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DEGRADATION OF OILY WASTE WATER IN AQUEOUS PHASE USING SOLAR (ZnO, TiO_2 and Al_2O_3) CATALYSTS

Ali A. Hassan, Haider T. Naeem[a], Raid T. Hadi

College of Engineering, Al-Muthanna University, Al-Muthanna, 72001Samawa, Al-Muthanna, Iraq.
E.mail: *dr.haider.naeem@gmail.com

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ABSTRACT

Oily waste water treatment beforehand injection into reservoirs of oil is required to diminish creation damage. This can be done using solar -catalytic procedure to lessen the oil droplets in oily waste water. In order to optimize the purification of waste water and, a new technique of degradation (the heterogeneous solar-catalysis) of the oil content was underlined. As catalysts we chose a semiconductor which are ZnO, TiO_2 and AL_2O_3 in the presence of solar as source of energy. The results show that the adsorption of the oil content on catalyst agent supported in absence of radiation solar is negligible. It was found that the removal of oil content by zinc oxide touched 95.2 % and 92.11%, 80.7% for titanium dioxide and aluminum oxide respectively in pH=7.42 and 120 min irradiation time. The capability of catalyst agent to eliminate organic was augmented after addition different catalyst agent. Generally, zinc oxide meaningfully by its high ability to adsorb suspended solids and organic compound from oily waste water, in addition, decreases the economic cost of waste water treatment. The kinetics of organic degradation follows pseudo-first order.

Keywords: Oily Waste Water; Wastewater Treatment; Advanced Oxidation Processes

1. INTRODUCTION

Crude oil is transformed into petroleum and other useful by-products through refining processes. Crude oils refining produces huge quantities of wastewater produced which consists of cool ing water, process water, storm water, and sewage [Tony et al., 2012, Fouad et al., 2014 and Hosny et al., 2016]. The volume of waste water is about 0.4–1.6 times the volume of crude oil processed [Aziz et al., 2012 and Diya'uddeen et al., 2011], then has a complex composition that comprises organic and inorganic materials, with the chief constituents being free and emulsified oils, salts and phenols. Among these apparatuses, the oil fraction, collected of hydrocarbons and fatty acids, is topic to more parliamentary limits for discharge [Jiménez et al., 2017, Darani et al., 2018]. The left over if not treated will reason thoughtful problems for the environment [Sapareng et al., 2018, Opoku et al., 2018]. The purpose of meet environmental rules along with reuse and recovering of oily waste water, numerous researchers have attentive on treating refinery waste water [Fakhru'l-Razi et al., 2009]. Conservative wastewater managements are not passable to treat confident chemical composites produced by human activity, which are finally deposited in the environment [Velo-Gala et al., 2014, Naeem et al., 2018]. Conventional technologies, including biological [Kang et al., 2005]. Coagulation-flocculation [Amuda et al., 2007], flotation [Silva et al., 2015 and Amin et al., Mofrad et al., 2017] and adsorption are frequently practical to remove aqueous contaminants [El-Din et al., 2017 and El-Sayed et al., 2017]. Despite extensive use of these approaches for the refinery wastewater treatment, however, these methods are non-destructive, subsequently they fair transfer the contaminant from water to solid matrix [Kestioğlu et al., 2005]. This curb has fortified the development of additional well-organized and environmental-friendly schemes for oily wastewater treatment. One opportunity for refinery waste water cleansing is chemical treatment as a post-treatment built on chemical oxidation processes [Rueda et al., 2015]. Advanced oxidation processes (AOPs) have appeared as a suitable waste water treatment alternative because it has demonstrated rapid degradation of recalcitrant and non-biodegradable compounds in waste water **[**Rozas et al., 2010**]**. The routine of the AOPs rises when the quantity of free radicals created upsurges. A conceivable way to upsurge the free radical (OH) manufacture is through using great energy electromagnetic waves [Coenen et al., 2013]. Advanced oxidation processes are biologically friendly manufacturing harmless end-products such as CO_2 and H_2O_2 [Tony et al., 2009] and these methods can result in practically comprehensive mineralization of organic contaminants and operative for a widespread range of organics [Youssef et al., 2016]. Many researchers studied the chemical on oily water treatment such as Palaniandy et al., [2015] investigates the use of solar-two catalyst titanium dioxide and photo-Fenton methods. Tony et al., [2009] evaluating the photo-catalytic application aimed at the mineralization of organic compounds. Palaniandy et al., [2016] appraising photo-oxidation of TOC and COD in refinery waste

water by using titanium dioxide and zinc oxide photo-catalyst. Coelho et al., [2006] studied refinery sour water by AOPs.

This study interested on oil removal from oily waste water solution by using solar catalytic oxidation. Find the optimum value of catalysts agent concentration by studying the belongings of pH and irradiation time on solar catalytic oxidation.

2. MATERIALS AND METHODS

2.1 Materials: Titanium dioxide TiO_2-P_25, Zinc oxide, Aluminum oxide, NaOH and H_2SO_4 (Merck-India). Distilled water was used for training of several solutions. The pH significance of the solutions was attuned by 1 N H_2SO_4 or 1 N NaOH.

