JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2021, 22(8), 278–286
https://doi.org/10.12911/22998993/140281
ISSN 2299-8993, License CC-BY 4.0

Received: 2021.06.16
Accepted: 2021.07.24
Published: 2021.08.10

Oil Recovery from Oilfield Produced Water Using Zinc Oxide Nano Particle as Catalyst in Batch and Continuous System

Hussein Ali Jabbar Alkhazraji[1], Mohammed Jaafar Ali Alatabe[1*]

[1] Department of Environmental Engineering, College of Engineering, Mustansiriyha University, P.O. Box 14150, Babal-Mu'adhem, Baghdad, Iraq

* Corresponding author's email: husseineng89.z@gmail.com

ABSTRACT

This article describes the design of photo catalyst reactor for oil removing from produced water. Real produced water containing a combination of organic compounds was treated with zinc oxide nanoparticles. In this study, ultraviolet radiations were used to find the efficiency of removing the oil content from the water produced that brought from the Al-Ahdab oilfield in kut/ Iraq by advanced oxidation process (AOP) using (ZnO/UV) in batch system and continuous system. In batch system were studied the effect of zinc oxide concentration (nanoparticles), time of irradiation, and pH. The highest removal rate of oil from the produced water (100%) was obtained during the following optimal conditions: ZnO NPs as catalyst = 55 mg/L, pH =3, at the time of irradiation of 90 minutes in batch experiments. In the continuous system, the effects of flowrate, number of UV-A lamp and time of reaction were studied, the results obtained were the efficiency of decomposition decreases with increasing the flow rate of solution in reactor, the maximum removal efficiency of the process (ZnO/UV) was 80% at 20 mL/min and irradiation time 120 min. In general, zinc oxide is beneficial through its high oil adsorption capacity in addition, It lowers the amount of oil in the produced water.

Keywords: photocatalytic, produced water, oil content, Advanced oxidation processes (AOPs), ZnO/UV.

INTRODUCTION

Produced water is a by-product of gas and oil production; throughout the crude oil extraction, water rises to the surface from deep formations. The treatment processes include basic separation techniques to remove oils, grease and all suspended and solid materials, as well as advanced processes to remove inorganic ions, organic compounds and radioactive materials [1, 2]. The amount of produced water ranges from 0.4 to 1.6, which is equivalent to twice the amount of oil extracted [3]. The produced water contains complex compounds comprising both inorganic and organic substances, with the main components of oils, free phenols, salts and emulsifiers [4]. If the remaining produced water is not treated, it will cause the studied problems concerning the environment [5]. Since the oilfield wastes pollute the environment, they must be handled before being removed. Treating this waste can lead to enhanced separation of oil/water, water recycling, environmental protection, oil recovery, and compliance with environmental legislation [6]. According to environmental legislation and concerns, there is no doubt that treating the produced water is important to reduce the resulting environmental damage. All strict environmental regulations require various types of treatment of wastes produced by gas and oil manufacturers before being released and injected into the reservoir [7]. The treatment of produced water is carried out for reducing the concentration of organic pollutants to acceptable levels [8]. The conventional treatment that was implemented was less effective in removing some contaminants from the produced water [9, 10]. There are numerous techniques available for separating the oil content from produced water, Including various

