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## An application of advanced oxidation process on industrial crude oily wastewater treatment

Heba A. El-Gawad<sup>1</sup>, Ebrahiem Esmail Ebrahiem<sup>2</sup>, Montaser Y. Ghaly<sup>3,4</sup>, Ahmed A. Afify<sup>3</sup> & R. M. Mohamed<sup>3</sup>✉

Advanced oxidation process, via photo-catalytic oxidation process was demonstrated in this study as one of the promising techniques of simulated oily wastewater treatment. Several effective factors such as initial oil concentration, catalyst dose, stirring speed (rpm), pH value and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) dose influencing on the photo-catalytic degradation rate of oily wastewater were investigated. The catalyst used in this work was titanium dioxide (TiO<sub>2</sub>). The solubility of oil in water was increased using emulsifier. Results indicated that the photo-catalytic oxidation process has a good removal percentage of oil from oily wastewater reached to 98.43% at optimum operating parameters of 1 g/L initial oil concentration, 850 rpm, 8 pH, 3 mL H<sub>2</sub>O<sub>2</sub> and 1.5 g/L of TiO<sub>2</sub> after 40 min of irradiation time. The degradation reaction follows a first order kinetics with a correlation coefficient (R<sup>2</sup>) of 93.7%. Ultimately, the application of photo-catalytic oxidation processes at these optimum operating parameters on an industrial oily wastewater collected from an effluent stream of Ras Shukair at Red Sea supplied by Asuit Petrochemical Company was done in Egypt. The results showed that the best oil removal (99%) was achieved after adding 3 mL of H<sub>2</sub>O<sub>2</sub> in a reaction time of 40 min compared to without adding H<sub>2</sub>O<sub>2</sub>.

Recent increases in human activity at the level of home sectors<sup>1</sup>, agricultural sectors<sup>2</sup> and municipal sectors<sup>3</sup> resulting increase in the organic contaminants in wastewater treatment facilities, which causes a discharge to water bodies that does not meet safety and environmental criteria. Due of its hazard, wastewater tainted with oil can actually harm the environment. With the need for more gas stations to service the expanding number of automobiles, the proportion of diesel/gas oil polluted effluent from these facilities has grown as well. Humans who use diesel or gas oil can have skin and eye irritation, however additional impacts have not been well studied<sup>4</sup>. Diesel is a toxicant since it contains polycyclic aromatic hydrocarbons (PAHs), which have the possibility of causing human cancer and are detrimental to human health<sup>5</sup>. For the outflow of oily effluent into surface waters or sewage systems, standards and regulations were created. These laws may differ from one nation to the next and even within one nation.

The necessity for wastewater treatment is dictated by the global increase in the release of slick wastewater, rigorous controls for gushing release, and constant drive for reusing treated wastewater. The selection of treatment methods for smooth wastewater is influenced by factors including wastewater composition, administrative challenges, prices, treatment effectiveness, and wastewater end use<sup>6</sup>. Conventional techniques for treating oily wastewater include dissolved air-flotation, emulsification, chemical coagulation, gravity separation, flocculation, sedimentation, and biological treatment<sup>7</sup>. However, these methods need long settling time, huge land space, and they involve severe sludge handling problems<sup>8</sup>. The produced sludge will need to be treated by novel methods such as adding nanoparticles to produce biogas from sludge<sup>9</sup> so, according to the quality of natural water and clean water deficiency the development of cheap wastewater treatment and technologies are required.

However, it is challenging to put together a single method or procedure to satisfy the required limitations for outflow because of the complexity of the organic content of oily wastewater. In this regard, researchers are continually working to create a successful therapeutic strategy. Advanced oxidation processes (AOPs), an alternative to traditional treatment methods, have been researched for the treatment of oil-contaminated wastewater. Highly reactive intermediates, such as hydroxyl radicals (HO<sup>•</sup>), sulphate radicals, O<sub>2</sub><sup>-•</sup>, H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub> are used in AOPs

<sup>1</sup>Department of Engineering Mathematics and Physics, Higher Institute of Engineering, El-Shorouk Academy, Cairo, Egypt. <sup>2</sup>Chemical Engineering Department, Faculty of Engineering, Minia University, Minya, Egypt. <sup>3</sup>Chemical Engineering Department, Canal High Institute for Engineering and Technology, Suez, Egypt. <sup>4</sup>Chemical Engineering and Pilot Plant Department, National Research Centre (NRC), Cairo, Egypt. ✉email: re7abmetwally@yahoo.com

