

Wastewater-(Direct Red Dye) Treatment-Using Solar Fenton Process

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Abstract:

The present research based its strategy in general on evaluating the feasibility of using the process of Fenton oxidation (solar-oxidation) as a technique to remove the residual organic pollutants that are available in direct red wastewater. The following values highlight the optimized Fenton parametric concentrations so as to maximize the removing of Direct Red wastewater: [DR] = 20 mg/L M, Fe^{2+} = 7.5 mg/L, H_2O_2 = 75mg/L, pH = 3 at room temperature. According to the above-mentioned conditions and during 30 minutes of reaction, the procedure managed to achieve degradation efficiency in excess of 75%. For the same time duration of 30 minutes, the DR degradation efficiency had been drastically surging from 59% up to 90.5% as a response to lowering the initial pH value from 7 to 3. As for the DR wastewater, the solar Fenton technique managed to carry out an approximate percentage of DR removal of 90.5% in contrast with a percentage of 38.5% in the case of Fenton oxidation technique.

Keywords: Dyes; Wastewater Treatment; Advanced Oxidation Processes

1. INTRODUCTION

One of the major issues which researchers had been focusing on is the negative impact of infected and toxic wastewater on environment. Organic dyes are but one prominent pollutant of industrial wastewater [1-2]. Top priority is reserved for such category of dyes because they can inflict massive harm onto bio organisms while many types of them had been classified as hazardous to human health too [3]. As far as textiles industry is concerned, direct dye still rules over other dyes used in printing and dyeing processes. Small-sized factories for dyeing & printing constitute the lion's share in dyeing industry where the trend is about home-made textiles. Ample quantities of synthetic dyes are usually consumed by multiple industries such as paper (10%), plastic matter (10%) and textile dyeing (60) [4].

The conventional treatments include adsorption, coagulation/flocculation, adsorption, biological and ultrafiltration. These processes are expensive and usually generate hazardous by-products [5-9]. Anyhow, these approaches are nondestructive as they simply transfer the non-biodegradable matter from one form into sludge which allows for a new kind of pollution that (needless to say) requires further treatment [10]. Apart from all other processes, advanced oxidation processes (AOPs) have been thoroughly studied as per their efficiency of treating the dyes. It is generally accepted that a process train comprising anaerobic/aerobic biological and advanced oxidation processes might be the only feasible option to deal with dyes [11]. These processes have the ability of completely degrading the organic pollutants into inorganic substances posing no harm such as H_2O and CO_2 under moderate conditions [12-13]. Moreover, advanced oxidation processes turned out to be very common in matters of industrial wastes treatment especially those containing organic dyes. AOPS is based on generating very strong oxidizing agents in the form of extremely reactive radicals [14]. The keys feature of AOPs for the degradation of contaminants in water is the utilization of free radicals ($OH\cdot$), which are powerful and non-selective oxidants able to decompose most organic compounds [15].

This study interested on dye removal from aqueous solution by using Fenton oxidation, solar Fenton oxidation and photolysis oxidation. Firstly find the optimum value of hydrogen peroxide concentration, studying the effects of pH and reaction time on solar Fenton processes. Secondly compare between these methods.

2. MATERIALS AND METHODS

2.1 Reagents

All chemicals used in this work were of analytical grade and used without further purification. Direct red and the chemical structure

is given in figure1, Hydrogen peroxide (Germany 45% wt. /wt.), ferrous sulphate (India 99 % purity), H_2SO_4 (SDFCL 98 % purity) and Sodium hydroxide (Thomsas baker), were used in this study

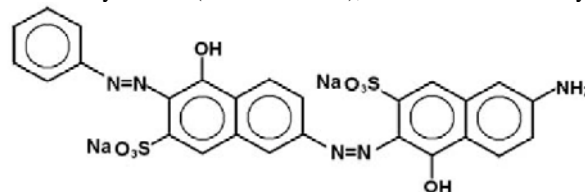


Figure 1: Discription of the structure of direct red.

2.2 UV/ H_2O_2 Bench-Scale Solar Batch Reactor

Advanced experiments were carried out onto oxidation processes of degradation using a 250 ml glass batch reactor which had 100 mL solution of direct red that was shaken at room temperature with an equivalent speed of stirring around 200 rpm lasting for duration of 30-150 min within the solar reactor. For the sake of obtaining uniform mixing, a magnetic stirrer was used with a glass beaker containing the solution. Prior to adding the reagents, a dilute NaCl or H_2SO_4 solution was introduced into the beaker for the sake of adjusting pH value. A digital pH meter (model WTW pH-720) had been used to measure the value of pH while a range of 50-100 mg/L of hydrogen peroxide was used too.