coagulation / flocculation methods [11, 12, 13], Adsorption [14], The biological separation process [15], and the process of separating the membrane [16]. However, none of the above-mentioned treatment methods are currently used for produced water treatment. There is an optional additional treatment stage, known as (AOPs) advanced oxidation processes [17, 18]. Advanced oxidation process have evolved to be environmentally friendly wastewater handling strategies that produce innocuous final results [19]. The fundamental strength of this chemical handling stems from the production of (*OH) hydroxyl radicals, it can effectively decompose and mineralize any organic pollutant into H_2O and CO_2. AOPs are divided into two kinds: homogeneous and heterogeneous procedures that can be directed without or with light illumination. Homogeneous procedure is a common photochemical reaction that occurs when iron particles and hydrogen peroxide (H_2O_2) react in the presence of light called (photo-Fenton) [20]. Heterogeneous photo-catalysis utilizing semiconductor catalysts (ZnO, TiO_2, CdS, and Fe_2O_3), It has proven ability to convert a wide range of powerful and mysterious organic materials into rapidly biodegradable formulations, and permanently mineralizes them into harmless substances, carbon dioxide and water [21]. Zinc oxide (ZnO) has received the best effective of photo-catalysis among semiconductor catalysts. It has a more efficient catalyst with regard to removing pollutants from water, because it generates (*OH) more efficiently, has high reactivity and mineralization rates, and it has greater active sites numbers with high surface interaction because of the high surface area relative to the volume [22]. Several researchers are debating the use of AOPs to eliminate organic pollutants: oxidation of photo Fenton [23] and ZnO & TiO_2 as solar photo catalysts [24]. AOPs have been used by other researchers for such purposes as removing phenol [11], mineralization [3], gasoline-contaminated water treatment [25]. It was also used to remove the remnants of olive presses [26]. The objective of this study was to use photo-oxidation processes to eliminate the oil content from the produced water that was brought from the Iraqi Al-Ahdab oilfield: first, to determine the best value of zinc oxide, the pH and the irradiation time effects in batch system; nevertheless, in continuous system, UV lamps number, flow rate of produced water, and UV radiation time effects were studied on the photo catalytic processes. It is important to remember that all organic compounds decomposed, which means the oil is completely removed from the water produced.

EXPERIMENT

The experimental work was divided into two parts: batch system and continuous system by (AOPs). The effect of ZnO concentration, pH and reaction time were studied in the batch process, while the impact of UV lamps, effect of flowrate, and effect of reaction time were studied in the continuous oxidation process.

Materials

The substance used in this research are zinc oxide nanoparticles powder with a particle size 35–45 nm (99% purity, USA), in order to adjust the pH NaOH (98% purity, India), H_2SO_4 (96% purity, Belgium) were used. Carbon tetrachloride (CCl_4) solvent (99% purity, India) was used for extracting the oil content from produced water. The chemicals were used without any other additive process.

The samples of produced wastewater were brought from the Ahdab oilfield in Waist province in middle of Iraq. In order to obtain a valuable treatment, the water samples obtained from the aforementioned oil field for these tests were preserved under environmental conditions similar to their original environment that contain oxygen and other values. Table 1 shows the classification of produced water.

Table 1. Properties of the produced water

Parameters.	Values mg/L
Oil concentration	53.56
pH	6.7
TDS	105216
Conductivity	164400
TSS	88
Oxygen dissolved in water	0.09
Sulphate	2745
Iron	0.33
Calcium	4800
Magnesium	2133

Methods

UV/ZnO NPs Batch Reactor

In this study, a batch reactor was used with a magnetic stirrer. In a glass beaker of 250-ml volume, photocatalytic experiments were carried out using the advanced oxidation technique, It is a glass batch reactor in a UV chamber with three UV lamps (TL 8W BLB, Philips, Poland), each with an output of 8 watts and a wavelength of 365 nm. Zinc Oxide Nanoparticles were utilized in range of 25–75 Mg/l at room temperature. The pH ranges of 3–8.5, and the irradiation period ranges from 30 to 150 minutes were employed. At first, 150 mL of produced water was poured into a 250 mL beaker and the pH was changed before adding the ZnO NPs catalyst, the solution pH was regulated with a pH meter (Model: BP3001, Singapore). The experiment was started by turning on the magnetic stirrer at 300 ppm to ensure uniform mixing of the solution in the beaker and turning on the UV lamps. After the experiment was completed, the sample was finely taken and analyzed using a UV spectrophotometer at 291 nm, as illustrated in Figure.

Continuous flow reactor system setup

Figure 2 shows the general sketch of the experimental design. The hollow chamber (6) was completely made of wood with the volume size of 90×70×70 cm^3 and painted black color from the inside to ensure that the UV light was not distracted. The box containing the continuous photocatalytic glass reactor was shown in Figure 3. The reactor is made up of two layers of glass, and its dimensions are 70×30×1 cm. The depth between these layers is 4 mm, the top layer glass is 6 mm thick, and the bottom layer is a reflexive mirror. The solution flows through the upper and lower layers. The solution was prepared in a feed tank (1) with a 15-liter capacity. In order to supply the produced water to the reactor, a water pump (2) was used and (5) is a calibrated flow meter used to control the flow levels of produced water passing through the reactor.