to damage and mineralize the organic contaminants in wastewater by oxidation processes<sup>10</sup>. These oxygen forms are accountable for oxidation and reduction of compounds attached on surface of catalyst. The main principal mechanism in UV-based radical AOP treatment processes is the use ultraviolet light to initiate generation of hydroxyl radicals by direct photolysis of hydrogen peroxide ( $H_2O_2$ ), photo-Fenton reactions or heterogeneous photocatalysis. For the treatment of drinking water and the facilities for reusing water, its technologies have been established and launched. Additionally, scientists and researchers working in the field of the environment are constantly researching a number of AOPs, including those linked to electrochemical processing, electron beam utilization, plasma, microwave, and ultrasound. Such processes include homogenous and heterogeneous processes which may be included by the UV light to enhance the reaction. This UV light may be sourced from natural sun light or from simulated artificial lamp source. The homogenous processes such as Fenton's reagent,  $H_2O_2$  and ozone and heterogeneous photo-catalysis using semiconductors such as  $TiO_2$ ,  $Fe_2O_3$ , CdS, GaP, ZnS and  $ZnO$ <sup>11</sup>.

When more biodegradable compound are arranged together or added up to mineralization with carbon dioxide and water, these catalysts cause extremely viable natural matter to deteriorate. The well-known kind of titanium dioxide ( $TiO_2$ ) used in photo-catalysis technology. It is the most energetic photo-catalyst ( $300\text{ nm} < \lambda < 390\text{ nm}$ ) that maintains stability during repeated catalytic cycles. It also exhibits high chemical, physical, and thermal stability, which ensures its widespread and effective use in the treatment of wastewater and water.

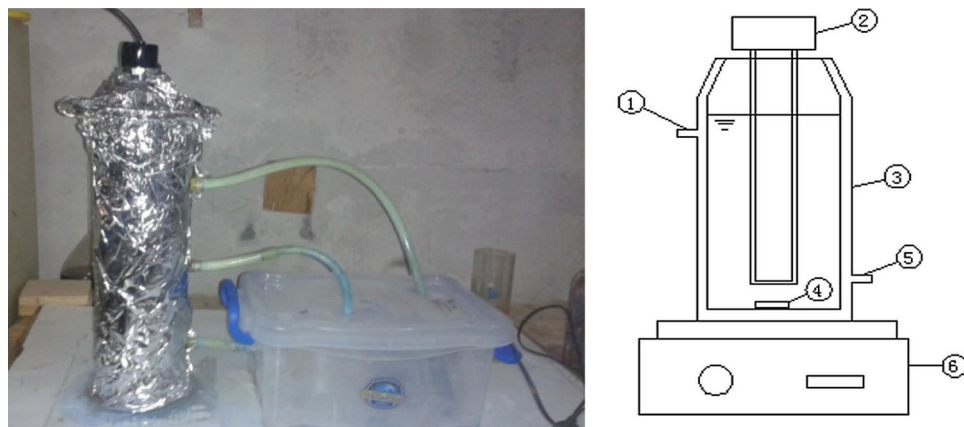
In contrast to other water treatment technologies, photo-catalysis has the capacity to perform two purification processes simultaneously: reduction and oxidation. By plating the metals onto the catalyst surface with the help of conduction-band electrons, the reduction is mostly effective for extracting the dissolved metals from water. The dissolved organic contaminant is mineralized using the photo catalyst's oxidation capabilities<sup>12</sup>.

In this study, the heterogeneous photo-catalysis oxidation technology (UV/ $TiO_2$ / $H_2O_2$ ) was used on a real sample of wastewater for oil mineralization which is coming from an effluent stream of Ras Shukair at Red See supplied by Asuit Petrochemical Company was done in Egypt. The catalyst, which is often a semiconductor, is exposed to radiation in order to produce electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites), giving redox reagents a lot of potential. The effect of the  $TiO_2$  catalyst dosage,  $H_2O_2$  dosage, stirring speed and initial oil concentration were investigated on this real sample.

## Experimental work

**Experimental set-up.** In this work, the experiments were conducted in a laboratory-scale reactor in a batch. Experimental set-up used is a closed cycle as shown in Fig. 1. It consists of a plastic tank with 6 L capacity. This tank includes contaminated feed water which will undergo treatment. The tank is linked to the inlet and outlet of a tubular reactor mounted on a hot magnetic stir plate (MSH-300N, BOECO, Germany) to maintain an unchanged composition. This tubular reactor is a precipices UV unit which consists of UV lamp to enhance the reaction and water input and output streams. The long and diameter of tube are 45 cm and 10 cm respectively. UV radiation (254 nm) was generated from UV lamp. Heraeus TNN 15/32, TQ 150 W medium-pressure mercury lamp (Germany) was used as the UV emitter and light source. The lamp was fixed perpendicularly and dipped at the top of the reactor. The lamp was completely dipped 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.