2.2 AOPs Efficiency and Kinetic Study

A UV spectrophotometer (UV-1800 Shimadzu, Japan) was used to measure the change in concentration of organic content in direct red during the advanced oxidation process. The results had been converted into the corresponding concentrations (C). Equation (1) given here below served in calculating DR Efficiency:

$$\eta = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Here, η represents the percentage of dye removal; C_o , measured concentration before the treatment (mg/L); C_t concentration value after treatment (mg/L). The Langmuir-Hinshelwood kinetics model was used to determine the kinetics of the photochemical degradation rate of dye removal. This is given in Eq. (2) here below: The pseudo-first-order rate constant, k_1 (min^{-1}). A plot of $\ln(C_o/C)$ versus time for each experiment lead to a straight line whose slope is K_1 [16].

$$\ln\left[\frac{C_o}{C}\right] = K_1 t \quad (2)$$

3. RESULTS AND DISCUSSION

The main factors affecting the efficacy of solar Fenton process are H_2O_2 and Fe concentrations, pH and temperature of the reaction medium.

3.1 The Effect of Initial Hydrogen Peroxide Concentration

To best clarify the role of H_2O_2 concentration on the solar-Fenton degradation of direct red taken in this investigation in the solar Fenton, this study implemented experiments with varying concentrations of initial hydrogen peroxide at constant values of initial pH, initial Fe (II) for the solar Fenton treatment within irradiation time of 120 min. Fig. 2 shows that the degradation efficiency represented by % DR removals is demonstrated when H_2O_2 concentration increases from 50 to 75 mg/L. This is justified by the effect of the additionally produced $OH\cdot$ radicals.

Anyhow, for concentrations more than this one for H_2O_2 , the reaction rate reaches a state of levels-off; sometimes it gets negatively influenced, by virtue of the progressive increase of hydrogen peroxide. This could be a result of recombination of $OH\cdot$ radicals as well as auto decomposition of H_2O_2 into water and oxygen [17]. Accordingly, a surplus amount of H_2O_2 may cause consumption of the active oxidizing hydroxyl radicals through a reaction other than the dye degradation reaction. Consequently, it all reduces the rate of the latter reaction. Due to that, a balance had been attained all the time between low levels of H_2O_2 and excess amounts of it. These observations are the same as that obtained by Shaker et al., 2011 [18].

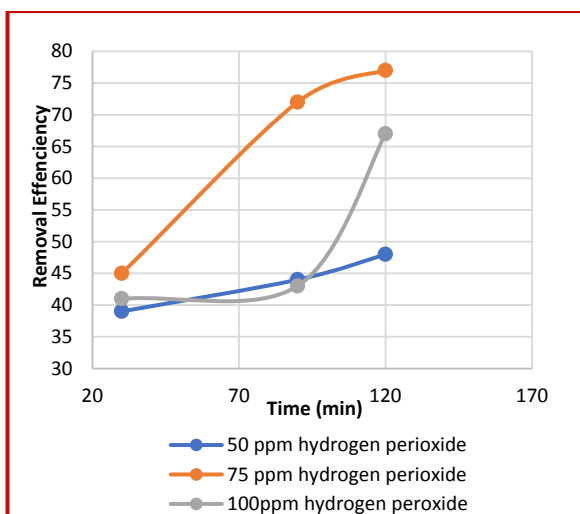


Figure 2: Effect of hydrogen peroxide on DR removal; pH = 6.2, room temperature, ferrous sulfate 10 mg/L, direct red 20 mg/L.

3.2 The Effect of Initial Amount of Fe Ion

The influence of the reaction catalyst concentration (as Fe^{2+}) on direct red removal had been investigated via adding $FeSO_4 \cdot 7H_2O$ solution in doses of 2.5–10 mg/L; all other reaction variables were kept fixed. Those variables included retention time, initial direct red, room temperature, pH, H_2O_2 concentration, room temperature and retention time. Figure 3 illustrate the results of residual concentration and removal efficiency as a function of $FeSO_4 \cdot 7H_2O$ dose.

