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Chemical Oxidation for Oil Separation from Oilfield-Produced Water / Homogeneous Process by Batch Technique

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Keywords:
Advanced oxidation process; Photo-fenton; Produced water; Spectrophotometer ultraviolet.

Highlights:

- An effective treatment approach by photo-Fenton oxidation method.
- Effects of irradiation time, pH value, hydrogen peroxide, Fe+2 doses, and UV intensity.
- Using of Photo-Fenton, Fenton, and Ultraviolet, Photo-Fenton of removing oil from produced water.

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Abstract: Water production is vital in environmental pollution because it contains many harmful contaminants to the environment and human health, such as oils, suspended solids, dissolved substances, and many other pollutants. The present study examined the advanced oxidation processes (AOPs) to purify the produced water from the Al Khabaz oilfield in the north of Iraq - Kirkuk province from oil content. Because of AOPs' ease of use, performance, and low price, it is a popular method for purifying this type of wastewater. This work used Photocatalytic homogeneous processes (Photo-Fenton (H_2O_2+Fe^{+2}+UV), Fenton (H_2O_2+Fe^{+2}) and Ultra Violet (UV)only) in the batch system under the best conditions (Time= 120 min, pH= 2.5, H_2O_2=20 ml in photo-Fenton process, H_2O_2= 80 ml in Fenton process, 2 UV lamps (capacity of each one=8 watt) in photo-Fenton, 10 UV lamps in direct UV process, and Fe^{+2}=18 mg in photo-Fenton & Fenton processes). The present work studied the impact of H_2O_2 & Fe^{+2} dosages, irradiation time, pH value, and intensity of UV on the oil removal effectiveness. It was found that the highest efficiency percentage in the Photo-Fenton process was 85.68, the percentage in Fenton was 75.01, and in the direct UV Photolysis was 56.64 percent. Therefore, it was concluded that the photo-Fenton process is the best approach to remove oil from produced water.

الأكسدة الكيميائية لفصل النفط عن المياه الناتجة عن حقول النفط / العملية المتجانسة بواسطة تقنية الدُفعات

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الخلاصة

تعتبر المياه المصاحبة للنفط من أخطر أنواع التلوث على البيئة، لأنها تحتوي على العديد من الملوثات الضارة بالبيئة وصحة الإنسان مثل (النفط، المواد الصلبة العالقة، المواد الذائبة، والعديد من الملوثات الأخرى). يتناول هذا المقال عمليات الأكسدة المتقدمة (AOPs) التي تمت دراستها لتنقية المياه المنتجة من حقل الخباز النفطي الواقع في شمال العراق - محافظة كركوك من المحتوى النفطي. نظرًا لسهولة استخدام AOPs والأداء والسعر المنخفض، فهي طريقة شائعة لتنقية هذا النوع من مياه الصرف الصحي. في هذا العمل تم استخدام عمليات التحفيز الضوئي المتجانسة (Photo-Fenton ($H_2O_2+Fe^{+2}+UV$)، Fenton ($H_2O_2+Fe^{+2}$)، وUltra Violet (UV) فقط) في نظام الدفعات تحت أفضل الظروف (الزمن = ١٢٠ دقيقة، الرقم الهيدروجيني = ٢,٥، H_2O_2 = 20 مل في عملية فوتو فنتون، H_2O_2 = 80 مل في عملية فنتون، ٢ مصباح UV (قدرة كل واحد = ٨ وات) في عملية فوتو فنتون، ١٠ مصابيح UV في عملية UV مباشرة، و Fe^{+2}=18 مجم في عمليات فوتو فنتون وفنتون). تم في هذا البحث دراسة تأثير جرعات H_2O_2 وFe^{+2} وزمن التشعيع وقيمة الرقم الهيدروجيني وشدة الأشعة فوق البنفسجية على فعالية إزالة النفط. حققت هذه الدراسة أعلى كفاءة في الفوتو-فنتون هي ٨٥,٦٨٪، الفنتون= ٧٥,٠١٪، والتحليل الضوئي فوق البنفسجي المباشر= ٥٦,٦٤٪. ونتيجة لذلك تم التوصل إلى أن عملية الفوتو فنتون هي أفضل طريقة لإزالة النفط من المياه المصاحبة للنفط.