2.2 Oily waste water: Oily waste water contaminated with oil droplets illustration was kindly got from the native Iraqi oilfield, Samawah oil field in Al-Muthanna governorate. The oily waste water used in these experimentations' existence carried from oilfield bare to the atmosphere and at that time reserved in an environment alike to their native habitat that encloses oxygen until the treatment process is valuable. Characterization of oily waste water is measured strongminded in the research laboratory of Samawah oil field at Al-Muthanna governorate are pH=7.42, iron=0.33 mg/L and sulphate=61.2 mg/L. The other substances available in refinery waste water are measured in the laboratory and shown in Table 1.

Table 1: The oily waste-water properties in this study.

Parameter	Value
Oil	167.89 (mg/L)
Turbidity	61.9 NTU
Solution oxygen content	0.065 (mg/L)
Specific gravity	0.997
conductivity	170000 µs/cm
TDS	110000 (mg/L)
viscosity	1.311 m Pa/S

2.3 UV/ TiO_2 bench-scale solar batch reactor: Solar catalytic squalor experimentations were approved out in 250 cm^3 glass batch reactor enclosed 150 cm^3solution from oily waste water surprised at an equal stirring velocity about 250 rpm for 30-120 min in the solar catalytic reactor. A magnetic stirrer was rummage-sale to confirm uniform mixing of solution in beaker. The pH was adjusted before adding the reagents by adding a dilute H_2SO_4 or NaOH solution in the beaker, the pH of solutions was restrained using WTWpH-720 digital pH meter. Different catalytic agent used in the range of (50-200) ppm.

2.4 Determination of organic concentration by means of UV-spectrophotometer analysis: 0.2 gm of sodium chloride was additional to 40mL refinery waste water in the separating funnel with the purpose of disruption the emulsion of oil. 4 ml of CCL_4 was extra and shadowed by vital shaking for 2min. After 25 min, when the solution unglued into two separate layers, the lower (oil) layer was occupied for the absorbance dimension, and from the calibration curve, oil content was obtained. The turbidity was slow using turbid meter (Lovibond, SN 10/1471, Germany) and recite the turbidity.

2.5 AOPs effectiveness and kinetic model: The alteration in the concentration of oil content in oily waste water during the solar catalytic process was measured using UV spectrophotometer (UV-1800 Shimadzu, Japan) and the consequences were transformed into the consistent concentrations (A). The oily waste water competence was designed using the subsequent (Eq. (1)):

$$\eta = \frac{A_\circ - A_t}{A_\circ} x100\% \qquad (1)$$

where η, percentage of oil removal; A_o, measured concentration before the treatment (mg/L); A_t concentration value after treatment (mg/L).The kinetics of the solar chemical degradation rate of oil removal was strongminded by means of the Langmuir–Hinshelwood kinetics classical, by way of given in the following (Eq. (2)): The pseudo-first-order rate constant, $k_1(min^{-1})$. A plot of $ln(A_o/A)$ against time aimed at each experimentation lead toward a straight line whose slope is K_1 [Jawad 2016 and Hassaan, 2017] .

$$ln\left[\frac{A_O}{A}\right] = K_1 t \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1. Solar squalor of oily waste water using agent catalysts: To elucidate the role of agent concentration on the solar squalor of oily waste water taken in this investigation in the solar-catalytic some experimentation were approved out by changing the catalyst agent concentrations at constant initial pH, initial waste water for the solar catalytic treatment within irradiation time of 120 min. As shown in Figs.1, 2 and 3 for zinc oxide, titanium dioxide and aluminum oxide respectively, the consequence of diverse concentrations of catalyst agent on the solar catalytic poverty of the oil pollutants was likewise experiential. The upsurge in catalyst slurry concentration in oily waste water samples consequences in superior surface of area and extra active sites obtainable for the oxidation of organic pollutants.

The catalyst concentrations were nominated founded on the effectiveness of the solar-catalytic oxidation to damage the pollutants of oily waste water [Alvarez et al., 2016]. Figures. 1, 2 and 3 presented that by cumulative catalysts agent concentration, squalor of oily waste water was augment-

ted. This is deliberate to be because of the greater surface area of the catalyst obtainable for squalor of the organic compounds in oily waste water solution. Investigations were approved out with dissimilar semiconductors viz. ZnO, TiO_2 and AL_2O_3 with the intention of choice the greatest active catalyst for the degradation of oily waste water. The solar -catalytic experimentations were approved out using unlike catalysts at a fixed waste water concentration (167.89 ppm), and catalyst packing in the range (50-200) ppm for different irradiation time. The consequences designate that zinc oxide displays greater photocatalytic activity than the others. Meanwhile the band gap of zinc oxide is high, the important efficiency of zinc oxide is meaningfully superior to titanium dioxide and henceforth higher efficiencies have been reported for zinc oxide.