In light of this, an increase of 84.% removal of DR in 7.5 mg/L of ferrous sulfate is obtained. The decolourisation in early stages is faster than in the late stage of the reaction. Since ferrous ion catalyses H_2O_2 to form hydroxyl radical rapidly in the first stage of reaction, further more decolourisation takes place in the early stage of reaction. With dosages of low ferrous sulfate, a longer treatment time is needed for complete decolourisation in the case

of direct red [19]. Higher additions of iron salt resulted in brown turbidity that stalled the absorption of UV light needed for photolysis and also caused the recombination of $OH\cdot$ radicals. In this case, Fe^{2+} reacted with $OH\cdot$ radicals as a scavenger [20]. Increasing ferrous salt dose up to 10 mg/L led to decreasing of DR removal at the adjustable conditions. It is desirable for the ratio of H_2O_2 to Fe^{2+} to be as low as possible so that the recombination of $OH\cdot$ radicals gets avoided and the sludge production from iron complex is also decreased. This way, it can be deduced that $OH\cdot$ generation (and subsequently, rate of oxidation too) rises in a significant manner and simultaneously with enhancing of Fe^{2+} ion concentration in the reaction [21].

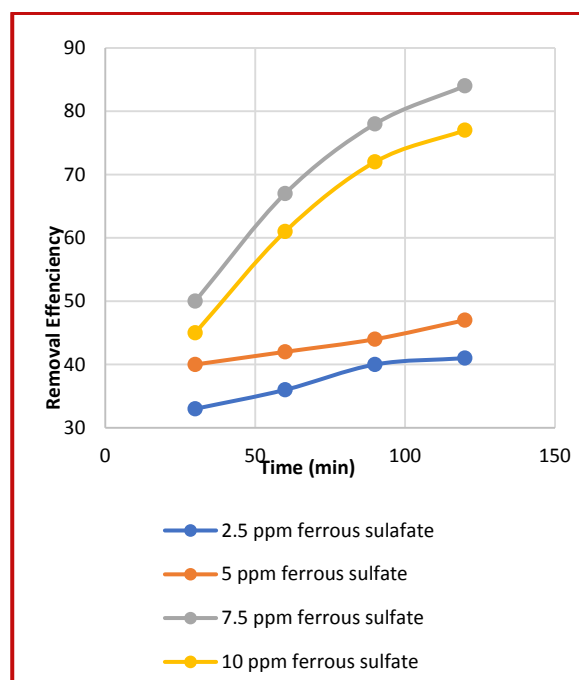


Figure 3: Influence of ferrous sulfate on DR removal; pH = 6.8, time = 120 min, room temperature, hydrogen peroxide 75 mg/L, direct red 20 mg/L.

3.3 Effect of pH on DR Removal

The solar Fenton method is considerably influenced by pH values since the optimal performance of the process demands a favored pH range. Both activities of decomposition of hydrogen peroxide and that of speciation of iron are affected by pH values. Figure 4 shows the effect of pH on the direct red removal efficiency. Examination of the figure shows that the removal efficiency increases with decreasing pH, the optimal pH being 3.0. These observations conform to those of Maha A. et al., 2012 [22] but are contrary to the findings of E. Hernández et al., 2017 [23] which state that the influence of pH value on removal of organic material is not remarkable. Multiple experiments had been conducted with variations on the pH range from 3 to 11 in order to assess the influence of pH on the efficiencies of DR percent removal as per direct red using solar Fenton's oxidation; all other parameters were maintained constant.

Figure 4 shows the results where one scan detects that a maximum removal efficiency (90.5%) has been achieved at pH=3. Just above this value, the DR efficiency has been reduced gradually down to a value of pH=11. An evident decrease of (35%) in efficiency of DR removal had been observed. The observed finding about using an acidic solution is that high removal percent in DR removal had been obtained given that the maximum amount of DR removal had been found to be with a pH equal to 3 but with more than this value the DR percent removal drops down

[24]. This drop can be attributed to the fact that at degraded values of pH result in high oxidizing property of H_2O_2 . On the other hand, iron reacts with the hydroxide ions (OH^-) at a high value of pH, eventually causing a precipitation of $Fe(OH)_2$ or of the iron hydroxide $Fe(OH)_3$. This does not react with H_2O_2 , thus reducing the rate of degradation [21]. The parameter of pH controls generating of free radicals; therefore it affects the oxidation. In addition to that, due to increase in pH, the oxidation potential of radicals decreases. At high value of pH, namely above 5.0, direct red resists degrading as a result of the precipitation of complex compounds and the declining of oxidation yield with pH increase can be clarified by the degeneration of H_2O_2 amount, also by the deactivation of the iron catalyst due to the formation of ferric hydroxide complexes which leads to a reduction of free radicals. This way, the influence of pH effect had been only examined in the range of 3 to 4.

