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Heterogeneous Photocatalytic Degradation for Treatment of Oil from Wastewater

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Abstract

In the present study, advanced oxidation process / heterogeneous photocatalytic process (UV/TiO_2/Fenton) system was investigated to the treatment of oily wastewater. The present study was conducted to evaluate the effect of hydrogen peroxide concentration H_2O_2, initial amount of the iron catalyst Fe^{+2}, pH, temperature, amount of TiO_2 and the concentration of oil in the wastewater. The removal efficiency for the system UV/TiO_2/Fenton at optimal conditions and dosage (H_2O_2 = 400mg/L, Fe^{+2} = 40mg/L, pH=5, temperature =30°C, TiO_2=75mg/L) for 1000mg/L load was found to be 77%.

Aluminum foil cover around the reactor and air bubbling were utilized in the experiments of photo Fenton UV/ H_2O_2/Fe^{+2} homogeneous and heterogeneous systems in order to improve the removal efficiency. The removal efficiency was improved to 81% for UV/TiO_2/Fenton system . The reaction was found to be of a first order throughout the systems.

Keywords: *Oily wastewater, Advance oxidation process, heterogeneous process, Aluminum Foil.*

1. Introduction

Oil is one of the important contaminants in water and causes the wastewater problems in environments. In practice, this can form various types of oily wastewaters; for instance, soluble oil in water, emulsion with or without surfactants or floating film [1].

Oils that are found in contaminated water can be grouped into [2]:

- Light hydrocarbons including light fuels such as gasoline, kerosene and jet fuel.
- Heavy hydrocarbons, fuels and tars including the crude oils, diesel oils, gas oil and asphalt.
- Lubricants and cutting fluid that generally falls into two classes: non-emulsifiable oils such as lubricating oils and greases, and emulsifiable oils such as water soluble oils, emulsifiable oils may contain soap, or various other additives.

The volume of diesel/gas oil contaminated wastewater from petroleum filling stations has increased in line with the number of such stations required to cater for the growing number of vehicles. According to data provided by International Energy Agency (IEA), the world consumption of diesel oil increased during the period 1990 to 2003 from 454,747 to 684,022 million liters.

In Iraq there is 507 car-wash facilities (except Kurdistan), (Ministry of Environment report 2011) and some of them discharge its wastewater (almost emulsifiable oils) to sewer systems without treatment.

Also as a result of human activities, there are many accidental discharges of hydrocarbon oil to the natural environment during its processing, transportation and storage. Photo in Fig. 1 , illustrate oil contaminated wastewater in Iraqi stream. Diesel /gas oil causes eye and skin irritation in humans, but otherwise its effects on humans are considered to be poorly investigated [3].

Diesel is considered to be harmful and possibly carcinogenic to humans and it contains PAHs that create a risk for human health because of their carcinogenic, mutagenic and teratogenic properties [4].

Standards and regulation were adopted for discharge of oily wastewater into surface water or sewage systems. These regulations may vary from country to country, and even within a country itself. The allowable hydrocarbons and its derivatives discharge into water bodies about 10 mg/L in Iraq [5].

Advanced oxidation processes (AOPs) have been investigated for the oil-contaminated wastewater treatment as an alternative to conventional treatment techniques. AOPs are characterized by the use of highly reactive intermediates, hydroxyl radicals (HO•), which attack the organic pollutants in the wastewater and mineralize them. Advanced oxidation processes (AOPs) have the advantage of rapid oxidation of pollutants to harmless end products. Such processes include homogenous processes such as Fenton’s reagent, H_2O_2 and ozone and heterogeneous photocatalysis using semiconductors such as TiO_2 and ZnO [6].

Fig. 1. Surface water oil contaminated in a AL-Fataha .

The principle of heterogeneous photocatalysis is based on the activation of a semiconductor particulate material (Cds, TiO_2, ZnO etc.) by the action of radiation with an appropriate wavelength. This activation is achieved with the absorption of photons by the semiconductor particle possessing enough energy to promote the conduction of an electron (e^-) from its valence band (VB) to the conduction band (CB) (a transition called band gap energy), creating holes in the valence band (h^+) that will act as oxidizing sites[7] .