Continuous flow Photocatalytic Process

The photocatalytic oxidation of oil was accomplished by dissolving the required amount of photocatalytic powder in 15 liters of produced water. The oil content of the solution was 53.56 ppm. The pH of the feed tank (1) was adjusted to 6.7 by adding a diluted H_2SO_4 solution, the appropriate amount of ZnO NPs equal to 25 mg/l was added into feed tank (1). In order to achieve consistent mixing, valve (4) was closed to allow the solution to circulate for 15 minutes. Then, the solution was allowed to flow into the photocatalytic glass reactor (6) from the feeding tank (1), after turning on the pump (2). The ultraviolet lamp source putted on the continues flow glass reactor (6) was switched on. The used flow rates were controlled with the calibrated flow meter; they amounted to 20, 30, 40, and 50 ml/min. A valve (7) was used to take samples for testing. All

Figure 1. Photograph of reactor Batch System

experiments were conducted at room temperature. An efficiency equation was used for measuring the efficiency of oil removal in produced water.

$$Oil\ Removal\ Efficiency = \frac{C_{initial} - C_{treated}}{C_{initial}} \times 100, \% \quad (1)$$

where: η - Oil removal efficiency; $C_{initial}$ - untreated Oil concentration; $C_{treated}$ - treated Oil concentration in (ppm).

The following procedure used to obtain the amount of oil concentration in the produced water was measured by using a spectrophotometer (GENESYS 10uv, USA) at the maximum absorption wavelength 291 nm. 0.5 grams of NaCl salt was added in the separating funnel to 100 ml of produced water in order to break the emulsion of the oil. Then 10 ml of carbon tetrachloride (CCl_4) was added, followed by shaking vigorously for 2 minutes. After, 20 minutes the solution was separate in two layers, the organic layer (lower layer) was used to measure the absorbance value; later, the oil content concentrations were calculated using a standard curve.

RESULTS AND DISCUSSION

Batch Photocatalyst experiments

The effect of ZnO NPs dosage on Oil Removal

In general, the dose of the photo catalyst is recognized for its effect on the decomposition of the pollutant according to the interactivity between concentration of the organic pollutants in the solution and quantity of active sites in the element; therefore, the catalyst performance along with the quantity of active sites [27]. The effect of various

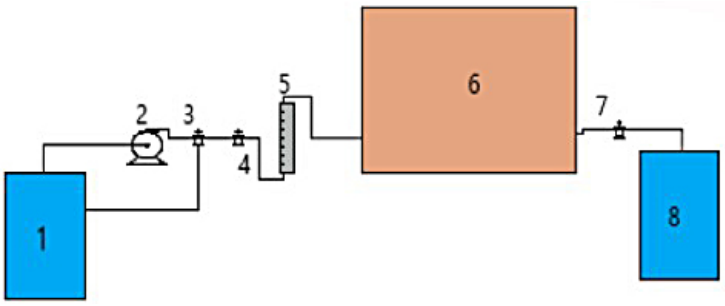

Figure 2. Sketch of designed continuous system., (1) Feeding. tank contain (P.W), (2) Pump.; (3) Divider.; (4) Valves.; (5) Calibrated flowmeter; (6) The hollow chamber inside is the photocatalytic reactor; (7) Valve for extracting samples, and (8) Tank contains treated (P.W)