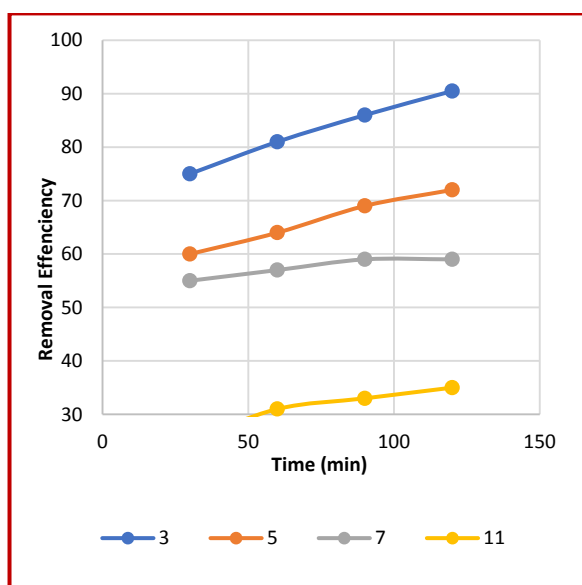


Figure 4: Effect of pH on DR removal; hydrogen peroxide = 75mg/L, irradiation time = 120 min, room temperature, ferrous sulfate 7.5 mg/L, direct red 20 mg/L.

3.4 Effect of Irradiation Time on Direct Red Removal

The study included the influence of irradiation time taken by the Solar-Fenton treatment in order to get the best removal of DR efficiency. In this process, the initial amount of H_2O_2 had been fixed (with pH too) at room temperature. The initial direct red concentration used in these experiments was 20 mg/L. As for the solar Fenton oxidation technique, the free radicals made (which already have an extremely high oxidizing ability) could oxidize into hardness with the breakdown of organic compounds taking a brief time. The relationship between irradiation time and the direct red percent removal within the experimental work is shown in Figure 5. For more concentrated or perhaps more complex wastes, it may take many hours for the reaction to remove wastes. Experiments were conducted to assess the best time duration for the solar Fenton efficiency in DR percent removal.

Figure 5 clarifies that the efficiency of DR removal is both slow and directly proportional. Due to that, the increase in efficiency of DR removal can be linked to DR oxidation via the free radicals. There had also been revisions reporting increasing oxidation time led to increasing efficiency of DR removing process which coincided with the observations of Javier Benitez et al., 2001[14].

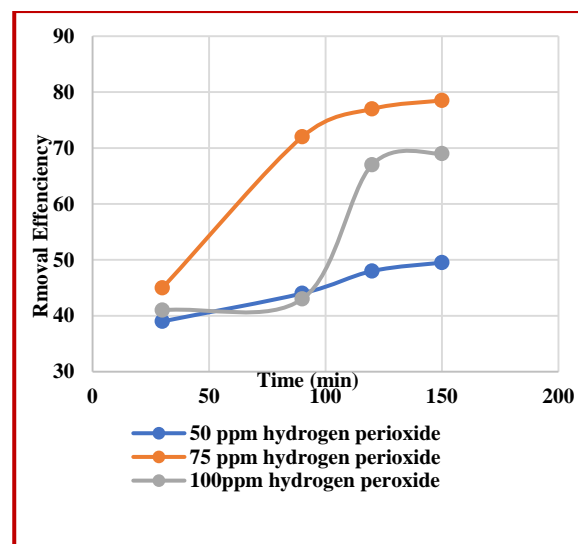


Figure 5: Influence of irradiation time on DR percent removal, pH = 6.2, room temperature, ferrous sulfate 5 mg/L.

3.5 The Effect of Initial Concentration on Direct Red

One vital parameter in Solar-Fenton technique processes is the pollutant concentration. Figure 6 shows the effect of initial dye concentration in this process. It is evidently noticed from this figure that the removal rate is decreased by the increase in dye concentration. Increasing the dye concentration from 10 to 40 led to decreasing the decolourisation from 81% to 45% for solar Fenton treatment. Hydroxyl radical is mainly responsible for dye decolourisation and its concentration remains constant for all dye concentrations. The number of dye molecules is increased by the increase in dye concentration and not the OH radical concentration, thus the removal rate decreases eventually.