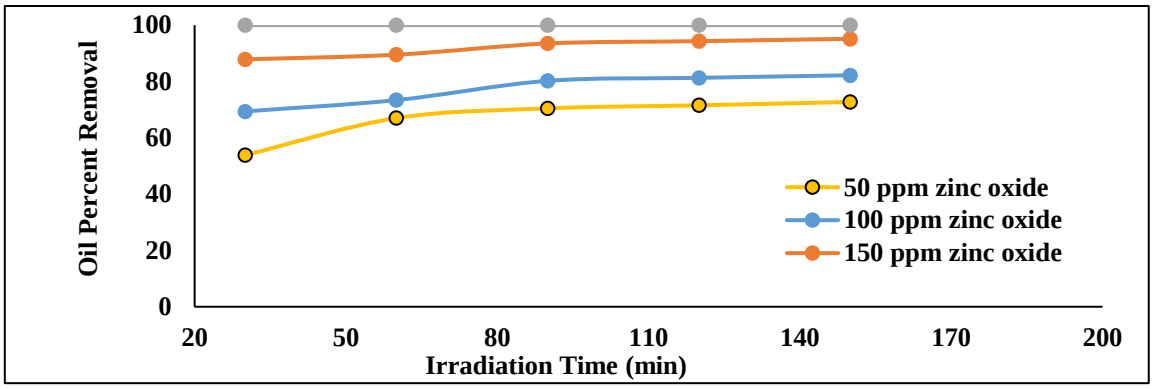

Figure 1: Effect of zinc oxide on oily waste water removal in pH = 7.42.

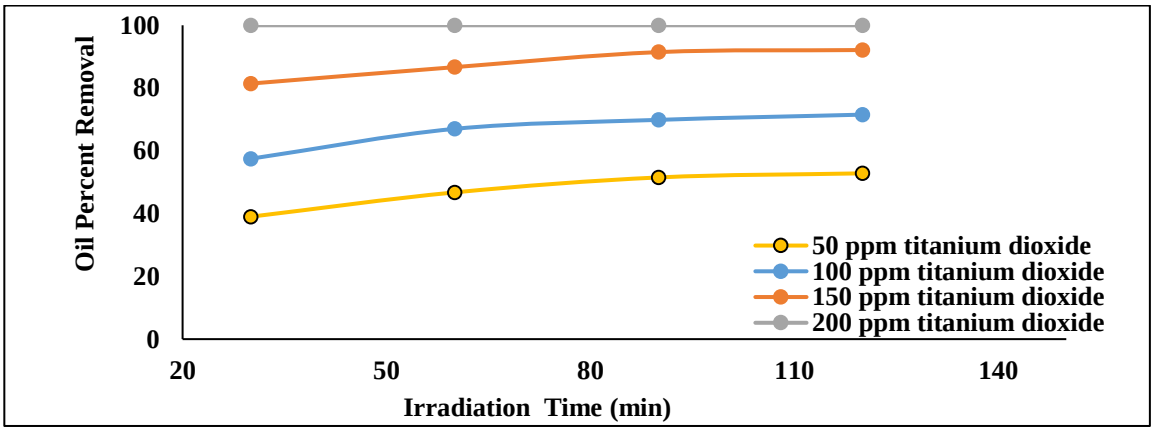

Figure 2: Effect of titanium dioxide on oily waste water removal in pH = 7.42.

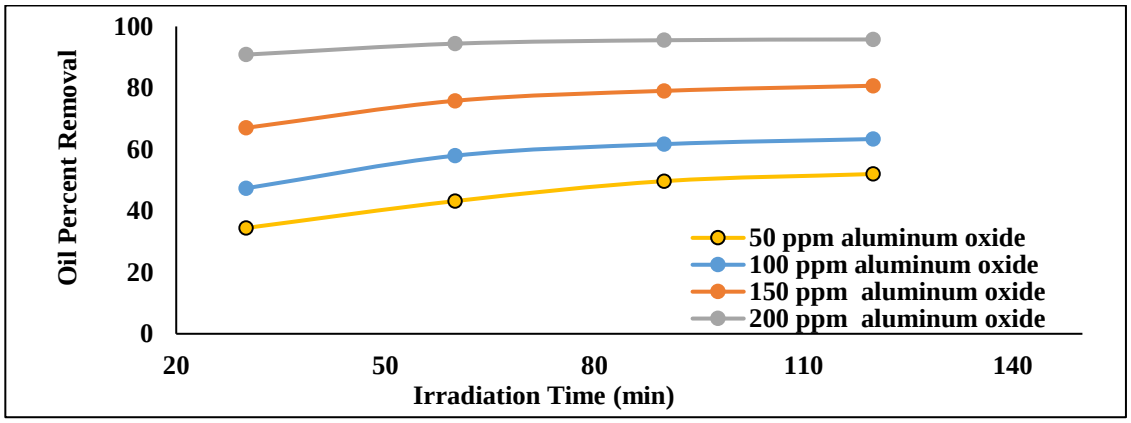

Figure 3: Effect of aluminum oxide on oily waste water removal in pH = 7.42.

3.2. Effect of pH on solar -catalytic treatment: The pH of the solution controls the manufacture rate of free radical in solar catalytic treatment. Hence, pH is an important parameter for oily waste water processes. The result of pH on the squalor of oily waste water by solar -catalytic processes is shown in Figs. 4, 5 and 6 for zinc oxide, titanium dioxide and aluminum oxide respect-

tively. Further upsurge of pH after 3 to 9 decreases the oil percentage from 97.2 to 85.8% for zinc oxide, 92 .12 to 67 % for titanium dioxide and 83.67 to 68.81% for aluminum oxide respectively. It is vibrant from Fig. 6 that inferior pH reasons the surge of oil squalor. Fewer pH improves active area of catalysts agent and irradiation area [Karimi et al., 2014]. Consequently, the surface charge of catalyst can be wide-ranging with pH difference, which touch the adsorption of particle on substance surface and effect the squalor rate efficiently. Consequently, the experimentations were showed to find out best pH of reaction mixture for the decay of oil content in refinery waste water. The investigational consequence specified that poverty of oil content in waste water greatly prejudiced by pH. The result presented that photo degradation rate was originating to upsurge lengthways with a decrease in pH for oily waste water.