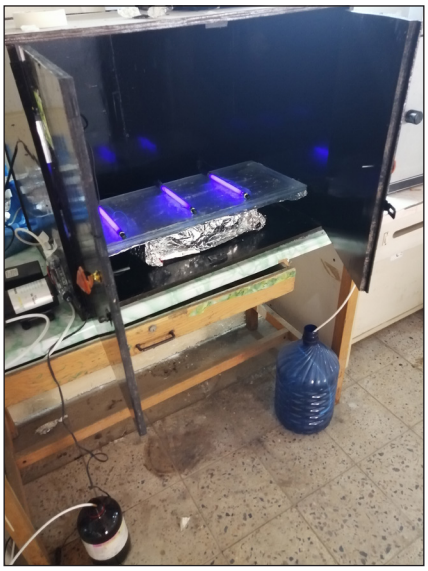

Figure 3. Photo of Photocatalytic glass reactor

ZnO NPs concentrations on the photo-chemical decomposition of oily produced water from 25 to 75 ppm (ZnO/UV) process was studied. The efficiency results are shown in Figure 4. At a pH of 6.7 and radiation time 90 min, the initial concentration of zinc oxide ranging from 25 to 55 ppm raises the oil removal efficiency from 81% at 25 ppm to reach the maximum efficiency of oil removal 94.875% at 55 ppm. Then, the oil removal efficiency decreased to 85% and 77.837% when increasing the concentration of ZnO NPs to 65 and 75 ppm, respectively.

The effect of UV radiation time

The influence of ultraviolet radiation time required to decompose the organic pollutants present in produced water was studied in range 30–150 minutes. The relationship between irradiation time and removal of oil content by photo catalysis using batch experiments was studied. Figure 5 shows that the irradiation time increased along with the oil removal percentage and that the maximum irradiation time is 150 minutes, while the best irradiation time is 90 minutes. This is consistent with the results [28, 29]. In general, the photocatalytic treatment requires minimal electricity consumption, which is approximately 60% of the total operating cost; however, the materials present in the solution can remain structurally similar to the primary organic compounds and thus, not degradable, if the pretreatment time is very short [23].

The Effect pH value on Oil Removal

In treating oily water, the pH is a significant key factor, in which the pH value for solution controls with the rate of production of free radicals that are created in the photocatalytic treatment. In order to obtain the maximum efficiency of oil removal, the pH effect was studied at various values on oil removal efficiency in photocatalytic processes by using ZnO NPs 55 ppm; radiation time 90 min with different pH. Figure 6 shows the maximum removal efficiency of oil content was 100% when pH was equal to 3.0,

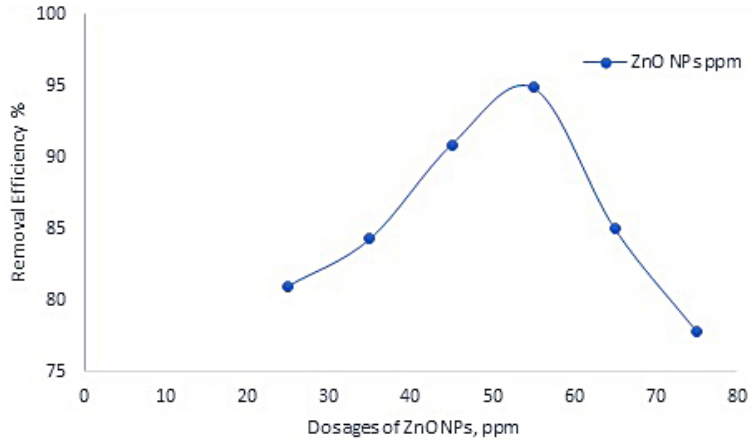

Figure 4. The effect dosage of ZnO on oil removal at pH = 6.7, 3 UV lamps, time radiation = 90 minute

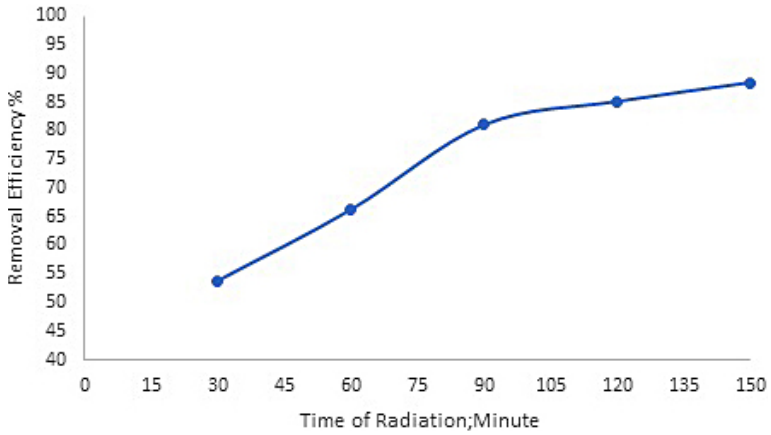

Figure 5. The effect of UV radiation time on removal % (ZnO NPs = 25 ppm; pH = 6.7; temp. = 20–25 °C)