As for the case with high concentrations of dyes within a context of a Solar-Fenton technique, the hydroxyl radical concentration gets lowered by virtue of a decrease in penetration of photons through the solution [19]. This occurs because of a relative lower concentration of $HO\cdot$ resulting due to the increase in DR concentration. These observations coincide with that obtained by Nadia A. et al., 2016 [25].

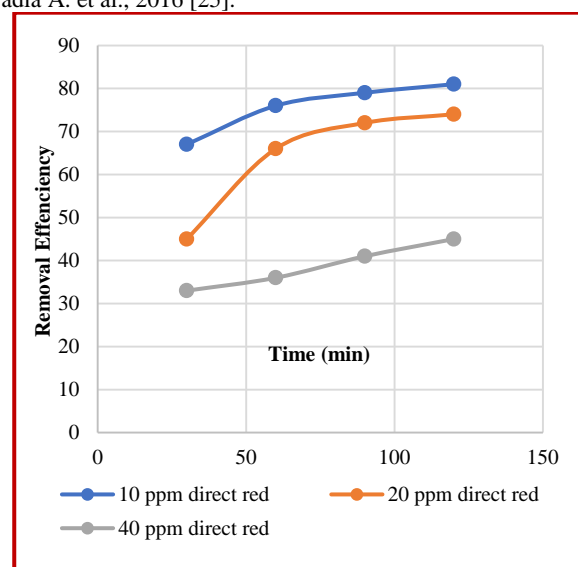


Figure 6: Impact of initial concentration on percent removal, hydrogen peroxide = 50 mg/L, pH = 6.2, room temperature, ferrous sulfate 10 mg/L.

3.6 Kinetic Study

The application of the kinetic model termed as Pseudo First Order model on hydrogen peroxide experiment is shown in Fig 7. A few experiments had been designed in order to assess the influence of the concentration of hydrogen peroxide on kinetic constants of DR removal percentage. Some of these experiments had been designed to be carried out with various concentrations of H₂O₂ (50, 70 and 100mg/L), the condition of initial direct red was set at 20 mg/L. The value of the parameter k₁ (min⁻¹) was determined by fitting the experimental data according to Eq (2). Figure 7 shows the values of ln(C₀/C) versus normalized lighting time

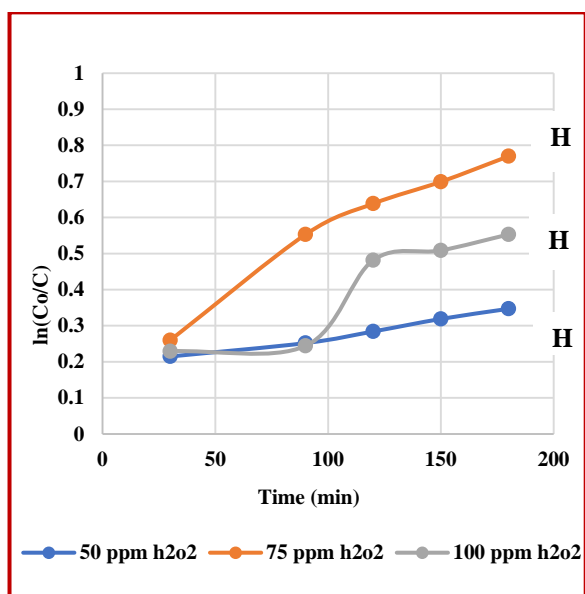


Figure 7: Pseudo' first order model for DR degradation of hydrogen peroxide experiments at pH = 7 at room temperature, ferrous sulfate = 10 mg/L, direct red 20 mg/L.

Table (1) provides the value for rate constants in the case with the model. The calculations of the coefficient of determination R² were employed to assess the best model. R² is an indicator of the degree of suitability of the equation for prediction. The closer to (1) the value is, the better would be the fit to the model.

Table 1: Rate constants of hydrogen peroxide experiments.

H ₂ O ₂	First order	
	K ₁ (1/min)	R ²
50	0.0009	0.9823
75	0.0034	0.953
75	0.0024	0.8367

According to contents of Figure 7 (and for this set of experiments specifically), the best concentration of H₂O₂ is 100 mg/L since the rate constant K₁ increases till it reaches the maximum (3.4x10⁻³ min⁻¹) at 75 mg/L of H₂O₂ then it encounters a decrease down to 100 mg/L of H₂O₂. This finding coincides with that of **Sushil A. et al., 2010** [26].

