013).

These contaminants cause serious toxic risks to the environment [4]. Methods for Petroleum refinery effluents (PRE) treatment include coagulation [5] adsorption [6], electrochemical oxidation [7], and biological techniques [8]. New technologies such as membranes [9] and catalytic wet air oxidation assisted by microwave irradiation [10] have also been adduced. Generally, these methods include the transfer of pollutants from one medium to another; therefore, another step is required for the removal of organic pollutants.

The advanced oxidation processes (AOPs), are currently considered to be a potential treatment method for the removal of pollutants which are characterized by production of the hydroxyl radical (·OH) as a primary oxidant.

The generation hydroxyl free radical through the dissociation of hydrogen peroxide (H₂O₂) catalyzed by Ferrous ion (Fe²⁺) in acidic medium, known as the Fenton oxidation reaction. Many research papers have pointed out the efficiency and effectiveness of Fenton oxidation processes for treating various wastewater and soil contaminated with phenols [11], diesel [12]; [13], Textile [14,15], pesticides [16] and landfill leachate [17]. The benefit of the Fenton process approach is that no energy input is necessary to activate H₂O₂. So, this method offers a cost-effective source of hydroxyl free radicals (·OH), using simple handling reagents.

The first goal of this project was the mineralization of Iraqi commercial diesel oil by Fenton oxidation. The optimum process parameters for Fenton oxidation depend upon various remediation objectives for mineralization. Therefore, the specific goals of this research were: i) to specify the optimum H₂O₂/Fe²⁺ molar ratio during Fenton operation of diesel oil at pH 3.5 by fixing H₂O₂ while changing Fe²⁺ concentration and vice versa; ii) to assess the influence of pH levels on the mineralization of diesel oil by Fenton process at the optimum molar ratio of H₂O₂/Fe²⁺; iii) to evaluate the removal efficiency of chemical oxygen demand (COD removal) under the best pH, molar ratio H₂O₂/Fe²⁺ and oxidation reaction time.

The second goal of this research was the degradation of oily wastewater taken from Baghdad south gas power plant-2 by Fenton processes. We applied the optimum operation parameters for Fenton oxidation processes depend upon our experimental data obtained in this research and these result is agreement with our previous report in 2016 [18]. Therefore, the optimal H₂O₂/Fe²⁺ molar ratio during Fenton oxidation of oily wastewater was 14.8 at pH 3.5, and the reaction time was one hour at room temperature.

2. Materials and methods

2.1. Reagents
All solutions were prepared using distill water. Iraqi commercial diesel oil was used as the model pollutant and sodium dodecyl sulphate \((C_{12}H_{25}Na_4S)\) as emulsifier. \(H_2O_2\) \((30\%\text{ w/w})\) and \(FeSO_4\cdot 7H_2O\) (Fischer Scientific), \(H_2SO_4\) and \(NaOH\) (BHD) were used as received.

2.2. Preparation of the oil-water emulsion

We prepared the oil-water emulsion according to Tony et al, 2009 method after making some modifications and as follows:

The synthetic oil water emulsion prepared by adding of 0.1 g sodium dodecyl sulphate emulsifier to 900 mL of distilled water to which a 100 mL of diesel oil was added progressively while mixing the solution at 300 rpm. The emulsion solution was then filtered using a filter paper (Whatman 22 μm), producing an emulsion with a chemical oxygen demand (COD) concentration of 1300± 23 mg O\(_2\)/L.

2.3. Fenton experiments for synthetic oil-water emulsion

Fenton experiments were carried out by using 250 mL of the synthetic oil-water emulsion in a 500mL beaker with magnetic stirrer speed and room temperature ranged from 30-35°C. The experiments were carried out according to the following procedure:

Firstly, to study the influence of the initial \(H_2O_2\) concentration (ranging from \(4.4\times10^{-2}\) to \(18.5\times10^{-2}\) M) on the degradation of diesel oil-water emulsion with initial concentration of COD 1300 ± 23 mg \(O_2/L\), Fenton oxidation experiments were carried out at a fixed \(Fe^{2+}\) concentration of \(7.4\times10^{-3}\) M and initial pH of 3.5. Each experiment was started by addition of the required amount of Iron(II) sulfate crystals previously weighed and dissolved separately in a beaker using the same solution contained the oil-water emulsion in the beaker of Fenton oxidation process and then added to the oil-water emulsion solution and stirred using a magnetic stirrer at 150 rpm. The pH of solution was adjusted to a desired level by using either 1 M \(H_2SO_4\) or 1 M \(NaOH\). The concentration of \(H_2O_2\) was calculated according to the predetermined concentration of \(H_2O_2\) and was added in a single step to the Fenton oxidation reactor. To observe the oil-water emulsion concentration during the decomposition process, a 5 mL sample was withdrawing at different times between (5 to 60 minutes). Secondly, experiments on the influence of \(Fe^{2+}\) concentration ranged from \(5.0\times10^{-4}\) to \(5.0\times10^{-2}\) M on decomposition rate of oil-water emulsion with initial concentration of COD 1300 ± 23 mg \(O_2/L\) were studied under the best experimental conditions of \(H_2O_2\) concentration of \(11\times10^{-2}\) M at pH 3.5. Samples were withdrawn at the same time interval as that in the first step.