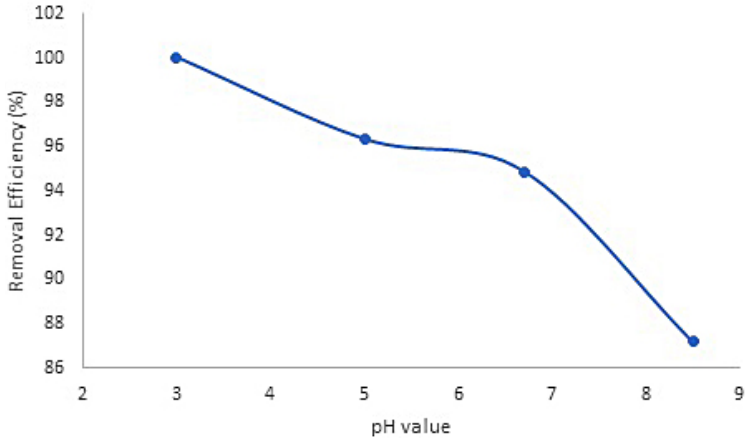

Figure 6. Effect various pH value on efficiency % (ZnO NPs = 55 ppm; radiation time = 90 min; temp.= 20–25 °C)

and reduced gradually to minimum removal efficiency 87.21% at pH = 8.5. Therefore, reducing the value of pH improves the active area of the catalyst agent; thus, at different pH, the catalyst surface charge can be in an effective wide range, which comes into contact with the adsorbent particles on the surface of the adsorbent and affects the removal efficiency rate; This agrees with [30].

Continuous system experiments

In this study, the continuous system of photocatalysis was studied, the effect of flow rate for water produced in the glass reactor as well as the effect of UV lamp number and the effect of reaction on the percentage of oil removal were studied. The factor for evaluating the continuous system was variable, while the others remained constant. The efficiency of removing oil content from the produced water was tested under various conditions.

The effect of UV lamps number

The impact of the UV lamp on oil removal efficiency in the catalyzed photocatalytic reactor was studied by change the of UV lamps number utilized (1, 2 and 3) on continuous photo catalysis (each with 8 Watt and wavelength = 365 nm). The procedure was tested to determine the number of UV lamps required for high oil removal efficiency. Parameters and quantity were kept constant (initial oil concentration in product water = 53.56 mg/L, pH = 6.7, flow rate = 20 mL/min, zinc oxide = 25 mg/L, time = 90 min at room temperature). Figure 7 illustrates the results of the removal efficiency of oil content from produced water increased along with the variable number of UV-A lamp from 1 to 3 due to the increase of free radicals. This is consistent with [31].

The Flow Rate effect on removal efficiency

The flow rate is an important parameter for investigating the percentage of oil recovery

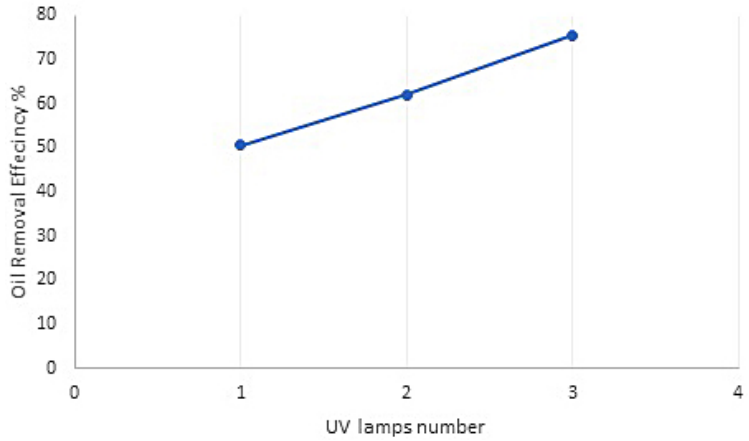

Figure 7. The effect of Uv lamps number with oil removal (ZnO NPs = 25 ppm; radiation time = 90 min; temp. = 20–25 °C)

