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A Competitive Study Using UV and Ozone with H_2O_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_2O_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_2O_2/UV were at pH=12. H_2O_2/ozone experiments exhibited better performance compared to the H_2O_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_2O_2/ozone experiments showed better removal efficiency than the H_2O_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 ozone, 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_2O_2 according to the following reaction (11):

$$H_2O_2 + h\nu \longrightarrow 2HO\bullet$$

In the UV-H_2O_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)**:**

$O3 + H_2O + h\upsilon \rightarrow O_2 + H_2O_2$ at ($h\upsilon$: λ <300 nm)

$2\ O_3 + H_2O_2 \rightarrow 2\ HO\bullet + 3\ O_2$

Some literature observed using AOP in different industrial applications. (14) studied the use of UV, $_{H2O2}$/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 O_3 and O_3/ H_2O_2 in the treatment of landfill leachate and found that the best COD removal was 46% at a H_2O_2/O_3 ratio of 0.8 and ozone dose of 0.6 g O_3/dm^3 compared to 29% when using UV. Treatment of olive oil mill wastewater using UV and H_2O_2\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 / H_2O_2. (17) studied the performance of using ozone in removal of petroleum-based pollutants from wastewater under the conditions of 23 $^{\circ}$C, 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 floatation after that 45 min of photo-Fenton process.

In this research, we employed AOP using H_2O_2/UV,H_2O_2/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).

H_2O_2/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 (H_2O_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:

$$Removal\ \% = \frac{C_i - C_f}{C_i} * 100$$

Where C_i is the initial concentration (mg/L)

C_f is the final concentration (mg/L)

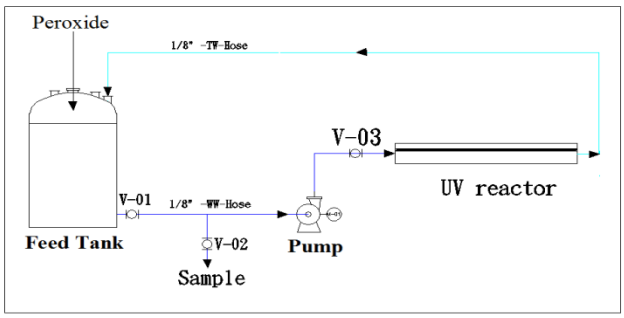

Figure 1. Schematic diagram of the H_2O_2/UV system

H_2O_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 m^3/hr. Ozone reacts with oil in the presence of H_2O_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.

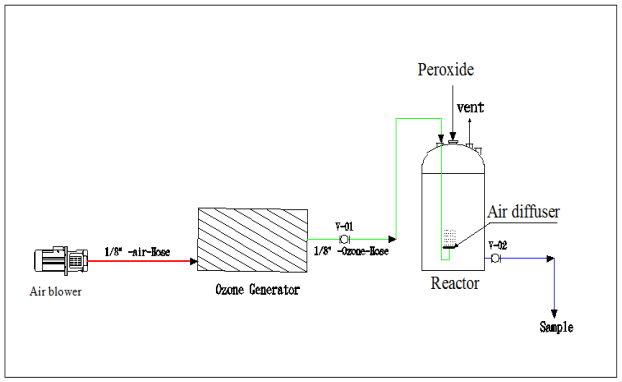

Figure 2. Schematic diagram of the H_2O_2/ozone system

Results and Discussion:

Performance of the UV/ H_2O_2 process

Effect of H_2O_2/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 (H_2O_2/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 H_2O_2can significantly enhance the degradation of the pollutants. When H_2O_2 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 H_2O_2.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.