The treatment of water produced from oil fields was studied via a photocatalytic process using TiO_2/UV, with the addition of H_2O_2. Chromatographic analyses showed the complexity of the wastewater, and most of the compounds present in the medium, remained unidentified. However, a considerable reduction in chromatogram peaks can be observed, showing pollutant degradation. They observed that addition of H_2O_2 in the photocatalytic process was unnecessary and even undesirable, owing to the corrosive and damaging effects of this substance on the catalysts (TiO_2) [8].

TiO_2/UV process was used to degrade the organic pollutants of a refinery wastewater by a circulating photocatalytic reactor.

In 2009, Tony et al.[9] studied the combined Fenton/UV augmented with TiO_2 and ZnO for mineralization of diesel-oil wastewater emulsion. The results show that the process is sensitive to the concentrations of the $Fe+^2$, H_2O_2 and TiO_2 or ZnO, but the process performs well over a wide pH range. The optimum conditions were found to be: 40 mg/L, 400 mg/L and 500 mg/L for $Fe+^2$, H_2O_2 and TiO_2 respectively and a pH of about 8.0. Under such conditions, with air being bubbled through the emulsion, an 84% reduction in the diesel oil-water emulsion COD concentration was achieved. The Fenton/UV process (without any TiO_2 or ZnO) achieved a 61% COD reduction. They illustrate that the issues relating to TiO_2 and Fe residuals in the wastewater effluent require further study. The objective of this work is to study the effectiveness of the AOPs in the degradation of oil in wastewater. The AOPs selected to carry out this study was heterogeneous photo-assisted system (UV/TiO_2/Fenton).

2. Materials and Methods

2.1. Reagents

Commercial gas oil was used in this study as the model pollutant for the degradation of oil from wastewater by AOP.

Gas oil was analyzed in Petroleum Research and Development Center / Ministry of Oil. The chemical compositions are Paraffins 62.5%, Aromatics 18.7% and Naphthenes 18.8%.

The paraffinic fraction composition of gas oil was identified by gas chromatography and revealed more than 66 alkane compounds, Fig.2. From this figure it can be observed that gas oil has a higher relative concentration in C9, C11, C12, C13, C14 and C15.

The functional groups present in gas oil were detected by FTIR analysis, Fig. 3.

Table 1 shows all the chemicals that used in the experiments. All the samples were prepared by dissolving requisite quantity in distilled water. The pH of the solution was adjusted by using H_2SO_4 solution.