الكلمات الدالة: الاشعة فوق البنفسجية، عمليات الاكسدة المتقدمة، مقياس الطيف الضوئي، فوتوفنتون، مياه مصاحبة للنفط.

1.INTRODUCTION

In the latest years, the increase in human activities, i.e., industrial, agricultural, and domestic sectors, has resulted in excessive organic pollutants in treatment facilities for wastewater, resulting in an outflow to the natural water resources that consider the required environmental and health regulations. Because of its perilous nature, oil-polluted wastewater could result in significant ecological snags [1]. Produced water (PW) is wastewater generated from crude oil extraction. Contaminants in produced water include many toxic elements, inorganic, and organic constituents, such as Oil minerals, Phenol, Sulfate, Phosphate, Heavy substances, Salts, and similar Minerals. Subsequently, a certain amount of water content will end up companying the oil extracted that includes an amount of aliphatic, aromatic, and Phenol. Wastewater is considered a worldwide threat due to its involvement in cancer causes and dangers to the ecological system and human health in general [2]. Such type of wastewater management needs inexpensive and ecologically friendly treatment methods to achieve the recycling and reuse goals. Four specific methods must be followed: reduction, disposal, preparation, and recycling. Numerous methods can be used for treating this kind of water to separate several organic components from produced water [3], such as coagulation [4, 5] adsorption [6, 7] biological separation [8] and membrane separation [9]. However, none of these treatment procedures sufficiently treat the generated water. Advanced oxidation processes (AOPs) are the optional additional phase of treatment [10]. AOPs have been investigated as an alternative to existing treatment methods for the treatment of oil-contaminated wastewater [11]. AOPs are characterized using powerful oxidizing products known as hydroxyl radicals (•OH), that damage and convert (organic matter) wholly or partly into a mineral or inorganic material or structure in wastewater. Both forms of AOPs, homogeneous and heterogeneous [12], could be applied with or without light exposure. The homogeneous Photo-Fenton, Fenton, and UV processes were utilized in the present study of oily effluent treatment at the oilfield. Many studies have discussed AOPs to terminate organic pollutants, such as ZnO [13] and TiO_2, as solar photocatalysts [14] and photo-fenton oxidation [15, 16]. Other researchers have also proposed AOPs to remove Phenol [17, 18], Mineralizing [19], and Dyes removal from aqueous medium [20]. Also, it was used to remove olive press residue [21]. The major objective of this study is to tear out oil from generated water at the Al-Khabaz oilfield in northern Iraq by employing (homogeneous process) Fenton, photo-Fenton, and photolysis (UV only). The investigation included finding an effective process with excellent removal effectiveness and examining the effects of reagent dose, UV strength, pH rate, and irradiation time on the process. It should be noted that the oil removal involves the breakdown of the total amount of organic contaminants.

1.1.Experiment

For the experimental process in the batched system procedure, AOPs were used. Reaction time, UV lamps' influence, pH value, and H_2O_2 and Fe^{+2} doses were all studied.

2.MATERIALS AND METHODS

2.1.Materials

The chemical substances used in this research were hydrogen peroxide (30% W/V, India), Fe^{+2} (99%, India), NaCl (99.5%, India), NaOH (98%, India), and H_2SO_4 (96%, Belgium) to modify the pH. The oil content in the generated water was separated using the organic solvent n-Hexane (CH_3. $(CH_2)_4$ .CH_3), 95% pure and imported from India. Samples of generated effluent were provided by the Al-Khabaz oilfield in the north of Iraq. Water-selected samples taken from the abovementioned oil field were employed in tests and stocked at conditions comparable to those found in its natural world, which included oxygen and other elements, to obtain a successful treatment. Table 1 lists the properties of produced water.

Table 1 Produced Water Characteristics.