**Instrumentations.** The pump is the first instrumentation used in the experiment for circulation of polluted water through a tubular reactor. It gives output flow rate of 2000 mL/min. The second instrumentation used is centrifuged (DLAB model) to separate  $TiO_2$  from oil solution to be measured on turbidity meter. The turbidity meter (TU-2016) was used to measure the oil concentration after centrifugation. The sensitive balance (Ohaus Corp Pine Brook, NJ, USA, Item AR 2140) was also used to weigh the number of grams of catalyst. The pH of the



**Figure 1.** Reactor of UV-based advanced oxidation process: (1) Cooling water out, (2) UV Lamp, (3) Reactor, (4) Stirrer, (5) Cooling water in, and (6) Magnetic stirrer.

sample was measured using a pH meter (model 3505 made by JENWAY Instruments, with a resolution of 0.01 and accuracy of  $\pm 0.02$ ). The pH meter was calibrated on daily basis via buffers of pH 4 and pH 7.

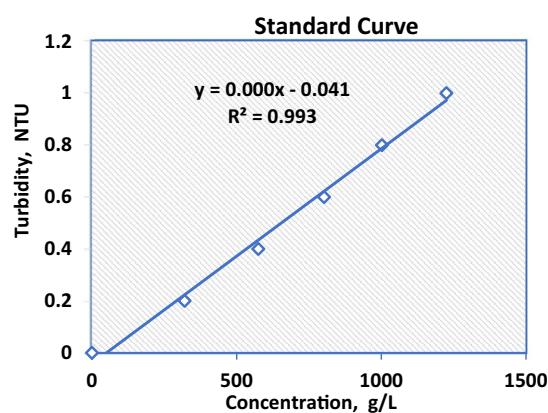
**Reagents.** The reagents used in this experiment are distilled water prepared in chemical engineering department laboratories,  $\text{TiO}_2$  catalyst (anatase type) having particle size of 0.005 mm and density of  $378 \text{ g/cm}^3$ , diluted  $\text{H}_2\text{SO}_4$  solution, NaOH solution and the oxidant  $\text{H}_2\text{O}_2$  solution used in this experiment were of analytical grade. All these reagents are pure grades delivered from Merck).

**Experimental procedure.** The light intensity of lamp ( $20 \text{ W/m}^2 \text{ hr}$ ) was set up to be nearly firm throughout the experiments. An oil solution was made up in stock solution of 1000 ppm concentration and was subsequently diluted to required concentrations using distilled water. In each experimental run, 5 L of oily wastewater sample with definite oil concentration was placed in the plastic feed tank. A definite dose of the  $\text{TiO}_2$  catalyst was added to the feed tank with strong mixing. Then, the hydrogen peroxide (1–4 mL) was added to the solution. To eliminate the effect of adsorption, the suspension was subjected to mix for about 3–5 min in the absence of UV lamp.

In the UV lamp experiment, the pump was joined to the tank and worked at specified vacuum rate, thus the contaminate solution was circulated from the plastic tank to tubular reactor and back to the plastic tank and the cycle was repeated. The solution was then subjected to stirring via a magnetic stirrer to mix the solution effectively. All the experiments were carried out at ordinary temperature ( $25^\circ\text{C}$ ). Each experiment lasted 60 min and samples (2 mL each) were drawn from the oil solution at regular intervals (10 min) through the sample valve. Then, the samples were centrifuged to separate  $\text{TiO}_2$  powder. Finally, leave the samples about 10 min to let  $\text{TiO}_2$  settle down. The removal of oil was demonstrated with the reduction in the oily wastewater turbidity.

**Analytical method.** Dilutions of concentrated samples of an oil solution with an initial concentration 1000 ppm is occurred to 10 samples from 1000 to 100 ppm and then the turbidity of each sample was measured. The standard oil calibration curve was made by means of recording the turbidity values for a range of known concentrations of oil solution as shown in Fig. 2. The turbidity readings of different samples after experiments were compared with the calibration curve and converted into concentration (ppm) terms.

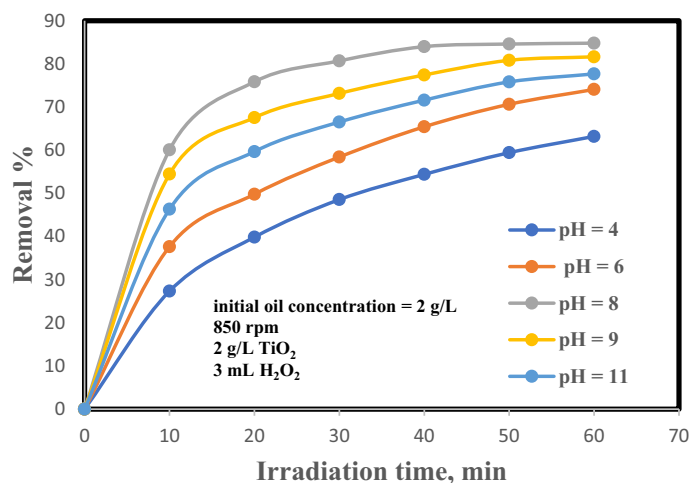
**Experimental runs.** The oil elimination from wastewater by means of advanced oxidation processes (AOPs) such as photo catalysis oxidation processes was investigated basing on various parameters described on the Table 1. The photo catalysis oxidation process was optimized in a batch-wise experiment to find the optimal factors viz. initial oil concentration,  $\text{TiO}_2$  catalyst dosage,  $\text{H}_2\text{O}_2$  dosage and stirring speed (rpm). The oil elimination efficacy was taking into account through optimization.