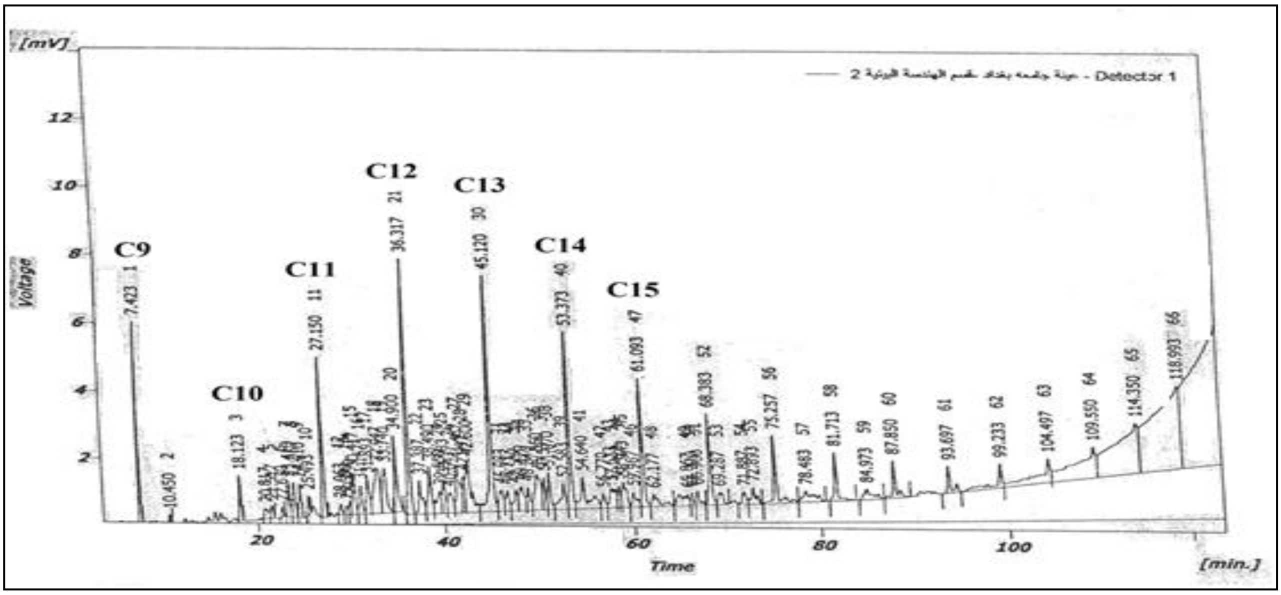


Fig. 2. The paraffinic fraction composition of gas oil.

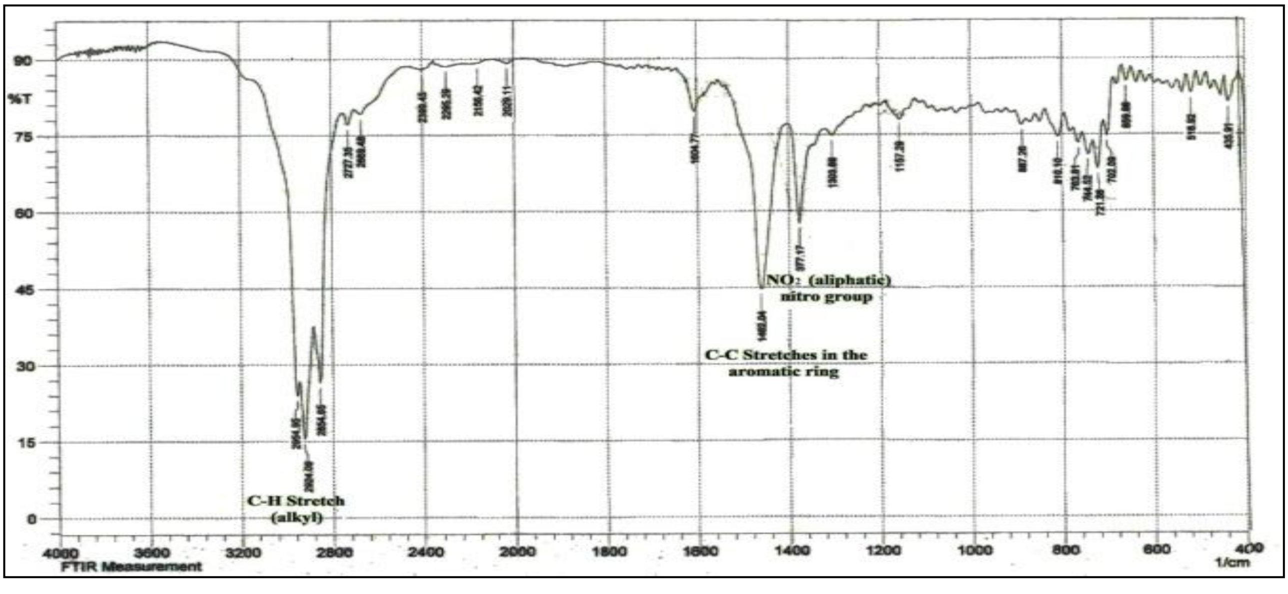


Fig. 3. The functional groups of gas oil detected by FTIR analysis.

Table 1,
List of chemicals used.