Parameter	Value
API at 15.6°C	27.0
Calcium	0
Electrical conductivity	84650 µs/cm
Density at 15.6°C	1.12235 g/cm³
Ferrous	0
Magnesium	1%
Turbidity	25.8
TSS	31 mg/l
Phosphate	0.103 mg/l
Sp. gr	1.1224
Sulphate	8946 mg/l
TDS	54210 ppm
Concentration of Oil	15 mg/l
pH	5.9

2.2. Experimental Methods and Procedure

2.2.1. ($UV/H_2O_2/Fe^{+2}$) Photo-Fenton Process

The experiment was performed in a batch reactor with mechanical stirring. Under ideal circumstances, photo-Fenton experiments were conducted in a 250 ml glass beaker using a UV chamber glass batch reactor with (2–10) Ultra-Violate bulbs, each with an output of (8) Watt and a wavelength range of 365 nanometers (TL 8W BLB, Philips, Poland). Fe^{+2} (2–20 mg) and H_2O_2 (20–100 ml) were utilized at the room temperature. The pH range employed was (2.5-9.5), and the exposure duration ranged from 30 to 120 minutes. A 250 mL beaker was first filled with 100 mL of the produced water, and the pH of the sol was regulated by a pH meter (Device Model: pHep®4 pH/Temperature Tester-HI98127). The test began with turning the UV bulbs on and the magnetized stirrer at 200 revolutions per minute to ensure the solution was evenly mixed in a glass beaker. After the experiment, a tiny sample was taken and analyzed at 236 nanometers with a UV spectrophotometer.

2.2.2. (Fe^{+2}/H_2O_2) Fenton Process

The materials mentioned in the photo-Fenton process were employed in this procedure without UV lights under ideal circumstances and at room temperature. To start the experiment, the magnetized stirrer was turned on at 200 revolutions per minute. After the experiment, a fine sample was taken and evaluated at 236 nanometers with a UV spectrophotometer.

2.2.3. Direct Ultraviolet Photolysis Processes

At this stage, just (2–10) UV lamps were employed without reagent addition under room temperature and ideal circumstances. To start the experiment, the magnetic stirrer and UV lamps were turned on by setting to 200 revolutions per minute. The substance was analyzed using a UV spectrophotometer at a wavelength of 236 nanometers. The experiments were conducted at room temperature. The effectiveness of detaching oil from generated water was determined by applying an efficiency equation.

$$\text{Oil effectiveness of removal}(\eta) = \frac{C_{In} - C_{Tr}}{C_{Tr}} \times 100\%$$

50 ml of produced water was blended with 0.25 grams of NaCl salt in the separatory tube to break down the oil emulsion. The medley was shaken up for (2) minutes after adding 5 ml of (n-Hexane). After 20 minutes, the mixture was divided into two layers. The upper layer (organic layer) was utilized to calculate the absorbance value and a calibration curve to determine the oil concentrations.

3. RESULTS AND DISCUSSION

3.1. Impacts of Ultraviolet Exposure Period

The effect of UV exposure and the time needed to eliminate organic contaminants from generated water was examined during a period of (30-120) minutes. A batch system was performed to explore the relation between the efficacy of oil elimination and the time of irradiation by photo-Fenton and the direct Ultraviolet photolysis techniques. Figure 1 shows that the effectiveness of oil removal from produced water is directly related to the irradiation period, related to the chemical oxidation of oil by releasing hydroxyl free radicals (•OH). The results showed that 120 minutes was the effective irradiation time for the degradation of organic compounds. At this time, oil removal efficiency reached its highest value. Oil removal efficiency is expected to increase more than this value if the produced water is exposed to ultraviolet radiation longer. As a result, more free radicals (•OH) would be produced due to numerous reactions taking place.

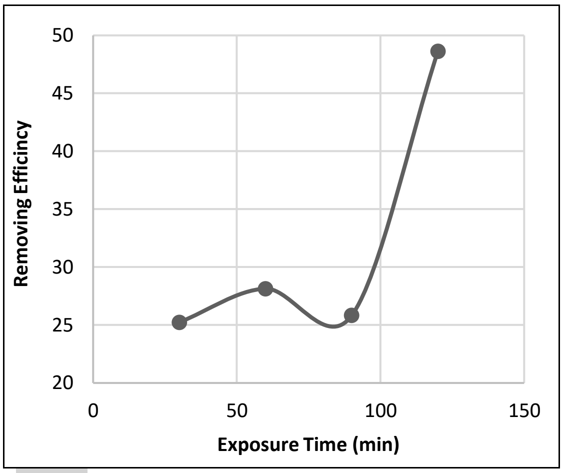

Fig. 1 Impacts of Ultraviolet Exposure Time.