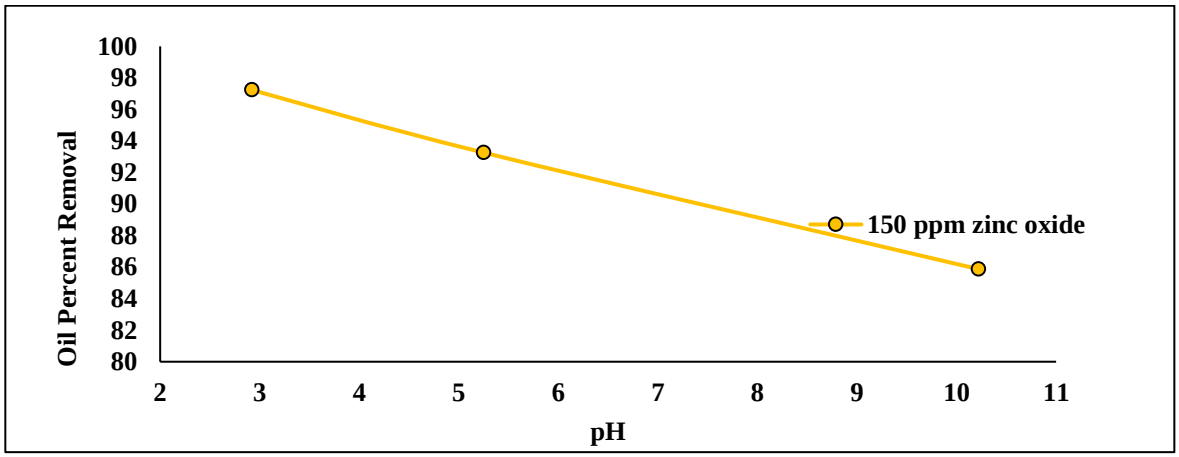

Figure 4: Role of pH on oily waste-water removal in 150 ppm zinc oxide, irradiation time 120 min.

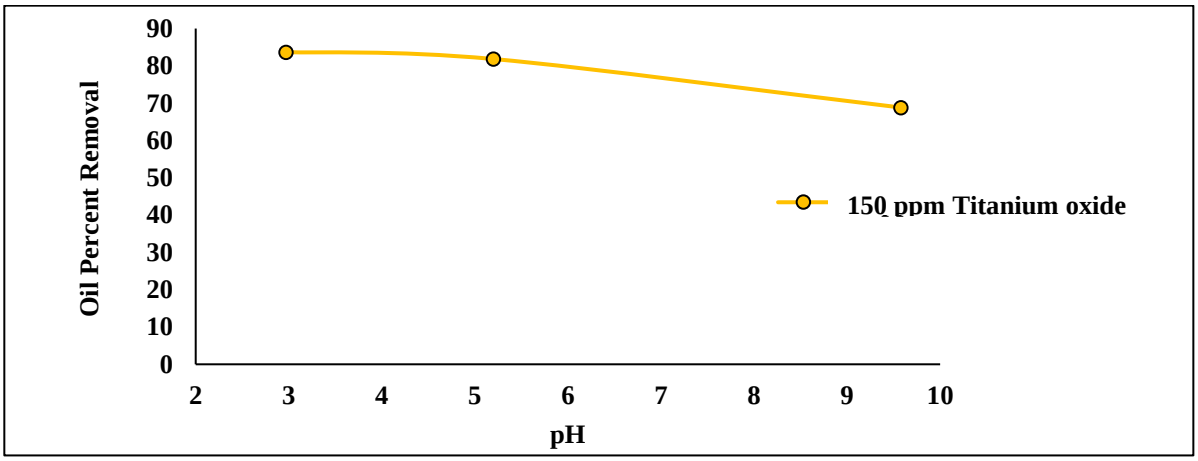

Figure 5: Role of pH on oily waste-water removal in 150 ppm TiO, irradiation time 120 min.

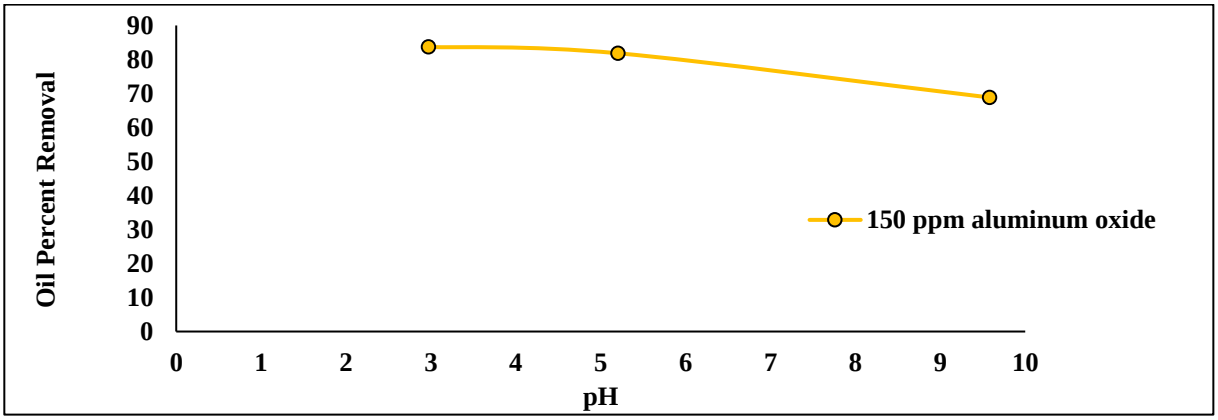

Figure 6: Effect of pH on oily waste water removal in 150 ppm Al_2O_3, irradiation time 120 min.