Compound	Formula	Vender
Hydrogen peroxide	H_2O_2	Scharlau (30 % wt/wt)
Ferrous chloroide tetrahydrate	$FeCl_2.4H_2O$	BDH (97% purity)
Sulfuric acid	H_2SO_4	Riedel-deHaen (99 % purity)

2.2. Equipments

The experiments were carried out in a batch mode laboratory-scale reactor, Fig.4 .The reactor consists of Pyrex glass cylinder 3 litter volumes mounted at magnetic stirrer with heater (MSH-300N, BOECO, Germany).

UV radiation (254 nm) was generated from UV lamps (TUV 11W 4P-SE, Philips, England), which was fixed vertically at the top of the reactor. The lamp was totally immersed in the cylindrical reactor. UV lamp was sheathed in quartz sleeve for protection. The distance between the lamp and the reactor was fixed to be 5 cm to ensure maximum light irradiation [10].

The turbidity of the solution for three experiments was measured using turbidity meter (Hanna microprocessor, Italy).

Initial pH of solution was monitored using a pH meter from (WTW Co., German, INOLAB 720).

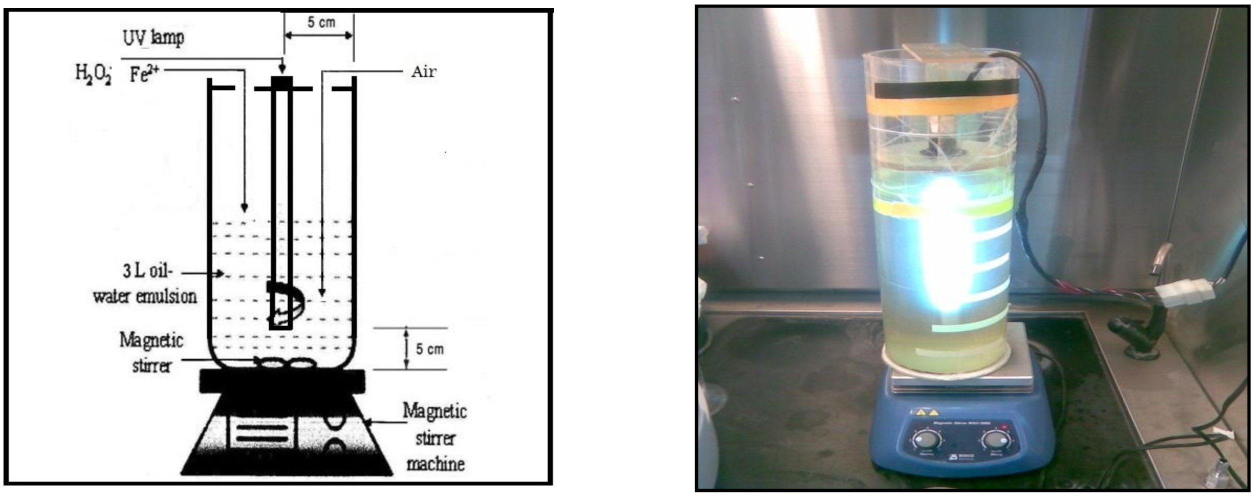
2.3. Experimental Procedure

The procedure was performed as follows:
The desired concentration of gas oil (500-2000) mg/L was prepared and the pH was adjusted before adding the reagents by adding a dilute H_2SO_4 solution in the reactor. The Fenton reagents were introduced to the solution by adding ferric chloride (10-100 mg/L) and then the hydrogen peroxide (100-800 mg/L).

The solution was then subjected to stirring using a magnetic stirrer at 200 rpm for 150 min. The heater was adjusted at the required temperature. Samples at a regular time intervals (30 min.) were taken for COD analysis.