3.2.Impacts of pH Value

The influence of pH at various values, i.e., 2.5, 4, 7.5, 8, and 9.5, on removal oil efficiency was tested in batch systems. Figure 2 shows that the highest oil removal efficiency was attained at a pH of 2.5; however, as the pH increased above this point, the oil removal efficiency rapidly declined. As a result, while the solution was in an acidic medium, it might have removed the most oil from the produced water. However, at pH values above 2.5, the removal efficiency started to decline, i.e., the amount of reactive free radicals produced would be low, leading to low removal efficiency because H_2O_2 has a high degree of oxidation at low pH levels. The creation of free radicals was influenced by the pH value, the hydrogen peroxide decomposition effectiveness, and iron ions formation.

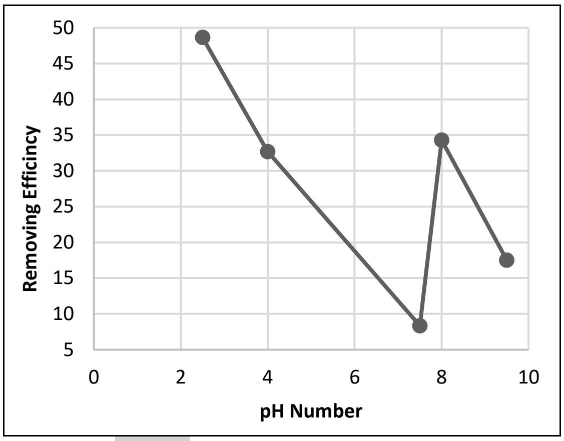

Fig. 2 Impacts of pH Value.

3.3.Impacts of Hydrogen Peroxide Doses

To determine the best amount of dosage required for oil breakdown in generated water, numerous tests were conducted on the homogeneous Photo-Fenton process and the Fenton process at different H_2O_2 dosages, i.e., 20, 40, 60, 80, and 100 ml. Figures 3 and 4 indicated that the Photo- Fenton, the best dose of hydrogen peroxide was 20 ml, i.e., the highest oil removal efficiency was attained at this dose. However, increasing the H_2O_2 dose reduced the oil removal effectiveness because the free radicals (•OH) reaction increase with excessive hydrogen peroxide doses (H_2O_2) would result in (•OH_2) radicals production, and these radicals were less effective than the (•OH) radicals [1]. However, in the Fenton process, the oil breakdown rate increased from 20 to 80 ml of H_2O_2, with the best removal obtained at a dose of 80 ml. When H_2O_2 concentration increased up to 80 ml, the degradation rate decreased because the increase in the hydrogen peroxide formed double radicals, which are less efficient in the treatment, forming a hazy substance due to forming these radicals, so re-combination occurred, decreasing the efficiency again.

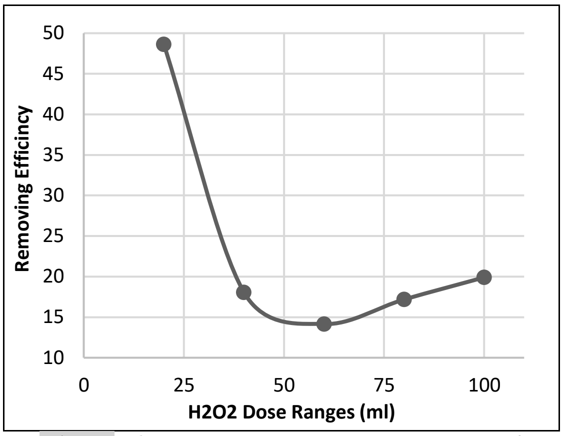

Fig. 3 Photo-Fenton Process: Impacts of (H_2O_2) Dose.

