A Competitive Study Using UV and Ozone with H$_2$O$_2$ in Treatment of Oily Wastewater

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Abstract:

In this study, ultraviolet (UV), ozone techniques with hydrogen peroxide oxidant were used to treat the wastewater which is produced from South Baghdad Power Station using lab-scale system. From UV-H$_2$O$_2$ experiments, it was shown that the optimum exposure time was 80 min. At this time, the highest removal percentages of oil, COD, and TOC were 84.69 %, 56.33 % and 50 % respectively. Effect of pH on the contaminants removing was studied in the range of (2-12). The best oil, COD, and TOC removal percentages (69.38 %, 70 % and 52 %) using H$_2$O$_2$/UV were at pH=12. H$_2$O$_2$/ozone experiments exhibited better performance compared to the H$_2$O$_2$/UV experiments. The results showed that 20 min was the best exposure time with removal percentages of 89.79 %, 83.33 % and 70% for oil, COD and TOC, respectively, and the optimum value of pH was at pH=8, where the pollutants removal percentages (i.e. 74.48 %, 80 % and 73.33 % respectively for the same previous pollutants). H$_2$O$_2$/ozone experiments showed better removal efficiency than the H$_2$O$_2$/UV experiments.

Key word: COD, Oil, Ozone, TOC, Ultraviolet

Introduction:

The continuous expansion in the hydrocarbon processes and the oil-related industries like car manufacturing, and oil refineries has led to increasing the risk of oil pollution on the aquatic environment(1). Oil is one of the most important pollutants in water that causes serious problems in the environment. Strict regulations were adopted by different countries for discharging wastewater that contains oil to the surface water. In Iraq, for example, the maximum allowable limit for discharging hydrocarbons and oils into surface water is 10 mg/L (2). Oil can be existing in water in different forms: free oil, emulsion and soluble. Free oil can easily be removed by gravitational methods like American Petroleum Institute (API) separator (3), dissolved air flotation (DAF) (4), skimmers (5). However, there are limited options to remove emulsified and soluble oil like adsorption (6), membranes (7,8) and advanced oxidation (9). Advanced oxidation process (AOP) is an efficient chemical treatment method for oil removal; AOP depends on formation of free radicals (HO•) which is a powerful and non-selective oxidant. Free radicals can be generated from oxygen, UV, hydrogen peroxide, and photo catalysis. Two or more of these free radicals generators can be used in combination to achieve more efficient treatment method (10). Combination of UV and hydrogen peroxide produces hydroxyl radicals by photolysis of H$_2$O$_2$ according to the following reaction (11):

\[ H_2O_2 + \text{hv} \rightarrow 2HO• \]

In the UV-H$_2$O$_2$ process, photon energy is high enough to break the chemical bonds of the organic compounds which enables the process to treat wastewater that contains different organic contaminations (12). Also, Ozone is another oxidizing and very reactive agent that can degrade even the persistent hydrocarbon pollutants. Ozone can be easily produced from oxygen using electrical discharge (13). Treatment by ozone is achieved through direct and indirect methods; in the direct methods hydroxyl and carboxylic groups are produced from attacking the organic compounds by ozone while in the indirect method, chain reactions
occurred to produce the hydroxyl radicals from dissolving ozone onto water and then attacking the organic pollutants according to the following reaction (10):

\[
\text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \text{ at (hv: } \lambda < 300 \text{ nm)}
\]

\[
2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\text{HO}^* + 3\text{O}_2
\]

Some literature observed using AOP in different industrial applications. (14) studied the use of UV, \text{H}_2\text{O}_2/\text{UV} and ozone in treatment of pharmaceuticals wastewater and they found that ozonation was the most effective process among the three tested processes. (15) studied the use of \text{O}_3 and \text{O}_2/\text{H}_2\text{O}_2 in the treatment of landfill leachate and found that the best COD removal was 46% at a \text{H}_2\text{O}_2/\text{O}_3 ratio of 0.8 and ozone dose of 0.6 g \text{O}_3/\text{dm}^3 compared to 29% when using UV. Treatment of olive oil mill wastewater using UV and \text{H}_2\text{O}_2/\text{UV} was investigated by (16). Their results showed that COD and TOC removal using UV were 22 and 34% respectively, while they were 48% for both COD and TOC when using UV / \text{H}_2\text{O}_2. (17) studied the performance of using ozone in removal of petroleum-based pollutants from wastewater under the conditions of 23 \text{ C}, \text{pH} of 7.2, 4.0 mg/L ozone dosage and 10 min reaction time. The highest pollutants percentage removal under these conditions was 83%. (18) studied the performance of flotation followed by photo-Fenton process in oil removal from oilfield produced water. Their results showed that 99% oil removal was achieved after 10 min of flotation after that 45 min of photo-Fenton process.

In this research, we employed AOP using \text{H}_2\text{O}_2/\text{UV}, \text{H}_2\text{O}_2/\text{O}_3 to treat oily wastewater from South Baghdad Power Station. A comparison was made between the two oxidants to evaluate the best treatment option in terms of oil, COD and TOC removal at different conditions.