3.7 Compare between Advanced Oxidation Methods

For the sake of studying and comparing the performance of degradation processes (including the solar-Fenton system), the research implemented three experiments in the course of treatment of direct red that contains organic constituents. These experiments were as follows: Solar-Fenton process (hydrogen peroxide and ferrous sulfate with UV irradiation in pH=3), the Fenton reaction (ferrous sulphate and hydrogen peroxide in the pH = 3 yet without UV irradiation) and finally the UV-photolysis (exclusive use of

UV irradiation in the pH = 6.2). All three experiments were conducted under room temperature. According to the findings of those experiments, the UV-photolysis failed to promote the complete mineralization. After a whole period of (150) min irradiation the percentage of removal according to the UV-photolysis experiment; the removal percentage corresponded to 12.5 % of DR removal. As for the Fenton reaction, a removal percentage of 38.5% was obtained after a period of (150) min irradiation time. This score was possible because of free radicals generation due to the reaction between hydrogen peroxide and the ferrous ions. The limiting reagent of Fenton for this process corresponds to ferrous ions, hydrogen peroxide and lower generate of free radical. Still, better results had been obtained due to this process using UV radiation combined with iron reagents. The solar Fenton processes managed to mineralize 90.5 % during the same irradiation period. The best removal efficiencies for direct red based on the findings mentioned above was solar Fenton.

4. CONCLUSIONS

The degradation of DR in aqueous solution by Solar Fenton reaction as practiced in this study had been applied according to various experimental conditions. These included: various values of pH for solutions, various values of dye concentration and dosages of H₂O₂ and Fe²⁺. An appropriate operating condition had been selected to be with: [DR] = 20 mg/LM, [Fe²⁺] = 7.5 mg/L, [H₂O₂] = 75 and pH = 3, all under room temperature. According to the above-mentioned conditions and during 30 minutes of reaction, the procedure managed to achieve degradation efficiency in excess of 75%. For the same time duration of 30 minutes, the DR degradation efficiency had been drastically surging from 59% up to 90.5% as a response to lowering the initial pH value from 7 to 3. Additionally, degradation kinetics pertaining to DR was proved through kinetics study to be following that of first order category. The findings of the study led to the conclusion that Solar-Fenton technique has a higher efficiency in contrast with Fenton process although both techniques may be applied for decolourisation of Direct Red.

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REFERENCES

- [1] L. Karimi, S. Zohoori, and M. E. Yazdanshenas, "Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nano-strontium titanate as the nanophotocatalyst," *J. Saudi Chem. Soc.*, vol. 18, no. 5, pp. 581–588, 2014.
- [2] N. Barka, S. Qourzal, A. Assabane, A. Nounah, and Y. Ait-ichou, "Photocatalytic degradation of an azo reactive dye, Reactive Yellow 84, in water using an industrial titanium dioxide coated media," *Arab. J. Chem.*, vol. 3, no. 4, pp. 279–283, 2010.
- [3] H. Benhebal et al., "Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol-gel process," *Alex. Eng. J.*, vol. 52, no. 3, pp. 517–523, 2013.
- [4] M. A. Hassaan, A. El Nemr, and F. F. Madkour, "Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in wastewater," *Egypt. J. Aquat. Res.*, vol. 43, no. 1, pp. 11–19, 2017.
- [5] A. A. Assadi, J. Palau, A. Bouzaza, and D. Wolbert, "Modeling of a continuous photocatalytic reactor for isovaleraldehyde oxidation: Effect of different operating parameters and chemical degradation pathway," *Chem. Eng. Res. Des.*, vol. 91, no. 7, pp. 1307–1316, 2013.
- [6] M. A. Hassan, T. P. Li, and Z. Z. Noor, "Coagulation and flocculation treatment of wastewater in textile industry using chitosan," *J. Chem. Nat. Resour. Eng.*, vol. 4, no. 1, pp. 43–53, 2009.