2.4. Analysis

Chemical Oxygen Demand of samples was analyzed by using COD Photometer. The appropriate amount of sample (0.2ml) was introduced into commercially available digestion solution (HR-Rang: 0-15000mg/L) containing potassium dichromate, sulfuric acid and mercuric sulfate. The mixture was then incubated for 120 min at 150°C in a COD reactor (model RD-125, Lovibond Company, Germany). After oxidation is complete, the COD concentration was measured colorimetrically at 605 nm using a DR/2010 spectrophotometer (model RD-125, Lovibond, Germany).



(a) (b)

Fig. 4. Laboratory scale batch reactor (a) Schematic diagram of batch reactor, (b) Photograph of batch reactor.

3. Results and Discussion

3.1. Effect of Initial Titanium Dioxide (TiO_2) Concentration

From our previous study [11] , the optimal conditions for homogenous process were (H_2O_2= 400 mg/L, Fe^{+2} = 40 mg/L, temperature = 30°C, oil concentration =1000 mg/L and pH = 3) and the removal efficiency for the system UV/ H_2O_2/Fe^{+2} at that optimal conditions was found to be 72%. Different concentrations of titanium dioxide (50, 75, 100 and 300) were used to show its effect on UV/ Fenton system at optimum conditions, Fig.5, from this figure it can be noticed that the removal efficiency increases to reach a maximum of 61% at 75 mg/L of TiO_2, then it tends to decreases to reach 27% at 300 mg/L TiO_2.

The increase in removal efficiency can be explained by the increase in the number of oil molecules that were absorbed by the TiO_2. Moreover, when TiO_2 is exposed to UV light, the light induction generates a hole in the valence band and an electron in the conduction band. The oxidation of adsorbed water or hydroxyl ions by holes in the valence band at the excited surface produces the hydroxyl radicals. The resultant radicals degrade the oil molecules which increases the removal efficiency. However, increasing the TiO_2 dosage beyond an optimal value has a negative effect on the degradation process.

This is due to the fact that excess TiO_2 particles increase the opacity of the suspension there by decreasing the light penetration into the solution, resulting in a reduction in the number of hydroxyl radicals, this explanations were also mentioned by [12]; [9].

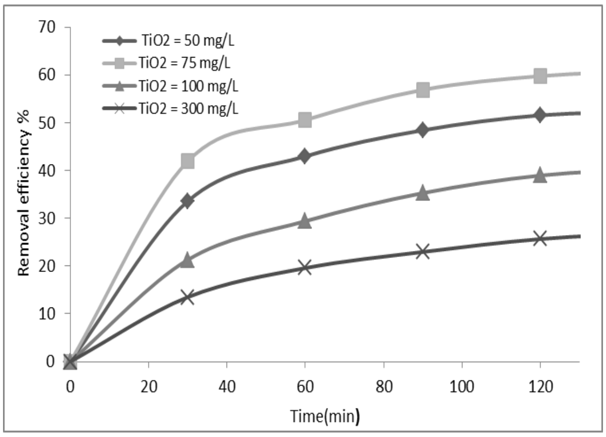


Fig. 5. Effect of initial titanium dioxide (TiO_2) concentrations on oil degradation by photocatalytic system at H_2O_2=400 mg/L, Fe^{+2}=40 mg/L, Temp. = 30°C, oil conc. = 1000 mg/L and pH=3.

3.2. Effect of the Initial pH

In order to study the effect of the initial pH in photocatalytic process, different values of pH (3, 4, 5, 6 and 8) were carried out at H_2O_2 = 400 mg/L, Fe^{+2} = 40 mg/L, TiO_2 = 75 mg/L and temperature=30°C. ,Fig. 6, from these figure it can be noticed that the removal efficiency increases to reach a maximum of 77% at pH=5.

The effect of pH cannot be generalized, it depends on the electrostatic interaction between the catalyst surface and the pollutant. Some authors recognized that the pollutants, which undergo hydrolysis under alkaline conditions, may show an increase in the rate of photocatalytic oxidation with an increase in the pH [13] ;[14].

The pollutants, which are weakly acidic, rate of photocatalytic oxidation increases at lower pH due to an increase in the extent of adsorption under acidic conditions [15]; [16] .