Materials and Methods:
Preparation of the Feed Solution
The oily wastewater was taken from South Baghdad Power Station and pretreated before being used in the advanced oxidation process. The initial oil concentration before the pretreating step was about 2000 ppm. The raw wastewater was filtered using sand filtration column with dimensions of length=40 cm, diameter=7 cm. The outlet from the sand filter was 98 ppm. Still, this water needed treatment before discharging to the environment; this treatment was conducted using advanced oxidation processes (UV and Ozone).

\text{H}_2\text{O}_2/\text{UV} Experiment
In the first stage, lab-scale system was used to do the experiments. This system consists of feed tank (3L) and a 15 W lamp to generate the UV ray at wavelength (240-280 nm). In order to study the influence of the time on the reducing of the contaminants, 2 L of the pretreated wastewater was fed to the system and was exposed to the UV ray at different times (0-100 min.). Hydrogen peroxide (\text{H}_2\text{O}_2) was added to the feed tank with an amount of 1 ml/L which provided the best removal efficiency. After each 20 min a sample was taken from the reactor to make the characterization on it. Oil concentration was measured using oil content analyzer Horiba OCMA-350, Japan. COD (chemically oxygen demand) and TOC (total organic carbon) for the treated samples were measured using spectrophotometer DR 5000 U. pH was studied in the range of (2-12) and was adjusted using HCl and NaOH solutions. All experiments were conducted at room temperature and at continuous mode with flowrate of 28 L/hr. Figure 1 shows schematic diagram of the lab-scale UV system that was used in this research.

Removal percentage of the various pollutants (oil, COD, and TOC) was calculated using the following equation:

\[
\text{Removal} \% = \frac{C_i - C_f}{C_i} \times 100
\]

Where \(C_i\) is the initial concentration (mg/L)  
\(C_f\) is the final concentration (mg/L)

\text{H}_2\text{O}_2/ozone Experiment
In the second stage, ozone has been used as a strong oxidizing agent to reduce oil, COD and TOC concentrations in the wastewater by pumping the ozone to the wastewater at a rate of 0.3 m³/hr. Ozone reacts with oil in the presence of \text{H}_2\text{O}_2 (1ml/L) to produce a hydroxyl radicals which attack the organic materials. For this purpose, ozone generator (Ozone techinc) was used to generate an electric spark in a dry air passing through a plastic pipe that is connected to the reactor.
A stone diffuser was used at the entrance of the ozone reactor to provide ozone as small bubbles before dissolving in water and reacting with the pollutants. In this experiment, different time intervals (5, 10, 15, 20, and 25 min) were used to study the influence of time on reducing the pollutants concentration, every 5 min, a sample was taken from the reactor for characterization (i.e. oil content, COD and TOC) until achieving the highest removal. The optimum time was chosen to conduct the further experiments of pH effect at the same range of the UV experiment. Figure 2 shows schematic diagram of the lab-scale ozone system that was used in this research.

Figure 2. Schematic diagram of the H₂O₂/ozone system

Results and Discussion:
 Performance of the UV/ H₂O₂ process
Effect of H₂O₂/UV Exposure Time
The first series of the experiments was to study the effect of UV exposure time on removal of oil, COD, TOC in wastewater in the range (0-100 min) by using advance oxidation (H₂O₂/UV) process. Fig.3 shows that the oil removal percentage gradually increase with exposure time from (10.20 % to 48.97 %) at 20-40 min and increase up to (66.32 %) at 60 min. The highest removal percentage (84.69 %) was achieved at 80 min. It can be observed that there is no more change in oil removal at further time. The same behavior was noticed for COD and TOC removal percentages. The achieved percentage removal for COD, and TOC are (56.33% and 50%) respectively at time 100 min as shown in Fig. 3. The combination of the UV process and H₂O₂ can significantly enhance the degradation of the pollutants. When H₂O₂ absorbs UV radiation, free radicals OH will be formed which attack the contaminants causing degradation processes. Therefore, we conducted oil irradiation with UV in the presence of H₂O₂. The reaction was achieved a higher level of removal, but in a longer degradation time (84.69 %) at 80 min(18), as shown in Figure 3.

Effect of pH
The effect of pH on removal efficiency of oil, COD and TOC in the wastewater was studied in the range of pH 2-12 at the optimum exposure time (80 min). It can be seen from Fig. 4 that when the pH increases from 2 to 12, the percentage removal of the oil, COD and TOC increases from 18.36 to 69.38 %, 33.33 to 70 % and 13 to 52 % respectively. It can be explained that, with increasing pH; two different effects are produced, first; the formation of more •OH which reacts with the hydro peroxide anion (HO₂——), leading to form hydrogen peroxide at high pH, which was higher than H₂O₂, second; the hydro peroxide anion (HO₂——) could scavenge the hydroxyl radicals observed that equation (19):

\[
\text{HO}_2^- + \cdot \text{OH} \rightarrow \text{HO}_2 \cdot + \text{OH}
\]

The reaction rate of hydro peroxide anion with peroxide is lower than that of ‘OH, the scavenging rate of 'OH also increased with higher pH (19). In addition, at alkaline conditions, the photolysis rate of the H₂O₂ increases, these results agree with the findings of Cesaro et al. 2013 (20).