Finally, the optimum molar ratio \(H_2O_2/Fe^{2+}\) was experimentally evaluated by varying either hydrogen peroxide or ferrous ion dosages, while one factor was varying at one time but keeping the other parameters constant. Experiments were carried out at various pH levels from 2.0 to 8.0 for the Fenton homogeneous oxidation. In the literature reviews, \(H_2O_2\) or \(Fe^{2+}\) was usually estimated by performed multiple experiments at a variable number of dosages at various ratios of \(H_2O_2\) or \(Fe^{2+}\) [12, 20, 21].

2.4. Fenton oxidation experiment for real oily wastewater

Fenton oxidation experiment was conducted by using 250 mL of oily wastewater taken from Baghdad south gas power plant-2 {the COD for this oily wastewater was 560 (± 15)} and placed in a beaker 500 mL with magnetic stirrer speed at 150 rpm and room temperature ranged from 30-35°C. The experiment was conducted according to the following procedure:

The following optimum parameters conditions of Fenton's oxidation reaction were applied: \([H_2O_2]: [Fe^{2+}] = 15\) and pH = 3.5. The procedure was as follows:

Oily wastewater was placed into in a 500 mL Bach reactor, and then acidified with \(H_2SO_4\) to adjust pH to 3.5, as Fenton's reaction is only effective in acidic pH range. After that, the optimum concentrations of \([H_2O_2] = 11\times10^{-2}\) M and \([Fe^{2+}] = 7.4\times10^{-3}\) M were added with continuous magnetic stirring. Within one hour the pH of treated wastewater was increased with 10 % solution of \(NaOH\) up to about pH 12. After sedimentation for 30 min the COD was determined in the clear solution.
2.5. Analytical methods
The chemical oxygen demand (COD) was quantified based on the standard photometric method 5220D [22]. The concentration of hydrogen peroxide was determined spectrophotometrically as described by Nogueira et al [23]. The total petroleum hydrocarbons TPH was measured using Horiba OCMA-350 Oil Content Analyzer.

3. Results and Discussion

3.1. Determination Chemical oxygen demand (COD) in the synthetic oil water emulsion
Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. COD predominantly is used to measure pollutants in wastewater and surface waters. We prepared a calibration curve using photometric method 5220D by plotting instrument response (Absorbance) against standard concentration potassium hydrogen phthalate as shown in Figure (2). Compute sample concentration by comparing sample response with the standard curve.

![Figure 2. Calibration curve for COD determination.](image)

Fenton’s reaction pathway mechanism to the reduction of COD is always summarized as below (Equations 1 to 3):

**Step 1:** $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH}^-$ (Fenton oxidation reaction)  

**Step 2:** COD (species) + \cdot\text{OH} → Partially oxidized species

**Step 3:** Partially oxidized species + \cdot\text{OH} → $\text{CO}_2 + \text{H}_2\text{O} + \text{inorganic salts}$

The efficiency and effectiveness of COD removal obtained during Fenton oxidation has been represented as shown in Equation (4):

$$\text{COD Removal (\%)} = \left( \frac{(\text{COD}_0 - \text{COD}_f)}{\text{COD}_0} \right) \times 100$$  

Where COD$_0$ is the initial concentration of chemical oxygen demand of the diesel oil (before oxidation) and COD$_f$ is its concentration during Fenton oxidation (after treatment) for time interval $t$.

3.2. Effect of $\text{H}_2\text{O}_2$ concentration on degradation of synthetic diesel oil water emulsion
Hydrogen peroxide concentration is a very important parameter in Fenton oxidation process of diesel oil. Enormous amount of $\text{H}_2\text{O}_2$ consumes hydroxyl radicals without destruction of the targeted organic matter. Thus, the removal efficiency of the targeted pollutant by the Fenton oxidation would be...
diminished [24]. While insufficient amount of \( \text{H}_2\text{O}_2 \) could not provide enough amounts of hydroxyl radicals for the maximum oxidation reaction. For this reason, the influence of \( \text{H}_2\text{O}_2 \) dosage on the decomposition of synthetic oil water emulsion was evaluated first.