In 2009 Tony et al.[9] have reported that the pH had marginal effect on the extent of degradation for diesel oil water emulsion over the range of pH studied in their work, the optimum pH for photocatalytic oxidation was found to be 8.0.

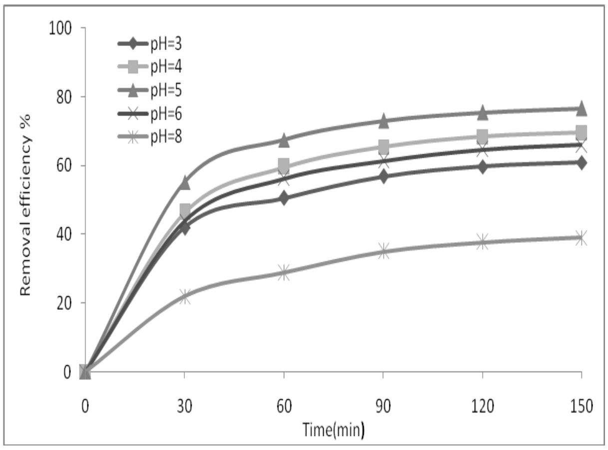


Fig. 6. Effect of the initial pH on oil degradation by photocatalytic system at H_2O_2=400 mg/L, Fe^{+2}=40 mg/L, Temp. = 30°C, oil conc. = 1000 mg/L and TiO_2=75 mg/L.

3.3. Effect of Air Bubble and Aluminum Foil

The performance of inducing air bubbles into the reactor and using aluminum foil cover around the reactor on the removal efficiency of oil were studied , Fig. 7. It can be noticed from Fig.(7) that the removal efficiency increases from 77% to

80% when using aluminum foil cover and reaches to 81 % when using air bubbling and aluminum foil.

Aluminum foil cover can enhance the degradation efficiency because it reflects irradiation exerting by the outer wall of the reaction vessel.

When air is bubbled into solution, the O_2 can scavenge the photon-produced electrons on the TiO_2 surface, thereby improving the overall reaction rate. In addition, the presence of O_2 in air noticeably works as an oxidizing agent for the organic molecules present in the solution [17].

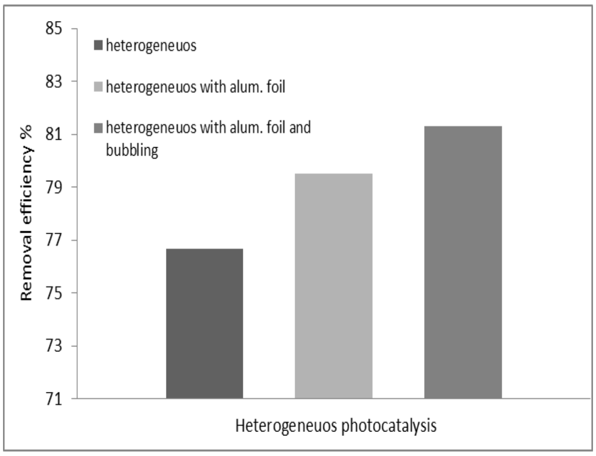


Fig. 7. Degradation of oil by heterogeneous photocatalytic system at H_2O_2=400 mg/L, Fe^{+2}=40 mg/L, Temp. = 30°C, oil con. = 1000 mg/L, TiO_2=75 mg/L , pH=5 and irradiation time =150 min.

3.4. Reaction Rate Constant for Homogenous and Heterogeneous Photocatalyst

The experimental data for diesel oil degradation can be fitted according to pseudo-first-order and pseudo-second-order.

The linearized form of pseudo-first-order and second-order kinetic models can be given in equations (1) and (2):

$$\mathrm{Ln}\left(\frac{COD}{COD_o}\right) = K\,t \qquad \ldots(1)$$

$$\frac{1}{COD} - \frac{1}{COD_o} = K_1 t \qquad \ldots(2)$$

Where COD_o is the initial concentration of gas oil and COD is the concentration at irradiation time t , K and K_1 are the pseudo-first- and pseudo-second-order rate constants in min^{-1} and $L.mg^{-1}$ min^{-1} respectively , t is the irradiation time (in min).