- [7] L. Kong *et al.*, "Producing sawdust derived activated carbon by calcinations with limestone for enhanced Acid Orange II adsorption," *J. Clean. Prod.*, vol. 168, pp. 22–29, 2017.
- [8] M. Kornaros and G. Lyberatos, "Biological treatment of wastewaters from a dye manufacturing company using a trickling filter," *J. Hazard. Mater.*, vol. 136, no. 1, pp. 95–102, 2006.
- [9] M. Simonič, "Efficiency of ultrafiltration for the pre-treatment of dye-bath effluents," *Desalination*, vol. 245, no. 1–3, pp. 701–707, 2009.
- [10] A. A. Aziz and W. M. A. W. Daud, "Oxidative mineralisation of petroleum refinery effluent using Fenton-like process," *Chem. Eng. Res. Des.*, vol. 90, no. 2, pp. 298–307, 2012.
- [11] E. Chatzisyneon, S. Foteinis, D. Mantzavinos, and T. Tsoutsos, "Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment," *J. Clean. Prod.*, vol. 54, pp. 229–234, 2013.
- [12] P. Palaniandy, H. B. A. Aziz, and S. Feroz, "Treatment of petroleum wastewater using combination of solar photo-two catalyst TiO₂ and photo-Fenton process," *J. Environ. Chem. Eng.*, vol. 3, no. 2, pp. 1117–1124, 2015.
- [13] J. Saïen and H. Nejati, "Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions," *J. Hazard. Mater.*, vol. 148, no. 1–2, pp. 491–495, 2007.
- [14] F. J. Benitez, J. L. Acero, T. Gonzalez, and J. Garcia, "Organic matter removal from wastewaters of the black olive industry by chemical and biological procedures," *Process Biochem.*, vol. 37, no. 3, pp. 257–265, 2001.
- [15] J. R. Alvarez-Corena, J. A. Bergendahl, and F. L. Hart, "Advanced oxidation of five contaminants in water by UV/TiO₂: reaction kinetics and byproducts identification," *J. Environ. Manage.*, vol. 181, pp. 544–551, 2016.
- [16] A. H. Jawad, N. S. A. Mubarak, M. A. M. Ishak, K. Ismail, and W. I. Nawawi, "Kinetics of photocatalytic decolorization of cationic dye using porous TiO₂ film," *J. Taibah Univ. Sci.*, vol. 10, no. 3, pp. 352–362, 2016.
- [17] E. E. Ebrahiem, M. N. Al-Maghrabi, and A. R. Mobarki, "Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology," *Arab. J. Chem.*, vol. 10, pp. S1674–S1679, 2017.
- [18] S. Haji, B. Benstaali, and N. Al-Bastaki, "Degradation of methyl orange by UV/H₂O₂ advanced oxidation process," *Chem. Eng. J.*, vol. 168, no. 1, pp. 134–139, 2011.
- [19] M. Muruganandham and M. Swaminathan, "Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology," *Dyes Pigments*, vol. 63, no. 3, pp. 315–321, 2004.
- [20] S. A. O. Galvão, A. L. Mota, D. N. Silva, J. E. F. Moraes, C. A. Nascimento, and O. Chiavone-Filho, "Application of the photo-Fenton process to the treatment of wastewaters contaminated with diesel," *Sci. Total Environ.*, vol. 367, no. 1, pp. 42–49, 2006.
- [21] M. M. Amin, 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.*, vol. 45, pp. 412–420, 2017.
- [22] M. A. Tony, P. J. Purcell, and Y. Zhao, "Oil refinery wastewater treatment using physicochemical, Fenton and photo-Fenton oxidation processes," *J. Environ. Sci. Health Part A*, vol. 47, no. 3, pp. 435–440, 2012.
- [23] E. Hernández-Francisco, J. Peral, and L. M. Blanco-Jerez, "Removal of phenolic compounds from oil refinery wastewater by electrocoagulation and Fenton/photo-Fenton processes," *J. Water Process Eng.*, vol. 19, pp. 96–100, 2017.
- [24] M. Muruganandham and M. Swaminathan, "Photochemical oxidation of reactive azo dye with UV–H₂O₂ process," *Dyes Pigments*, vol. 62, no. 3, pp. 269–275, 2004.
- [25] N. A. Youssef, S. A. Shaban, F. A. Ibrahim, and A. S. Mahmoud, "Degradation of methyl orange using Fenton catalytic reaction," *Egypt. J. Pet.*, vol. 25, no. 3, pp. 317–321, 2016.
- [26] S. K. Kansal, A. H. Ali, and S. Kapoor, "Photocatalytic decolorization of biebrieh scarlet dye in aqueous phase using different nanophotocatalysts," *Desalination*, vol. 259, no. 1–3, pp. 147–155, 2010.