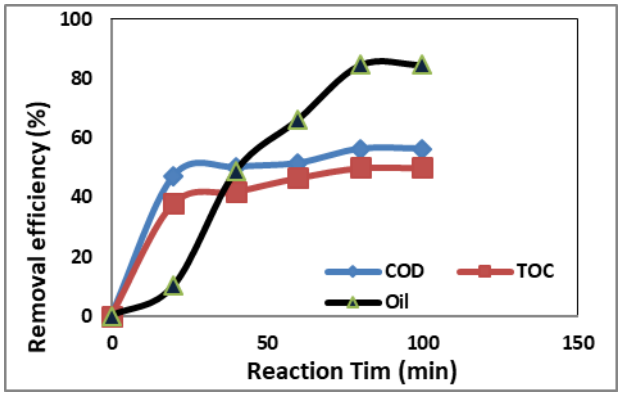

Figure 3. Effect of reaction time on removal efficiency of COD, TOC, and oil usingH_2O_2/UV process.

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 2-12at 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 (HO_2^-), leading to form hydrogen peroxide at high pH, which was higher than H_2O_2, second; the hydro peroxide anion (HO_2^-) could scavenge the hydroxyl radicals observed that equation (19):

$$HO_2^- + \bullet OH \longrightarrow HO_2^{\bullet} + OH$$

The reaction rate of hydro peroxide anion with peroxide is lower than that of $^{\bullet}OH$, the scavenging rate of $^{\bullet}OH$ also increased with higher pH (19). In addition, at alkaline conditions, the photolysis rate of the H_2O_2 increases, these results agree with the findings of Cesaro et al. 2013 (20).

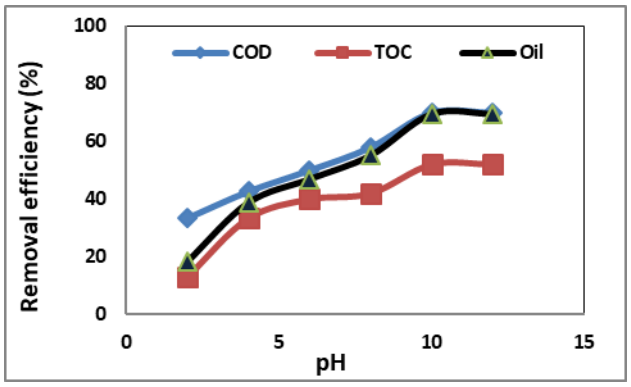

Figure 4. Effect of pH on removal efficiency of COD, TOC, and oil using H_2O_2/UV process.

Performance of the H_2O_2/ozone Process

Effect of H_2O_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).

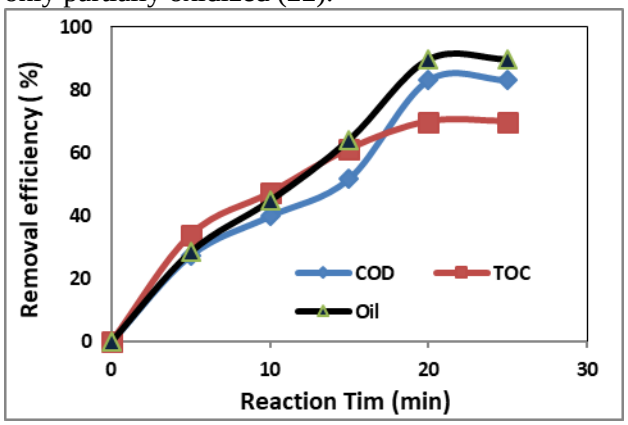

Figure 5 Effect of reaction time on removal efficiency of COD, TOC, and oil using O_3/H_2O_2process.

Influence of pH

The efficiency of O_3/H_2O_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 to12 (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).