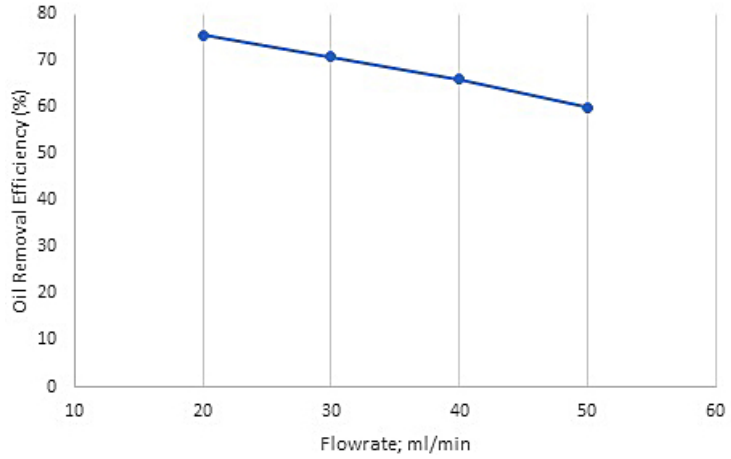

Figure 8. The Flow rate effect on the removal efficiency (ZnO = 25 mg/l, and 3 UV lamps, radiation time = 90 min)

from the water produced passing through the glass continuous photocatalytic reactor. By adjusting the flowrate of the produced water for the following ranges of 20, 30, 40, 50 ml/min, the oil removal efficiency was analyzed by using ultraviolet light (3 UV lamps, each of 8 watts with wavelength of 365 nm). Figure 8 shows that the high flow rate of the produced water in the continuous reactor has an adverse effect on the quality of oil removal. Moreover, the results showed that the efficiency of removing oil content increases with decreasing flow rate of the produced water, and vice versa. The flow rate of 20 ml/min of the solution obtains the highest removal efficiency of the oil content at 75.6% and decreases gradually. Thus, it is evident that the residence time of pollutant particles in the water produced with ZnO NPs is an important factor, and this coincided with [32].

The effect reaction time on removal efficiency

The reaction time of the water produced in a glass continuous reactor depends on the size of the reactor and the rate of solution flow into reactor. The effect of reaction time was studied under the following conditions: oil concentration in water produced = 53.56 mg/L, 3 UV lamps, pH = 6.7, room conditions, ZnO NPs = 25 ppm. Figure 9 illustrates the resulting indicate that the primary degradation rate is high, which is likely due to the increased interaction between the water produced and the surface of the photo catalyst. The efficiency of oil removal in the first 30 minutes was 49.11%. After increasing the cumulative volume retention time of the photo reactor at 60 minutes, the oil removal efficiency increased to 61.73% and then to 75.6% at 90 minutes. After increasing the radiation time to 120 minutes, the oil degradation level was remarkably constant at 80% of efficiency of oil removal. This is in agreement with [33].

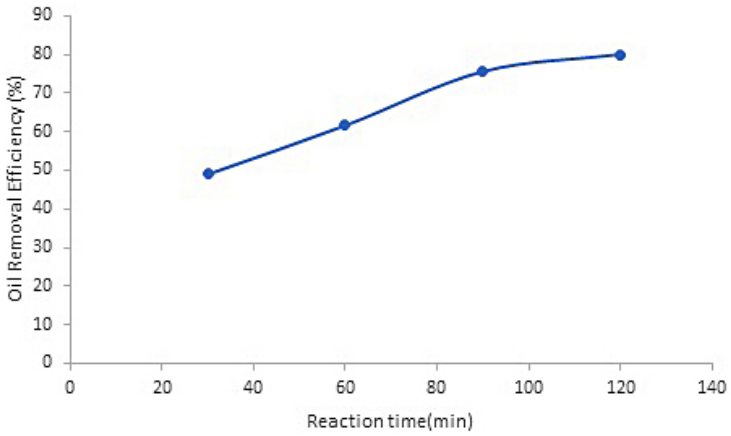

Figure 9. The reaction time effect on efficiency of oil removal (ZnO = 25 mg/l, 3 UV lamps, temp. = 20–25 °C)