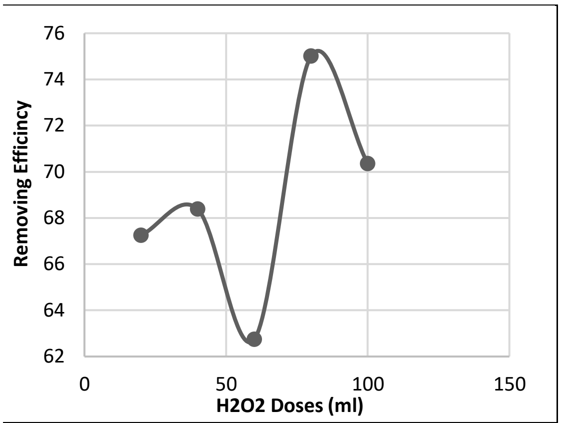

Fig. 4 Fenton Process: Impacts of (H_2O_2) Doses.

3.4.Impacts of Fe^{+2} Doses

Numerous trials were conducted to explore the effect of ferrous sulfate (Fe^{+2}) dosages on the photo-Fenton process and Fenton at doses ranging from (2, 4, 6, 12, 18) mg. Figures 5 and 6 show that increasing the doses of Fe^{+2} enhances the effectiveness of oil removal (the best dose is 18 mg) for each method, Fenton and photo-Fenton, due to the formation of many free radicals at this point, which causes increasing in oil removal efficiency. In the two processes observed when Fe^{+2}= 4 mg sharply dropped in removal efficiency perhaps due to the deposition of salts during the treatment.

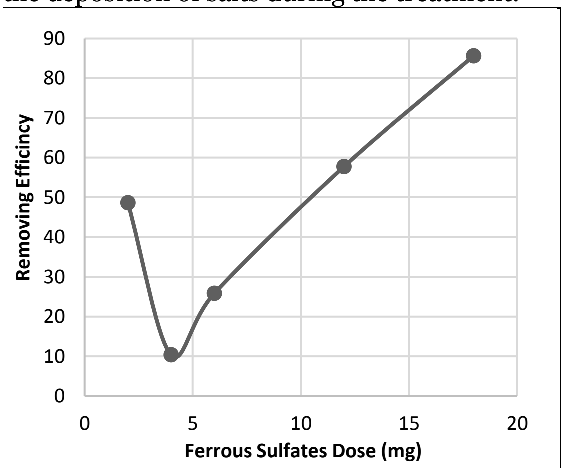

Fig. 5 Photo-Fenton Process: Effects of Fe^{+2}.

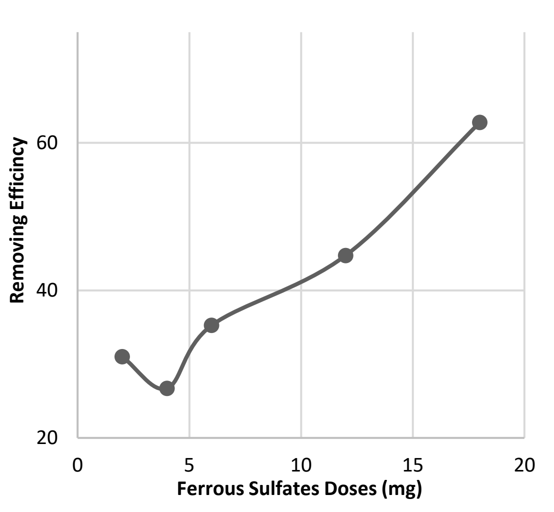

Fig. 6 Fenton Process: Impact of Fe^{+2}.

3.5.Impacts of Ultraviolet Intensity

The number of ultraviolet bulbs in photo-fenton and ultraviolet direct photolysis processes (2, 4, 10) bulbs (16, 32, 80) Watts effects were examined. Figure 7 shows that the effectiveness of removal oil declined with an increase in UV's intensity in the photo-Fenton process, i.e., the best intense was 16 Watt, 2 lamps) because the produced water was untreated by any primary treatment process; it might contain many contaminants and ions that interact with chemicals and oppose the ultraviolet rays due to forming double radicals, which are less efficient in the treatment process; however, in the ultraviolet direct photolysis processes, when UV intensity increased, the effectiveness of oil removal increased, i.e., the highest removal happened using a UV intensity of 80 Watt, due to the increased formation of free radicals, which increased the removal process efficiency, as shown in Fig. 8.