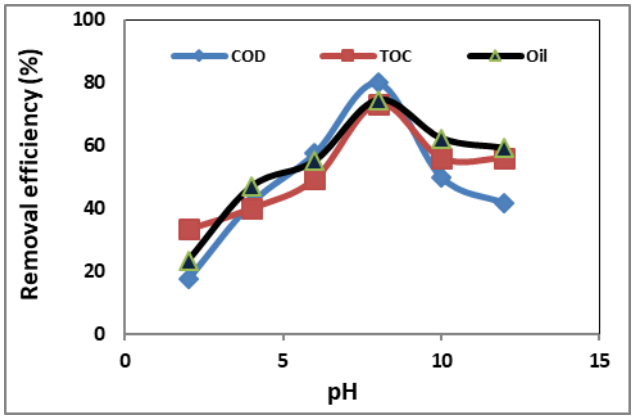

Figure 6. Effect of pH on removal efficiency of COD, TOC, and oil using O_3/H_2O_2process.

Conclusion:

The target from this study is to make a comparison between combined effects of H_2O_2/UV, and ozone//H_2O_2advanced oxidation methods of oily wastewater treatment. It can be concluded from the results that the experimental results of oil removal by ozone /H_2O_2 is more effective with removing percentage(89.79 %) at (20 min) than photolysis withH_2O_2/UV (84.69 %) at (80 min), while the results show high efficiency removal percentages of the COD and TOC by H_2O_2/ozone83.33 % and 70% respectively comparing with lower percentage 56.33% and 50 % by usingH_2O_2/UV. There are many parameters that influence the oxidation process; one of them is pH as the experimental results illustrate that the H_2O_2/ozone optimized results is at pH =8, while H_2O_2/UV is at pH=12. We recommend studying the use of the hybrid UV/ozone in the presence of H_2O_2process 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 re-publication 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 الاكسدة المتقدمة لبيروكسيد الهيدروجين باستخدام الاشعة فوق البنفسجية والاوزون في معالجة مياه الصرف الزيتية

بان عبد الوهاب جاسم مصطفى حسين الفريجي علي اسماعيل سكران وليد ابراهيم عبد الله

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الخلاصة:

يتضمن البحث دراسة تأثير عمليات الاكسدة المتقدمة لبيروكسيد الهيدروجين باستخدام الاشعة فوق البنفسجية والاوزون في معالجة مياه الصرف الزيتيةمنمحطة جنوب بغداد باستخدام منظومة مختبرية،علماانالتجاربتمت بطريقة التشغيل المستمر (Continuous Process) وبدرجةحرارةالغرفة.اشارت النتائج الى ان الوقت الافضل لازالة الملوثات باستخدام الاشعة فوق البنفسجية(UV) وبيروكسيد الهيدروجين هو 80 دقيقةحيث انالنسبة المئوية للازالة كانتعاليةعند هذا الوقت للزيت بينما لكل منقيم المتطلب الكيمياوي للاوكسجين و الكاربون الكلي العضوي كانت84.69 % و 56.33 % و 50 % على التوالي. وايضا تم دراسة تأثير الدالة الحامضية على ازالة الملوثات بمعدل (12-2) و كانت نسب الازالة الافضل باستخدام H_2O_2/UV عند الدالة الحامضية = 12 و كانتنسب ازالةالزيت و COD وTOCهو 70 % 70, % , 52% على التوالي.ان نتائج التجربة باستخدام الاوزون مع بيروكسيد الهيدروجين بينت ان وقت التعرض الافضل كان20 دقيقة مع نسب ازالة مثلى 89.79 % 83.33 , % 70,للزيت ،COD وTOC على التوالي في حين ان النتائج عند الدالة الحامضية = 8 و كانتنسب ازالة الملوثات78.48 % 80, % 73.33, % على التوالي لنفس الملوثات السابقة وهي الاعلى من بين قيم الدوال الحامضية المستخدمة .انتجارب الاوزون وبيروكسيد الهيدروجين اعطت نتائج افضل مقارنة بتجارب الاشعة فوق البنفسجية وبيروكسيد الهيدروجين.

الكلمات المفتاحية : الاشعة فوق البنفسجية ، الاوزون ، الزيت ، المتطلب الكيمياوي للاوكسجين ، الكاربون الكلي العضوي.