**Figure 2.** Oil standard calibration curve.

Parameter studied	Ranges
Initial oil concentration, g/L	0.5–2
$\text{TiO}_2$ catalyst dose, g/L	0.5–2
$\text{H}_2\text{O}_2$ dose, mL	1–4
Stirring speed, rpm	650–1000

**Table 1.** Experimental parameters studied and their ranges.



**Figure 3.** Influence of pH solution on the removal efficiency of oil.

## Results and discussion

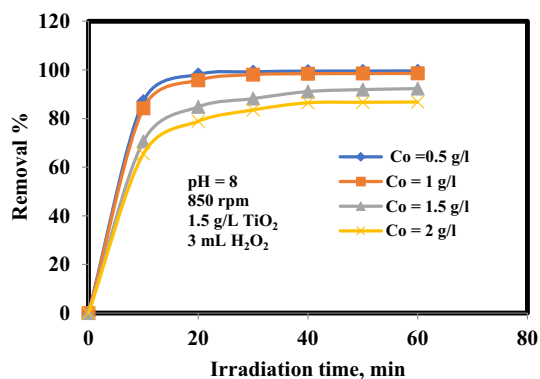
### Influence of pH solution.

The pH of solution is a significant factor affecting on the photolysis. In order to inspect the influence of pH on photo-catalytic oxidation of the oily solution, a photo-catalytic experiment was achieved with a variety of pH from 4 to 11 in the existence of  $\text{TiO}_2$  at concentration of 2 g/L,  $\text{H}_2\text{O}_2 = 3$  mL, initial oil concentration of 2 g/L, and at 850 rpm. Figure 3 depicts the influence of pH on the elimination percentage. The acquired results elucidated that increasing the pH of the solution up to pH 8 leads to a raised in oil elimination up to 84% at 40 min irradiation time. At lower pH, corrosion of  $\text{TiO}_2$  happened and photo-catalytic reaction was blocked owing to the dissolution of  $\text{Ti}^{2+}$  in the solution as well as the reduction of oil adsorption over  $\text{TiO}_2$ . This leads to a lower of decomposition rate<sup>13, 14</sup>.

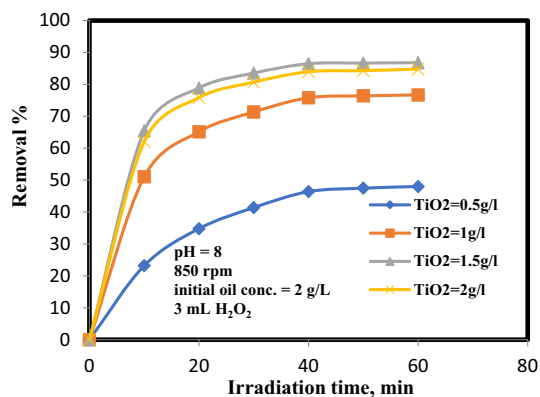
The oil removal percentage is increased with pH as OH<sup>-</sup> concentration rise on the  $\text{TiO}_2$  surface in the basic media by photo-induced trapping hole<sup>15</sup>. Oils also consist of the sulphate group in their structure, which are negatively charged in basic conditions (pH > 8). So, efficient oil adsorption is hampered from static electricity causes. Then, at a moderate pH, i.e., between 7 and 8 ideal conditions for oil adsorption and photo production of hydroxyl radicals, obtaining the highest rate of oil elimination versus pH. Moreover, it is obvious that the rate photo-catalytic oxidation rises as the pH of the oily wastewater rises to 8.

### Influence of initial oil concentration.

To examine the influence of the initial oil concentration ( $C_o$ ) in photo-catalytic process, the various values of initial oil concentration (0.5, 1, 1.5 and 2 g/L) were carried out at 8 pH,  $\text{H}_2\text{O}_2 = 3$  mL,  $\text{TiO}_2 = 1.5$  g/L and 850 rpm. Figure 4 depicts this influence of  $C_o$  of oil on the elimination percentage. It is obvious that the rise in oil concentration reduce the elimination percentage. Once the oil concentration was raised from 0.5 to 2 g/L, the oil removal was reduced from 99.5 to 86.48% within 40 min of decomposition time. With an increase in  $C_o$ ; more and more oil is adsorbed on the  $\text{TiO}_2$  surface. This leads to less generation of OH<sup>-</sup>, as there are only fewer active sites for the adsorption of hydroxyl ions and the generation of hydroxyl radicals. Moreover, as  $C_o$  raised, incident photons were adsorbed by oil before they can reach the catalyst surface. Then, the absorption of photons by the catalyst reduces, and therefore the oil decomposition rate decreased<sup>12, 16, 17</sup>.