3.3. Effect of irradiation time on Oil degradation: The consequence of time on solar oxidetion treatment was showed in the range (30-150 min) to specify the time compulsory for squalor of organic pollutants in oily waste water formerly keeping the other limitations and quantity constant. The association between organic percent and contact time by solar oxidation procedure was examined using batch experiments to achieve the equilibrium as exposed in Figures 7, 8 and 9. Oil percent removal increased with irradiation time increase that causes to produce free radical in longest time. The best irradiation time was 120 minutes at steady state value for reaction. The contact time is significant finding is that there is no obligation to treat the refinery waste water for a period of time lengthier than 2 hr., as the consequences achieved change little after this time.

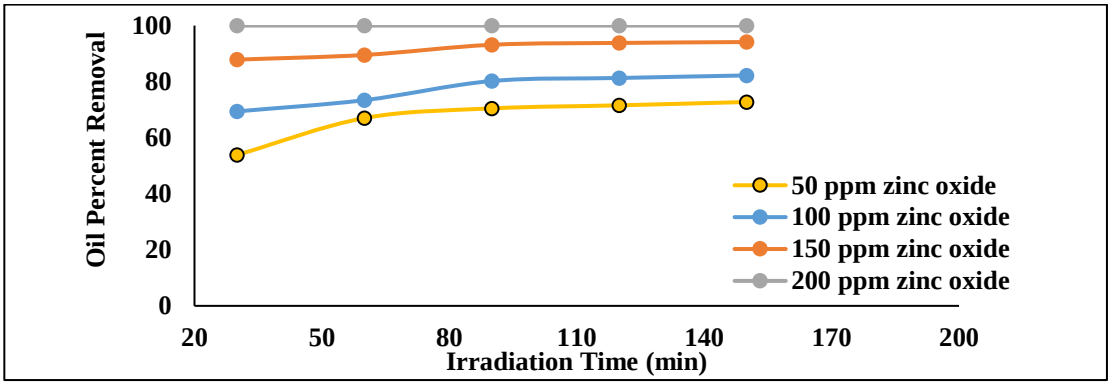

Figure 7: Effect irradiation time of on oily waste water removal in 150 ppm zinc oxide, pH=7.42.

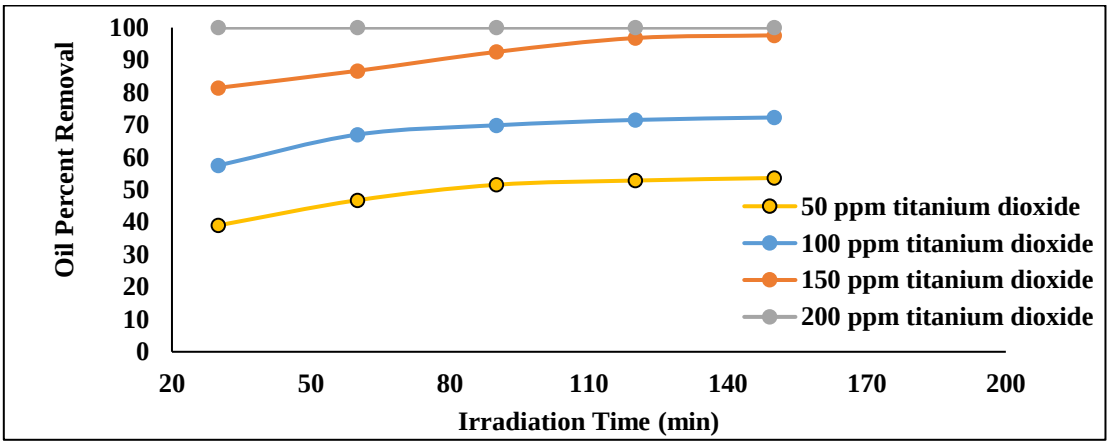

Figure 8: Irradiation time for oily waste water removal in 150 ppm titanium dioxide, pH=7.42.