4.CONCLUSIONS

The present study used modern oxidation techniques in processing due to its environmentally beneficial for removing organic contaminants from generated water, including homogeneous Fenton, photo-Fenton, and photolysis only ultraviolet processes. These processes in the batch system were utilized to investigate eliminating oil from produced water at the Al Khabaz oilfield in the Kirkuk governorate of Iraq. To achieve the highest oil removal the batch reactor was employed at the best conditions for this work. The results of the research showed that:

1- The Photo Fenton (H_2O_2/Fe^{+2}/UV) homogeneous photocatalysis process was conducted under the best conditions to find the best time that gave the highest efficiency for oil removal, i.e.,120 min. It was found that the best pH value = 2.5, H_2O_2 dose = 20 ml, Fe^{+2} dose = 18 mg, and the UV intensity = 16 Watt in a batch system to achieve the highest removal efficiency obtained, i.e., 85.68%, with the best operation conditions at room temperature.

2- The Fenton (H_2O_2/Fe^{+2}) homogeneous process was conducted under the best conditions, i.e., pH= 2.5, time= 120 min, and at room temperature, by finding the best dose of H_2O_2, i.e., 80 ml and the dose of Fe^{+2}, i.e., 18 mg, in a batch system based on the highest removal efficiency obtained, i.e., 75.01%.

3- The direct photolysis process (only UV) was conducted under the best conditions, i.e., pH= 2.5, time= 120 min, and at room temperature). It was found that the best UV intensity, i.e., 80 Watt, in a batch system based on the highest removal efficiency obtained, i.e., 56.64%.

The present study results showed that photo-Fenton oxidation is an effective treatment approach. The effects of the irradiation period, pH value, Hydrogen Peroxide (H_2O_2) and (Fe^{+2}) doses, and ultraviolet intensity were examined.

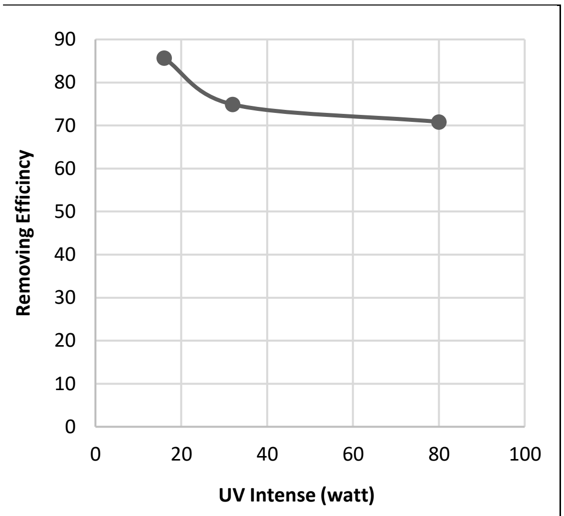

Fig. 7 Photo-Fenton: Impacts of Ultraviolet Intense.

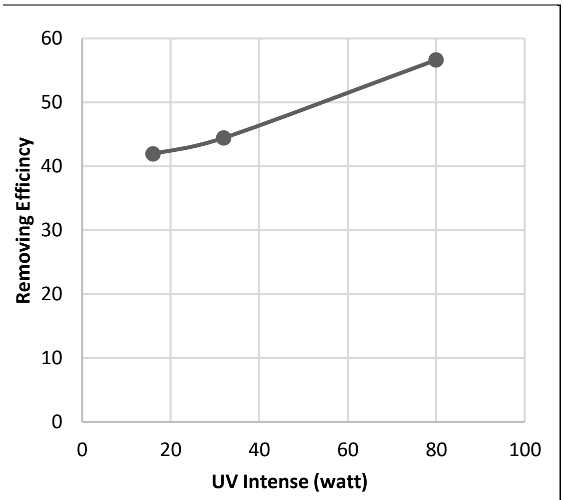

Fig. 8 Ultraviolet Direct Photolysis Impacts of UV Intense.

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