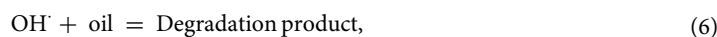
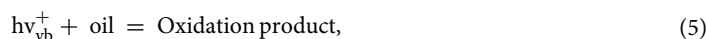
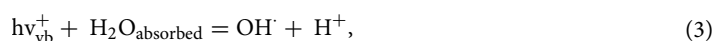


**Figure 4.** Influence of initial oil concentration on the removal efficiency of oil.



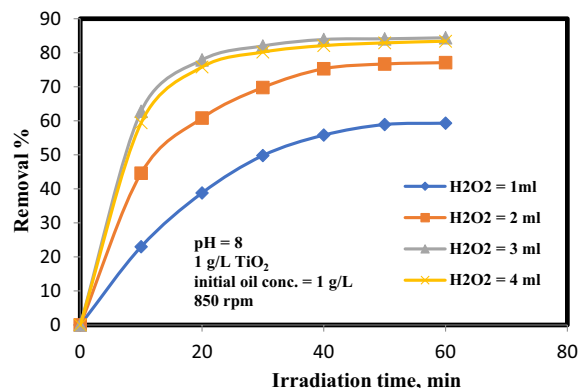
**Figure 5.** Influence of titanium dioxide (TiO<sub>2</sub>) concentrations on oil degradation.

**Influence of TiO<sub>2</sub> catalyst dose.** The catalyst capacity influence on oil removal decomposition on TiO<sub>2</sub> with range of (0.5–2 g/L) was inspected at 8 pH, 850 rpm, initial concentrations of oil and H<sub>2</sub>O<sub>2</sub> were 2 g/L and 3 mL, respectively. The semiconductor quantity as catalyst is a key factor in heterogeneous photo-catalytic oxidation investigations. It should be noted that, the catalyst capacity affects number of active sites on the photo-catalyst and the permeation of radiation through the suspension<sup>12</sup>. Figure 5 presents that the oil disposal ratio was improved when the catalyst quantity in the reactor elevated up to 2 g/L/Lower TiO<sub>2</sub>. The raise in disposal percentage was due to the enhancement of OH<sup>•</sup> generation due to higher TiO<sub>2</sub> catalytic activity. During the exposure of TiO<sub>2</sub> to UV light, the positive hole and an electron are produced in the valence band ( $h\nu_{vb}^+$ ) and the conduction band ( $e_{cb}^-$ ). The hydroxyl radicals are produced due to the oxidation of adsorbed water or hydroxyl ions by holes in the valence band on the excited surface as described below<sup>18</sup>. The produced radicals break down the oil particles, raising the disposal rate. Despite this, raising the dose of TiO<sub>2</sub> beyond an optimum value (1.5 g/L) has a negative impact on the decomposition process. This is a consequence of the fact that overflow TiO<sub>2</sub> molecules raise the obscurity of the suspension there by reducing the light permeation into the solution, which leads to a decrease in the number of OH<sup>•</sup>, and these explications have also been stated in the preceding researches<sup>19,20</sup>.



Any further rise in the catalyst concentration leads to a reduction in the oil disposal efficacy which can be illustrated by means of the light scattering generated by the suspended photo resist catalyst<sup>21</sup>. Simultaneously, as a result of the raise in the turbidity of the suspension, there is a reduction in light penetration due to the increase in the scattering effect, and thus the size of the photo-activated suspension reduces<sup>22</sup>. A concentration of 1.5 g/L of TiO<sub>2</sub> exhibited the bested oil elimination execution. When an excess the TiO<sub>2</sub> quantity was uptake, the surface area was saturated, then the intensity of light was thus attenuated due to reduced light penetration and raised light scattering<sup>23</sup>.