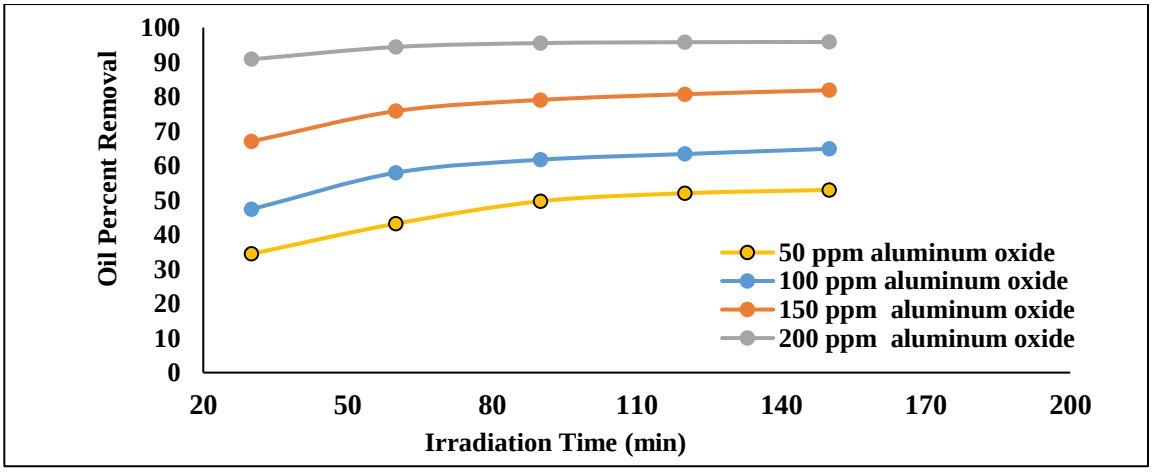

Figure 9: Irradiation time for oily waste water removal in 150 ppm aluminum oxide, pH=7.42.

3.4 Kinetic study: The application of the kinetic model; pseudo first order models on catalysts agent experiment are shown Figs 10, 11 and 12. In the direction of regulate the result of zinc oxide concentration on the kinetic constants of oil percent, some experimentations were intended at a dissimilar ZnO concentration (50,100 and 150 ppm) and ailment of initial waste water concentration = 167.89 mg/L. Figure 10 demonstrates that the rate constant K_1 upsurges until it influences the all-out ($2.9x10^{-3}$ min^{-1}) at 150 ppm of ZnO, representtative that the best concentration of ZnO aimed at this traditional of experiments is 150 ppm.

The value of the parameter k_1 (min-1) was strongminded by fitting the investigational data confe-rring to Eq (2). The values of ln (A_o/A) against regularized lighting time are shown in Fig. 10. And the value of k_1 for two catalysts titanium dioxide and aluminum oxide in the same condition as showed in Figs 11 and 12 respectively.

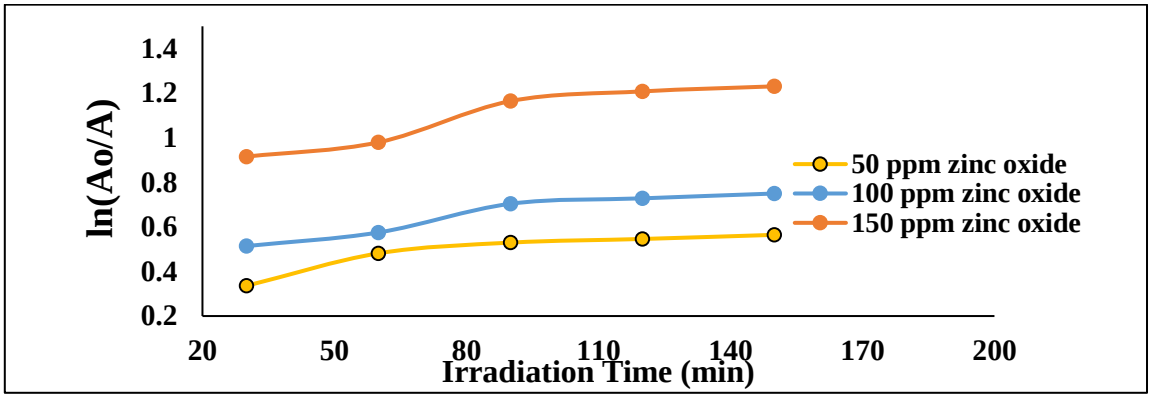

Figure 10: Pseudo first order model for oily waste water degradation of zinc oxide experiments at pH = 7.42.

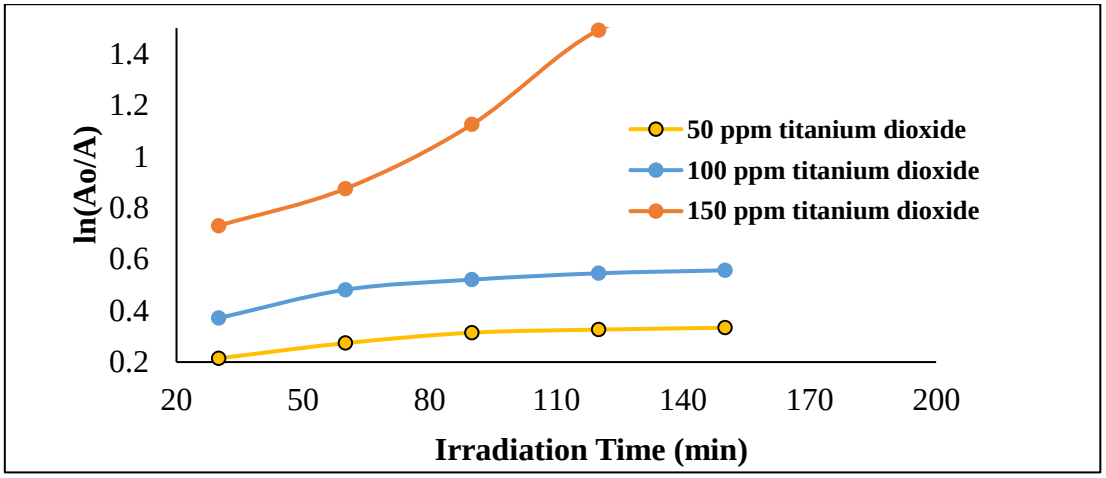

Figure 11: Pseudo first order model for oily waste water degradation of titanium dioxide experiments at pH = 7.42.