CONCLUSIONS

In this study, the recovery of oil content from the water produced in Al Ahdab oilfield was studied by using heterogeneous catalytic ZnO nanoparticles for batch and continuous processes. The zinc oxide oxidant with the ultraviolet light (ZnO/UV) was used to destroy the organic pollutants in produced water. Decomposition of the oil content in produced water was performed in a glass reactor. The advanced oxidation process is an environmentally friendly method to eliminate the organic pollutants present in produced water and ZnO is a highly efficient oxidizing agent, reliable and stable semiconductor for elimination of organic pollutants under UV irradiation. In a batch system, very low catalyst concentration of ZnO NPs = 55 mg/L with pH = 3 as the optimum operating conditions achieved 100% removal efficiency of oil content. In continuous treatment system, flow rate, UV lamps number and reaction time effects were studied, the maximum oil removal percentage was 80% at 120 minutes.

REFERENCES

1. Rodriguez A.Z., Wang H., Hu L., Zhang Y., Xu P. 2020. Treatment of produced water in the permian basin for hydraulic fracturing: Comparison of different coagulation processes and innovative filter media. Water, 12(3), 770.
2. Hu L., Yu J., Luo H., Wang H., Xu P., Zhang Y. 2020. Simultaneous recovery of ammonium, potassium and magnesium from produced water by struvite precipitation. Chem. Eng. J., 382, 123001.
3. Aziz A.R.A. & Daud W.M.A.W. 2012. Oxidative mineralisation of petroleum refinery effluent using Fenton-like process. Chem. Eng. Res. Des., 90(2), 298–307.
4. Jiménez S. et al. 2017. Integrated processes for produced water polishing: Enhanced flotation/sedimentation combined with advanced oxidation processes. Chemosphere, 168, 309–317.
5. Sapareng S., Ala A., Kuswinanti T., Rasyid B. 2018. The ability of trichoderma sp and pleurotus sp for the decomposition of oil palm empty bunches. Pak. J. Biotechnol, 15(2) 543–548.
6. Okiel K., El-Sayed M., El-Kady M.Y. 2011. Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. Egypt. J. Pet., 20(2), 9–15.
7. Fathy M., El-Sayed M., Ramzi M., Abdelraheem O.H. 2018. Adsorption separation of condensate oil from produced water using ACTF prepared of oil palm leaves by batch and fixed bed techniques. Egypt. J. Pet. 27(3), 319–326.
8. Shokrollahzadeh S., Golmohammad F., Naseri N., Shokouhi H., Arman-Mehr M. 2012. Chemical oxidation for removal of hydrocarbons from gas–field produced water. Procedia Eng., 42, 942–947.
9. Alvarez-Corena J.R., Bergendahl J.A., Hart F.L. 2016.Advanced oxidation of five contaminants in water by UV/TiO_2: reaction kinetics and byproducts identification. J. Environ. Manage., 181, 544–551.
10. Karimi L., Zohoori S., Yazdanshenas M.E. 2014. Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nano-strontium titanate as the nanophotocatalyst. J. Saudi Chem. Soc., 18(5), 581–588.
11. Hernández-Francisco E., Peral J., Blanco-Jerez L.M. 2017. Removal of phenolic compounds from oil refinery wastewater by electrocoagulation and Fenton/photo-Fenton processes. J. Water Process Eng., 19, 96–100.
12. Fouad Y.O. 2014. Separation of cottonseed oil from oil–water emulsions using electrocoagulation technique. Alexandria Eng. J., 53(1), 199–204.
13. Mousa K.M., Al-Hasan A.A. 2017. Oilfield produced water treatment by coagulation/flocculation processes. Proceedings of the Second Conference of Post Graduate Researches (CPGR'2017), College of Engineering.
14. El-Din G.A., Amer A.A., Malsh G., Hussein M. 2018. Study on the use of banana peels for oil spill removal. Alexandria Eng. J., 57(3), 2061–2068.
15. Li Q., Kang C., Zhang C. 2005. Waste water produced from an oilfield and continuous treatment with an oil-degrading bacterium. Process Biochem., 40(2), 873–877.
16. Coto M., Troughton S.C., Duan J., Kumar R.V., Clyne T.W. 2018. Development and assessment of photo-catalytic membranes for water purification using solar radiation. Appl. Surf. Sci., 433, 101–107.
17. Poyatos J.M., Muñio M.M., Almecija M.C., Torres J.C., Hontoria E., Osorio F., 2010. Advanced oxidation processes for wastewater treatment: state of the art. Water. Air. Soil Pollut., 205(1), 187–204.
18. Rueda-Márquez J.J., Sillanpää M., Pocostales P., Acevedo A., Manzano M.A. 2015. Post-treatment of biologically treated wastewater containing organic contaminants using a sequence of H_2O_2 based advanced oxidation processes: photolysis and catalytic wet oxidation. Water Res., 71, 85–96.
19. Tony M.A., Purcell P.J., Zhao Y.Q., Tayeb A.M., El-Sherbiny M.F. 2009. Photo-catalytic degradation of an oil-water emulsion using the photo-fenton treatment process: Effects and statistical optimization. J. Environ. Sci. Heal. Part A, (44) 2, 179–187.
20. Czaplicka M. 2006. Photo-degradation of chlorophenols in the aqueous solution. J. Hazard. Mater., 134(1–3), 45–59.