**Influence of H<sub>2</sub>O<sub>2</sub> dose.** The additive of H<sub>2</sub>O<sub>2</sub> is a significant to improve the photo-catalytic oxidation efficiency since it is used as electron acceptor<sup>24</sup>. Different concentration of H<sub>2</sub>O<sub>2</sub> (1–4 mL) were added to the solution and irradiated with UV light. Figure 6 displays the influence of H<sub>2</sub>O<sub>2</sub> on the oil disposal percentage under the operating parameters of oil initial concentration equal 1 g/L, TiO<sub>2</sub> equal to 1 g/L, 8 pH, and stirring speed of 850 rpm. From this figure, it can be observed that the removal of oil deposits lifted decomposition raised as the concentration of H<sub>2</sub>O<sub>2</sub> raised from 1 to 3 mL achieving an extreme removal percentage of 83.8% at 3 mL after 40 min of irradiation time. The additive of H<sub>2</sub>O<sub>2</sub> above this value had a negative effect as mentioned in many previous researches<sup>11,12,20</sup>. The reason for this phenomenon is that of hydroxyl radicals produced by the



**Figure 6.** Influence of H<sub>2</sub>O<sub>2</sub> concentrations on oil decomposition.

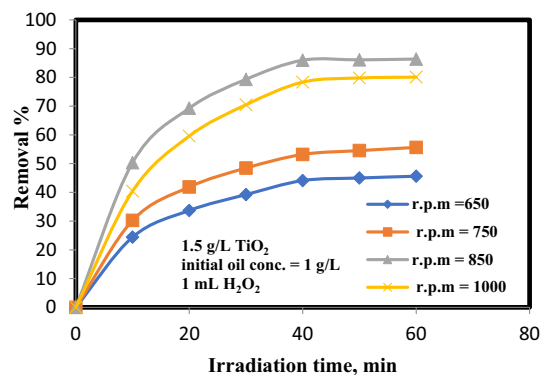
direct photodegradation of hydrogen peroxide are the prime types answerable for the decomposition process. The reason for this phenomenon is that of hydroxyl radicals produced by the direct photo-degradation of hydrogen peroxide are the prime types answerable for the decomposition process. It has been anticipated that rising the H<sub>2</sub>O<sub>2</sub> concentration minimizing the rate of oil decomposition owing to the reaction of hydrogen peroxide with these radicals producing HO<sub>2</sub><sup>·</sup>. Since HO<sub>2</sub><sup>·</sup> radicals are not as reactive a HO<sup>·</sup>, then low decomposition may acquire, thus acting as an inhibitory agent. Another reason, as H<sub>2</sub>O<sub>2</sub> concentrations increase, the light intensity decreases, because H<sub>2</sub>O<sub>2</sub> also soak up lights in the system and leads to lower the degradation efficiency. Increasing the light intensity had a positive effect on photo-degradation and enhanced the reaction rate<sup>25</sup>.



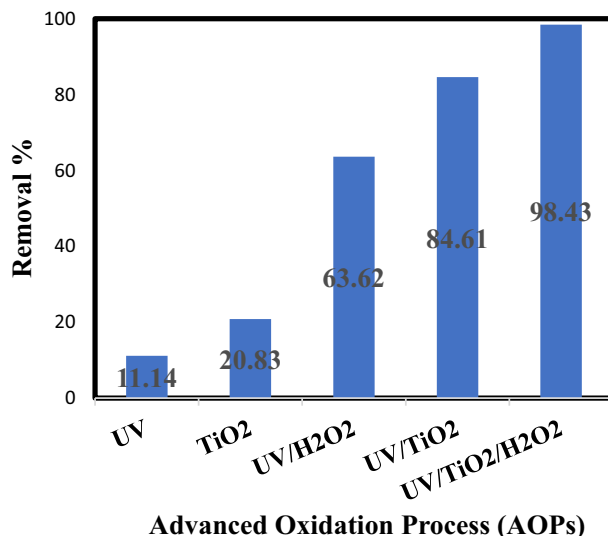
If H<sub>2</sub>O<sub>2</sub> does is low, HO<sup>·</sup> forming will also be minimum, which will reduce the treatment efficacy. Therefore, equilibrium must be preserved between surplus and depressed levels of H<sub>2</sub>O<sub>2</sub><sup>10, 26</sup>.

**Influence of agitation velocity (rpm).** To decide the agitation velocity influence of on oil removal %, tests were executed at C<sub>o</sub> oil concentration of 1 g/L, 1.5 g/L of TiO<sub>2</sub>, 8 pH, and 1 mL of H<sub>2</sub>O<sub>2</sub>. The final results are demonstrated in Fig. 7 that elucidate that the removal efficiency of oil raises to accomplish a greatest of 85.98% at stirring speed of 850 rpm after 40 min irradiation time after that it tends to drop to 78.36% at 1000 rpm.