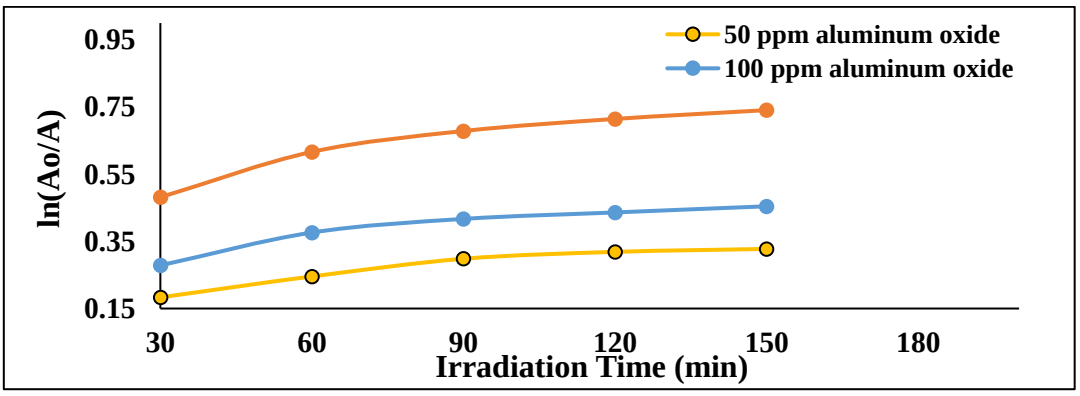

Figure 12: Pseudo first order model for oily waste water degradation of aluminum oxide experiments at pH = 7.42.

The morals of rate coefficients in the case of the model are providing in Tables (2) for zinc oxide. The finest classical was appraised finished the scheming of the constant of determination R^2. R^2 is an indicator to in what way healthy the equation can be used for forecast. The earlier the value is to 1, the

improved is the appropriate to the model. From figure above the high efficiency of oily waste water when using the zinc oxide, for that reason, ZnO was only discussed in the next sections.

Table 2 Rate constants of zinc oxide experiments.

ZnO	First order	
	K_1 1/min	R^2
50	0.0017	0.7987
100	0.0021	0.9
150	0.0029	0.91

4. Conclusions

In this effort, the poverty of organic content in refinery waste water solution by Solar catalytic reaction has been deliberate on not the same investigational conditions, with dosages of ZnO, TiO_2 and AL_2O_3, changed pH value of solutions and diverse irradiation time. A appropriate working condition was designated as: oily waste water= 167.89 ppm, catalyst agent= 150 mg/L, pH =7.42 at 120min irradiation time, the high oil removal is 95.2 %, 92.11% and 80.7% for titanium dioxide and aluminum oxide respectively. The Kinetic education specified that the poverty kinetics of oily waste water shadowed the first-order kinetics. Founded on the consequences the subsequent deductions have been haggard. Though solar- catalytic processes can be used aimed at the degradation of oil content from refinery waste water, the Solar-catalytic process is more efficient.

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REFERENCES

Alvarez-Corena, J.R., J.A. Bergendahl and F.L. Hart, Advanced oxidation of five contaminants in water by UV/TiO_2: reaction kinetics and by-products identification. *J. Environ. Manage.* 181: 544–551 (2016).

Amin, M.M., M.M.G. Mofrad, H. Pourzamani, S. M. Sebaradar and K. Ebrahim, Treatment of industrial wastewater contaminated with recalcitrant metal working fluids by the photo-Fenton process as post-treatment for DAF. *J. Ind. Eng. Chem.* 45: 412–420 (2017).

Amuda, O. and I. Amoo, Coagulation/ flocculation process and sludge conditioning in beverage industrial wastewater treatment. *J. Hazard. Mater.* 141(3): 778–783 (2007).

Aziz, A.A. and W.M.A.W. Daud, Oxidative mineralisation of petroleum refinery effluent using Fenton-like process. *Chem. Eng. Res. Des.* 90 (2): 298–307 (2012).

Coelho, A., A.V. Castro, M. Dezotti, and G.L. Sant'Anna Jr, Treatment of petroleum refinery sourwater by advanced oxidation processes. *J. Hazard. Mater.* 137(1): 178–184 (2006).

Coenen, T., W. Van de Moortel, F. Logist, J. Luyten, J.F. Van Impe and J. Degrève, Modeling and geometry optimization of photochemical reactors: Single-and multi-lamp reactors for UV–H2O2 AOP systems *Chem. Eng. Sci.* 96: 174–189 (2013).

Diya'uddeen, B.H., W.M.A.W. Daud and A.A. Aziz, Treatment technologies for petroleum refinery effluents: a review. *Process Saf. Environ. Prot.* 89(2): 95–105 (2011).

El-Din, G.A., A.A. Amer, G. Malsh and M. Hussein, Study on the use of banana peels for oil spill removal. *Alex. Eng. J.* (2017).

Fakhru'l-Razi, A., A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, and Z.Z. Abi-din, Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* 170(2): 530–551 (2009).

Fathy, M., M. El-Sayed, M. Ramzi, and O.H. Abdelraheem, Adsorption separation of condensate oil from produced water using ACTF prepared of oil palm leaves by batch and fixed bed techniques. *Egypt. J. Pet.* (2017).