21. Malato S., Fernández-Ibáñez P., Maldonado M.I., Blanco J., Gernjak W. 2009. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal. today., 147(1), 1–59.
22. Rao A.N., Sivasankar B., Sadasivam V. 2009. Kinetic study on the photocatalytic degradation of salicylic acid using ZnO catalyst. J. Hazard. Mater., 166, (2–3), 1357–1361.
23. Ebrahiem E.E., Al-Maghrabi M.N., Mobarki A.R. 2017. Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology. Arab. J. Chem., 10, 1674–1679.
24. Aljuboury D. al deen A., Palaniandy P., Aziz H.B.A., Feroz S. 2016. Withdrawn: Comparison and performance of petroleum wastewater treatment using photocatalytic TiO_2, photo Fenton, TiO_2/Fenton and TiO_2/Fenton/ZnO processes. Water Resources and Industry.
25. Tiburtius E.R.L., Peralta-Zamora P., Emmel A. 2005. Treatment of gasoline-contaminated waters by advanced oxidation processes. J. Hazard. Mater., 126 (1–3), 86–90.
26. Chatzisymeon E., Foteinis S., Mantzavinos D., Tsoutsos T. 2013. Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment. J. Clean. Prod., 54, 229–234.
27. Ling H., Kim K., Liu Z., Shi J., Zhu X., Huang J. 2015. Photocatalytic degradation of phenol in water on as-prepared and surface modified TiO2 nanoparticles. Catal. Today., 258, 96–102.
28. Hassan A.A. & Al-zobai K.M.M. 2019. Chemical oxidation for oil separation from oilfield produced water under UV irradiation using Titanium dioxide as a nano-photocatalyst by batch and continuous techniques. Int. J. Chem. Eng., vol. 2019.
29. Faisal M., Khan S.B., Rahman M.M., Jamal A., Abdullah M.M. 2012. Fabrication of ZnO nanoparticles based sensitive methanol sensor and efficient photocatalyst. Appl. Surf. Sci., 258(19), 7515–7522.
30. Hassan A.A., Naeem H., Hadi R. 2018. Degradation of oily waste water in aqueous phase using solar (ZnO, TiO_2 and Al_2O_3) catalysts. Pakistan J. Biotechnol., 15, 909–916.
31. Mitrović J., Radović M., Bojić D., Anđelković T., Purenović M., Bojić A. 2012. Decolorization of textile azo dye reactive orange 16 with UV/H2O2 process. J. Serbian Chem. Soc., 77(4), 465–481.
32. Mohammed R.M. Al-zobai K.M.M. 2020. Photocatalytic degradation of organic pollutants in petroleum refinery using TiO_2/UV and ZnO/UV by batch and continuous process. Solid State Technol., 63(3), 5390–5404.
33. Monteiro R.A.R., Rodrigues-Silva C., Lopes F.V.S., Silva A.M.T., Boaventura R.A.R., Vilar V.J.P. 2015. Evaluation of a solar/UV annular pilot scale reactor for 24 h continuous photocatalytic oxidation of n-decane. Chem. Eng. J., 280, 409–416.