To find out the optimum molar ratio of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) during the degradation of diesel oil, first, the amount of \( \text{Fe}^{2+} \) was kept constant at \( 7.4 \times 10^{-3} \) M, while the concentration of \( \text{H}_2\text{O}_2 \) was varied so that the \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) molar ratio ranged from 6 to 25. At the lowest dose of \( \text{H}_2\text{O}_2 \) ranged from \( 4.4 \times 10^{-2} \) up to \( 11 \times 10^{-2} \) M, the diesel oil degradation increased when increase the concentration of hydrogen peroxide as shown in Figure (3). The positive enhancement of the removal efficiency on the degradation of diesel oil wastewater may be attributed to the higher yield of hydroxyl radical produced from higher amount of \( \text{H}_2\text{O}_2 \) [14]. When \( \text{H}_2\text{O}_2 \) concentration was greater than \( 11 \times 10^{-2} \) M (Figure 3), the degradation values decreased due to the over dosed \( \text{H}_2\text{O}_2 \) was scavenging hydroxyl radicals excessively. Therefore, \( 11 \times 10^{-2} \) M \( \text{H}_2\text{O}_2 \) was chosen as the optimum concentration and used in the next experiments to assess the influence of \( \text{Fe}^{2+} \) concentration on the diesel oil degradation.

![Figure 3. The COD Removal, % of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) molar ratio used versus Time (Minute), obtained during diesel oil degradation by Fenton process, keeping \( \text{Fe}^{2+} \) constant and ranging \( \text{H}_2\text{O}_2 \). Initial conditions: \[\text{Diesel Oil}] = 1300 \pm 23 \text{ mg O}_2/\text{L}; \ [\text{Fe}^{2+}] = 7.4 \times 10^{-3} \text{ M}; \text{and pH} = 3.5.\]

3.3. Effect of \( \text{Fe}^{2+} \) concentration on degradation of synthetic diesel oil water emulsion

The amount of ferrous ion is also an important parameter in Fenton’s oxidation because it directly impacts the yield of hydroxyl radical, \( ^{\cdot}\text{OH} \), by catalytically dissociating \( \text{H}_2\text{O}_2 \) as shown in Equation 1. While \( \text{Fe}^{2+} \) also would act as scavengers of \( ^{\cdot}\text{OH} \) radicals if it was overdosed [25].

Figure (4) demonstrates that the oil degradation increase with the \( \text{Fe}^{2+} \) concentration, increasing the dose of \( \text{Fe}^{2+} \) (from \( 5.0 \times 10^{-4} \) up to \( 7.4 \times 10^{-3} \) M) while increased the diesel oil degradation as shown in Figure (4). The slower degradation after the concentration \( 7.4 \times 10^{-3} \) M suggests that \( \text{Fe}^{2+} \) is over dosed by consuming considerable amount of \( ^{\cdot}\text{OH} \) radicals in the aqueous media. As a consequence, the amount of \( ^{\cdot}\text{OH} \) radicals available to oxidize oil wastewater was diminished. Therefore, \( 7.4 \times 10^{-3} \) M \( \text{Fe}^{2+} \) was chosen as the optimal \( \text{Fe}^{2+} \) concentration.
3.4. Effect of pH on degradation of synthetic diesel oil water emulsion

Several experiments were carried out at five pH levels (2.5, 3.5, 4.5, 5.5, 6.5 and 7.5) at optimum conditions (time = 60 min, H$_2$O$_2$/Fe$^{2+}$ molar ratio = 15:1). The results of these experiments are showed in Figure (5). When the pH of solution greater than 3.5 the efficiency of degradation is reduced for example the COD removal percentage were reduced from 64.5% to 33.1 at pH 3.5 and 7.5 respectively. The reasons could be related to the reduced rate of the production of •OH radicals, due to of the formation of the ferric hydroxo complexes Fe(OH)$_3$ at higher pH [27]. The peroxonium ion makes peroxide electrophilic which enhances its stability, and reduces the reactivity with Fe$^{2+}$ ion [28]. Therefore, pH 3.5 was considered as optimum pH for the next experiments.