Fouad, Y.O., Separation of cottonseed oil from oil–water emulsions using electrocoagulation technique. *Alex. Eng. J.* 53(1): 199–204(2014).

Haider T. Naeema and Ali A. Hassan, effectiveness & economy of sawdust wood adsorbents in removing anionic dyes of aqueous solutions. Pak. J. Biotechnol. 15(2): 311-320 (2018)

Hassaan, M.A., A. El Nemr and F.F. Madkour, Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in waste water. *Egypt.J. Aquat. Res.* 43(1): 11–19 (2017).

Hosny, R., M. Fathy, M. Ramzi, T. A. Moghny, S. E.M. Desouky and S.A. Shama, Treatment of the oily produced water (OPW) using coagulant mixt-ures. *Egypt. J. Pet.* 25(3): 391–396 (2016).

Jawad, A.H., N.S.A. Mubarak, M.A.M. Ishak, K. Ismail, and W.I. Nawawi, Kinetics of photocatalytic decolourization of cationic dye using porous TiO_2 film. *J. Taibah Univ. Sci.* 10(3): 352–362 (2016).

Jiménez S. *et al.*, Integrated processes for produced water polishing: Enhanced flotation/sedimentation combined with advanced oxidation processes. *Chemosphere* 168: 309–317 (2017).

Karimi, L., S. Zohoori and M.E. Yazdanshenas, Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nanostrontium titanate as the nanophotocatalyst. *J. Saudi Chem. Soc.* 18(5): 581–588 (2014).

Kestioğlu, K., T. Yonar and N. Azbar, Feasibility of physico-chemical treatment and advanced oxidation processes (AOPs) as a means of pretreatment of olive mill effluent (OME). *Process Biochem.* 40(7): 2409–2416 (2005).

Khoso, M. Hassan, Meng Fanrui, Lubna Muhi Rasoul, The sterategic role of fibroblast growth factor-21in obesity, Pak. J. Biotechnol. 15(3): 855-864 (2018).

Li, Q., C. Kang and C. Zhang, Waste water produced from an oilfield and continuous treatment with an oil-degrading bacterium. *Process Biochem.* 40(2): 873–877 (2005).

Palaniandy, P., H.B.A. Aziz, S. Feroz, and others, Evaluating the TiO_2 as a solar photocatalyst process by response surface methodology to treat the petroleum waste water. *Karbala Int. J. Mod. Sci.* 1(2): 78–85 (2015).

Palaniandy, P., H.B.A. Aziz, S. Feroz, S.S.A. Amr and others, Evaluating photo-degradation of COD and TOC in petroleum refinery waste water by using TiO_2/ZnO photo-catalyst. *Water Sci. Technol.* 74(6): 1312–1325 (2016).

Palaniandy, P., H.B.A.Aziz and S. Feroz, Treatment of petroleum wastewater using combination of solar photo-two catalyst TiO_2 and photo-Fenton process. *J. Environ. Chem. Eng.* 3(2): 1117–1124 (2015).

Rozas, O., D. Contreras, M.A. Mondaca, M. Pérez-Moya and H.D. Mansilla, Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions. *J. Hazard. Mater.* 177(1–3): 1025–1030 (2010).

Rueda-Márquez, J.J., M. Sillanpää, P. Pocostales, A. Acevedo and M. A. Manzano, 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 (2015).

Sapareng, S., Ambo Ala, Tutik Kuswinanti, the ability of trichoderma sp and pleurotus sp for the decomposition of oil palm empty bunches. Pak. J. Biotechnol. 15(2): 543-548 (2018)

Silva, de S.S., O. Chiavone-Filho, E.L. de Barros Neto and E.L. Foletto, Oil removal from produced water by conjugation of flotation and photo-Fenton processes. *J. Environ. Manage.* 147: 257–263 (2015).

Tony, M.A., P.J. Purcell and Y. Zhao, Oil refinery wastewater treatment using physicochemical, Fenton and photo-Fenton oxidation processes. *J. Environ. Sci. Health Part A* 47(3): 435–440 (2012).

Tony, M.A., P.J. Purcell, Y. Zhao, A.M. Tayeb, and M. El-Sherbiny, Photo-catalytic degradation of an oil-water emulsion using the photo-fenton treatment process: effects and statistical optimiza-tion. *J. Environ. Sci. Health Part A* 44(2): 179–187 (2009).

Tony, M.A., Y.Q. Zhao, P.J. Purcell and M.F. El-Sherbiny, Evaluating the photo-catalytic application of Fenton's reagent augmented with TiO_2 and ZnO for the mineralization of an oil-water emulsion. *J. Environ. Sci. Health Part A* 44(5): 488–493 (2009).

Velo-Gala, I., J.J. López-Peñalver, M. Sánchez-Polo and J. Rivera-Utrilla, Comparative study of oxidative degradation of sodium diatrizoate in aqueous solution by H_2O_2/Fe^{2+}, $H_2O_2/Fe^{3+,}$ Fe (VI) and UV, H_2O_2/UV, $K_2S_2O_8$/UV. *Chem. Eng. J.* 241: 504–512 (2014).

Youssef, N.A., S. A. Shaban, F. A. Ibrahim and A.S. Mahmoud, Degradation of methyl orange using Fenton catalytic reaction. *Egypt. J. Pet.* 25(3): 317–321 (2016).