Figure 3. Effect of reaction time on removal efficiency of COD, TOC, and oil using H₂O₂/UV process.

Figure 4. Effect of pH on removal efficiency of COD, TOC, and oil using H₂O₂/UV process.
Performance of the H$_2$O$_2$/ozone Process

Effect of H$_2$O$_2$/ozone Reaction Time

Reaction time is an important parameter in the process of removing of wastewater pollutants. In this research we studied the influence of ozonation exposure time on the removal of oil, COD and TOC. It can be observed from Fig. 5 that during the first minutes of the reaction, increasing of reaction time enhances the reducing of oil, COD and TOC with high speed of separating; after that a rapid increase in the removal percentage was observed because of the ozone activity. Later, the removal rate kept increasing until the reaction time reached 20 min. It can be explained that, consuming of ozone leads to generate the free radicals which react with the organic compounds (21). At 20 min, the removal rate was stable for all pollutants as shown in Fig. 5. The highest percentage removals were 89.79 %, 83.33 % and 70 % for oil, COD and TOC respectively. After this time, the removal rate did not change significantly thereafter. This can be explained by that some organic compounds are more prone to oxidation than others, while some are only partially oxidized (22).

![Figure 5](image1.png)

**Figure 5 Effect of reaction time on removal efficiency of COD, TOC, and oil using O$_3$/H$_2$O$_2$ process.**

Influence of pH

The efficiency of O$_3$/H$_2$O$_2$ at the optimum reaction time (20 min) was studied at different pH (2-12). Figure 6 shows that at pH= 8, a big change was observed in the removing percentages for oil, COD and TOC (74.48%, 80%, 73.33%) respectively, then the removing percentages were decreased with increasing pH from 10 to 12 (62.24 to 59.18 %), (50 to 41.66 %) and (61.33 to 56 %) respectively. It can be illustrated that the number of O$_3$ molecules that are decomposing to generate •OH radicals increases at higher pH values which improve the removing efficiency (23). Decreasing in COD removing percentage at high pH is attributed to that the ozone changes the suspends solid materials to dissolved materials followed by destroying the big solid materials to small molecules (23).

![Figure 6](image2.png)

**Figure 6. Effect of pH on removal efficiency of COD, TOC, and oil using O$_3$/H$_2$O$_2$ process.**

Conclusion:

The target from this study is to make a comparison between combined effects of H$_2$O$_2$/UV, and ozone//H$_2$O$_2$ advanced oxidation methods of oily wastewater treatment. It can be concluded from the results that the experimental results of oil removal by ozone /H$_2$O$_2$ is more effective with removing percentage (89.79 %) at (20 min) than photolysis with H$_2$O$_2$/UV (84.69 %) at (80 min), while the results show high efficiency removal percentages of the COD and TOC by H$_2$O$_2$/ozone 83.33 % and 70% respectively comparing with lower percentage 56.33% and 50 % by using H$_2$O$_2$/UV. There are many parameters that influence the oxidation process; one of them is pH as the experimental results illustrate that the H$_2$O$_2$/ozone optimized results is at pH =8, while H$_2$O$_2$/UV is at pH=12. We recommend studying the use of the hybrid UV/ozone in the presence of H$_2$O$_2$ process in the treatment of the oily wastewater.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for republication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

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دراسة مقارنة بين عمليات الأكسدة المتقدمة لبيروكسيد الهيدروجين باستخدام الاشعة فوق البنفسجية والاوزون في معالجة مياه الصرف الزيتية

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الخلاصة:

يتضمن البحث دراسة تأثير عمليات الأكسدة المتقدمة لبيروكسيد الهيدروجين باستخدام الاشعة فوق البنفسجية والأوزون في معالجة مياه الصرف الزيتية من محطة جنوب بغداد باستخدام منظومة مختبرية، تم اجراء التجارب بطريقة التشغيل المستمر (Continuous Process) ولتوافر درجة الحرارة. أشارت النتائج إلى أن الوقت الأفضل لإزالة الامولبات باستخدام الأوزون هو 10 دقائق حيث أن نسبة الازالة كانت 87.6%، وتنفيذ الأوزون مع بيروكسيد الهيدروجين و بيروكسيد الهيدروجين هو 80 دقيقة حيث أن نسبة الازالة كانت 84.69%، و 80 دقيقة حيث أن نسبة الازالة كانت 84.69%. وعند التوالي، وايضا تم دراسة تأثير الدالة الحامضية على ازالة الامولبات.  

الكلمات المفتاحية: الأشعة فوق البنفسجية, الاوزون, الزيت, المتطلب الكيمائي للاوكسجين, الكاربون الكلي العضوي.