Figure 4. The COD Removal, % of H$_2$O$_2$/Fe$^{2+}$ molar ratio used versus Time (min), obtained during diesel oil removal by Fenton oxidation, keeping H$_2$O$_2$ constant and ranging Fe$^{2+}$. Initial conditions: [Diesel Oil] = 1300±23 mg O$_2$/L; [H$_2$O$_2$] = 11×10$^{-2}$ M and pH = 3.5.

Figure 5. The COD Removal (%) versus different pH obtained during diesel oil degradation by...
Fenton process, Initial conditions: [Diesel Oil] = 1300 ± 23 mg O₂/ L; [H₂O₂] = 11×10⁻² M; [Fe²⁺] = 7.4×10⁻³ M and time = 60 min.

3.5. Effect of reaction time on degradation of synthetic diesel oil water emulsion
The time effect was studied through experiments were conducted at different time period (5, 10, 30, 60, 90, 120, 180 and 240 min). It can be seen from Figure (6) that COD reduction occurs principally at an initial period (10-60 min). As shown in Figure (6) there is no significant different after 60 min, the COD removal for Fenton process lay between 65.3% and 73.5% at initial period 60 and 240 min respectively.

![Figure 6. The COD Removal, % versus Time (min) obtained during diesel oil degradation by Fenton process, optimum conditions: [Diesel Oil] = 1300 ± 23 mg O₂/ L; [H₂O₂] = 11×10⁻² M; [Fe²⁺] = 7.4×10⁻³ M and pH=3.5.](image)

3.6. Degradation of real oily wastewater using Fenton oxidation
The real oily wastewater in this study was collected from Baghdad south gas power plant-2 and its composition is unknown. The oily wastewater chemical characteristics are summarized in the Table (1), as well as the standard deviations associated to each analyses technique.

The degradation of real oily wastewater using Fenton oxidation at the optimum condition of [H₂O₂] = 11x10⁻² M; [Fe²⁺] = 7.4x10⁻³ M, pH=3.5 and reaction time at 60 min also summarized in Table (1). The COD after 60 min at optimum conditions were sufficient to remove 86% of the initial COD of the oily wastewater as shown in Table (1). While total petroleum hydrocarbons, TPH were removal 97 % of the oily wastewater.

| No. | Characteristics                  | Values before treatment | Values after treatment |
|-----|----------------------------------|-------------------------|------------------------|
| 1   | pH                              | 7.3 (± 0.2)             | 8.1 (± 0.2)            |
| 2   | Total Dissolved Solids, TDS (mg/L) | 506 (± 2)               | 222(± 1.5)             |

Table 1. Chemical characteristics of the real oily wastewater in this study before and after the application of the Fenton oxidation treatment with the corresponding experimental deviation presented in parenthesis.
|   | Total Suspension Solids, TSS (mg/L) | 48 (± 0.8) | 0 (± 0.1) |
|---|-----------------------------------|------------|-----------|
| 4 | Electrical Conductivity, EC (μS/cm) | 1260 (± 3) | 588 (± 1.2) |
| 5 | Chemical oxygen demand, COD (O2 mg/L) | 560 (± 15) | 75 (± 15) |
| 6 | Total Phenol (mg/L) | 3.2 (± 0.1) | 0.06 (± 0.2) |
| 7 | Total petroleum hydrocarbons, TPH (mg/L) | 742 (± 5) | 23 (±2) |
| 8 | Sulfate SO$_4^{2-}$ (mg/L) | 147 (± 0.5) | 133 (± 0.2) |
| 9 | Nitrate NO$_3^-$ (mg/L) | 21 (± 0.5) | 22.1 (± 0.4) |
| 10 | Chlorides (mg/L) | 129 (± 1) | 110(± 1.2) |

### 4. Conclusion

In this study, the Fenton oxidation process have been successfully applied for the degradation of highly polluted synthetic and real oily wastewater. From the experimental data illustrated in this research, one of the most important conclusion is the optimum H$_2$O$_2$/Fe$^{2+}$ molar ratio was experimentally determined to be 15 according to the analytical methods presented in this study. Fenton process has so powerful oxidation that it is able to degrade of diesel oil, and oxidize the high molecular organics into low molecular organics, or decompose some organics directly into CO$_2$ and H$_2$O. The optimum conditions for removal 65% of diesel oil at 60 min is [H$_2$O$_2$] = 11×10$^{-2}$ M; [Fe$^{2+}$] = 7.4×10$^{-3}$ M and pH=3.5.

The degradation of real oily wastewater using Fenton oxidation at the optimum condition were removed 86% of the initial COD and 97 % of total petroleum hydrocarbons TPH of the oily wastewater.

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