**Comparison of the different AOPs.** Numerous types of AOPs such as UV, TiO<sub>2</sub> photocatalysis, UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub>, processes have been inspected for oil decomposition in oily wastewater. A comparison of these different AOPs was made under optimal operating conditions (1 g/L initial oil concentration, 850 rpm, 8 pH, 3 mL H<sub>2</sub>O<sub>2</sub> and 1.5 g/L of TiO<sub>2</sub> after 40 min of irradiation time) as elucidated in Fig. 8. The results noted that the TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub> process exhibited the superior oil removal efficiency (98.43%) in oily wastewater. The same figure explain that the addition of H<sub>2</sub>O<sub>2</sub> to the UV/TiO<sub>2</sub> process increase obviously the removal percent of oil because H<sub>2</sub>O<sub>2</sub> plays as electron acceptor. This phenomenon can be elucidated that decomposition of oil is fundamentally controlled by means of the hydroxyl radicals generated by the conjunction of



**Figure 7.** Influence of rotational speed on oil decomposition.



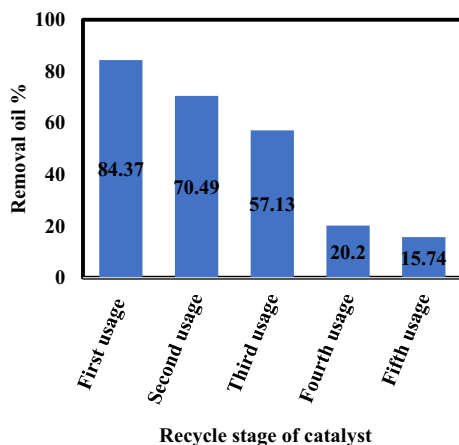
**Figure 8.** Influence of UV, TiO<sub>2</sub> photocatalysis, UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub>, processes on an oil elimination percentage.

TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in the H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>/UV system. As shown also from the same figure that the percent oil removal in case of TiO<sub>2</sub> alone (dark process) is occurred due to the effect of TiO<sub>2</sub> adsorption only. On the other hand, at light photo-assisted processes in the presence of UV light, the oil removal is taken place by the effect of generation of the powerful oxidizing agent (free hydroxyl radicals OH·) e.g. (UV/TiO<sub>2</sub>, UV/ H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> processes). The produced hydroxyl radicals is the main reason for degrading the organic contaminants and the pollutants in the wastewater sample as stated in the literature<sup>27</sup>.

**Photo-catalyst recycle.** The lifetime of catalyst is a definitive agent in defining the capacity of the photo-catalytic degradation process for the oily wastewater and for assessing its feasibility in real world purposes. A high-cost reduction can also be got if the photo catalyst can be utilized for a longer period. The catalyst disruption through photo catalytic decomposition can greatly raise the operational cost as a result of the persistent alteration of required catalyst.

The centrifugation process and re-suspension raises the accumulation of the particles and so, decreases the specific surface area. They proposed that the photo catalyst disruption could be relieved by means of superior dispersal or particle-rinsing techniques.

Various catalyst reactivation techniques have been implemented. The Organic contamination of the catalyst can be remedied via calcinations, combustion of organic matter and maintaining the stability and reusability of the catalyst<sup>28,29,30</sup>. However, this process expends extra energy. Therefore, here the catalyst was recycled 5 times. The catalyst was recovered by rinsing with dilute Hydrochloric acid and water, and there the recyclability was examined. It is noticed that the removal oil percentage decreased to 60%. It was observed that the removal oil percentage decreased to 84.37%, 70.49%, 57.13%, 20.2% and 15.74% upon the 1st, 2nd, 3rd, 4th and 5th



**Figure 9.** Influence of photo-catalyst recycle on oil removal percentage.

Reaction rate equation	Kinetic equation	Rate constant	R <sup>2</sup>
First order equation	$\ln C_t = 0.713 t$	$0.713 \text{ min}^{-1}$	0.937
Second order equation	$\frac{1}{C_t} - \frac{1}{C_0} = 0.11 t$	$0.11 \text{ L min}^{-1} \text{ g}^{-1}$	0.881

**Table 2.** The rate of reaction of 1 g/L initial oil concentration.

photo-catalyst recycling, respectively as clarified in Fig. 9. In our study it is recommended to reuse the catalyst for three times.

### Kinetic studies

Table 2 clarifies the reaction rate of 1 g/L initial oil concentration, TiO<sub>2</sub> of 1.5 g/L, 850 rpm and H<sub>2</sub>O<sub>2</sub> of 3 mL. The linear form of first- and second order kinetic models can be presented in Eqs. (10, 11).