A plot of $\ln\left(\frac{COD}{COD_o}\right)$, and $\frac{1}{COD} - \frac{1}{COD_o}$ versus time for each experiment lead to a straight line whose slope is K and K_1 respectively. The regression analysis of the concentration curves versus reaction time indicates that the decomposition rate of this compound could be described by first order kinetics. The results are shown in Table2.

4. Conclusion

UV/TiO_2/Fenton(heterogeneous hotocatalysis) was used to examine the performance of AOP for the degradation of oil in wastewater .The reaction was influenced by the input concentration of H_2O_2, the amount of the iron catalyst Fe^{+2}, pH, temperature, the amount of TiO_2 and the concentration of oil in the wastewater. The reaction was found to be of a first order throughout the systems.

The removal efficiency for the system UV/TiO_2/Fenton at optimal conditions and dosage (H_2O_2 = 400mg/L, Fe^{+2} = 40mg/L, pH=5, temperature =30°C, TiO_2=75mg/L) for 1000mg/L load was found to be 77%.

To improve the performance of AOPs, aluminum foil cover around the reactor and air bubbling were utilized. The removal efficiency was improved to 81% for UV/TiO_2/Fenton systems respectively.

Table 2,
Pseudo-first-order, pseudo-second-order rate constants (effect of aluminum foil and air bubbles in homogeneous system and heterogeneous system)

Homogenous process; H_2O_2=400mg/L , Fe^{+2}=40mg/L , Temp.=30°C , pH=3

Treatment	**Removal efficiency**	**First order**		**Second order**	
		$Kx10^3min^{-1}$	**R^2**	**$K_1x10^6Lmg^{-1}min^{-1}$**	**R^2**
With alumn. Foil	75	16.1	0.930	15.3	0.914
With alumn. Foil + air bubble	79	17.5	0.911	19.2	0.922

Heterogeneous photocatalyst ; H2O2=400mg/L , Fe+2=40mg/L , Temp.=30oC , pH=5 ,TiO2=75mg/L

Treatment	**Removal efficiency**	**First order**		**Second order**	
		Kx103min-1	**R2**	**K1x106Lmg-1min-1**	**R2**
With alumn. Foil	80	18.4	0.926	18.5	0.918
With alumn. Foil + air bubble	81	20.2	0.927	25.0	0.891

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ازالة الزيوت من المياه الملوثة باستعمال طريقة التحفيز الضوئي الغير متجانس

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الخلاصة

تم في هذا البحث التحقق من امكانية استخدام طريقة الأكسدة المتقدمة / الغير متجانسة ($UV/TiO_2/Fenton$) لمعالجة مياه الصرف الملوثة بالزيت. تم دراسة تاثير تركيز بيروكسيد الهيدروجي H_2O_2 ، التركيز الابتدائي لايون الحديد المحفز F^{2+}، والدالة الحامضية ودرجة الحرارة، تركيز مادة TiO2والتركيز الاولي للزيت في مياه الملوثة. تم التوصل الى ان اكفئ إزالة كانت عند تركيز بيروكسيد الهيروجين =٤٠٠ ملغم /لتر وتركيز الحديد المحفز =٤٠ملغم /لتر ودالة حامضية =٥ و درجة حرارة =٣٠ درجة مئوية وتركيز ثاني اوكسيد التيتانيوم ٧٥ ملغم / لتر عند تركيز اولي للزيت =١٠٠٠ ملغم/ لتر بلغت ٧٧%.

بهدف زيادة الكفاءة تم تغطية جدار المفاعل بورق الالمنيوم اضافة الى ضخ الهواء مع المواد المتفاعلة، وبذلك ازدادت نسبة الازالة للنظام $UV/TiO_2/Fenton$لتبلغ 81 % .