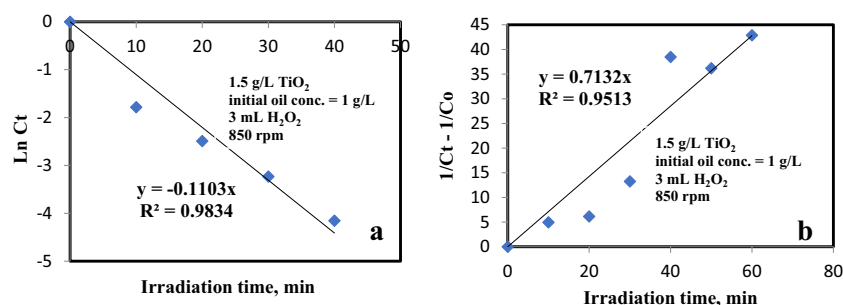
$$\ln C_t = K_1 t, \quad (10)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = K_2 t, \quad (11)$$

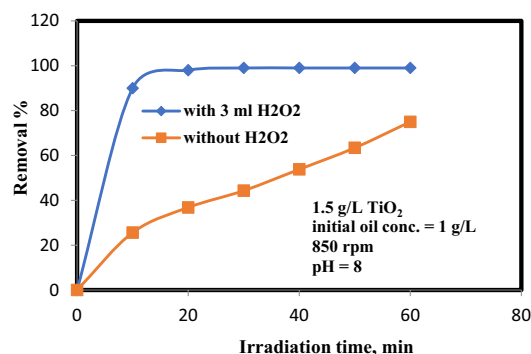
where C<sub>0</sub> is the initial concentration of oil and C<sub>t</sub> is the concentration at irradiation time t, K<sub>1</sub> and K<sub>2</sub> are first and second order rate constants in min<sup>-1</sup> and L g<sup>-1</sup> min<sup>-1</sup>, respectively, t is the degradation time (in min). A plot ln C<sub>t</sub> and  $[\frac{1}{C_t} - \frac{1}{C_0}]$  against time for each experiment leads to a straight line whose slope is K<sub>1</sub> and K<sub>2</sub>, respectively. The regression analysis of the concentration curves against degradation time marks that the rate of reaction can be depicted by means of first order kinetics. The result is shown in Fig. 10.

### Case study

Treatment of an oily wastewater collected from an effluent stream of Ras Shukair at Red Sea supplied by Asuit Petrochemical Company was investigated. The sewer water from these industries naturally contains fats, oils and greases mixed with a variety of dissolved substances (organic and/or inorganic) in suspension in high concentrations. If they are not treated before being discharged into an open ground or into water streams, it leads to environmental issues and health risks. To avert these types of issues, a process is done for pre-treating oily sewer water. The treatment process was carried out at optimum operating parameters mentioned above (1 g/L



**Figure 10.** The reaction rate of 1 g/L initial oil concentration at optimum operating parameters. (a) First order equation (b) Second order equation.



**Figure 11.** Addition of H<sub>2</sub>O<sub>2</sub> effect on an oil removal %.



of initial oil concentration,  $\text{TiO}_2$  of 1.5 g/L, 8 pH, and 850 rpm). The final results are demonstrated in Fig. 11. These elucidate that the maximum removal % of oil (99%) achieved by adding 3 mL of  $\text{H}_2\text{O}_2$  in a reaction time of 40 min. The oil removal % without adding  $\text{H}_2\text{O}_2$  was 75%. This proved that the addition of  $\text{H}_2\text{O}_2$  is a significant to improve the AOP efficiency.

## Conclusion

Firstly, UV/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  was utilized to inspect the AOP performance of oil decomposition in simulated wastewater in the current study. The optimum factors for the process were found to be as follows: 1 g/L of initial oil concentration,  $\text{TiO}_2$  of 1.5 g/L, 850 rpm, 8 pH, and  $\text{H}_2\text{O}_2$  of 3 mL. At these optimum factors, 98.43% of oil was removed from oily wastewater after a reaction time of 40 min. This study found that photo-catalytic oxidation by UV/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  is effective in oily wastewater treatment. Secondly, the treatment of oily sewer water collected from an effluent stream of Ras Shukair at Red See supplied by Asuit Petrochemical Company was investigated at these optimum parameters. The maximum removal percentage (99%) was achieved in a reaction time of 40 min with 3 mL  $\text{H}_2\text{O}_2$ . By rinsing the catalyst five times in diluted hydrochloric acid and water, the catalyst's recyclability was assessed. According to our studies, the catalyst should be used three times. Thirdly, analysis of oil degradation kinetics was also performed so as to elucidate an optimum operating factors effect on the rate constant of the decomposition reaction. Decomposition reaction follows a first order kinetics with  $R^2$  of 93.7%.

## Data availability

Datasets are available in the manuscript. Any additional information and data are available upon reasonable request. The data and materials can be shared with the corresponding author upon reasonable request.

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## Author contributions

E.E.E. and M.Y.G. conceptualized the study. H.A.E.-G. and R.M.M. contributed to data acquisition. H.A.E.-G., E.E.E., M.Y.G., A.A.A. and R.M.M. conducted the data analysis and generated the tables and figures. A.A.A. contributed with writing, review and editing. All authors have read and agreed to the published version of the manuscript.

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## Competing interests

The authors declare no competing interests.

## Additional information

**Correspondence** and requests for materials should be addressed to R.M.M.

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