Global NEST Journal, Vol 27, No X, pp 1-9

Comparative Study of Fenton and Photo-Fenton Processes for the Treatment of Distillery Wastewater: Pollutant Removal Efficiency and Kinetic Analysis

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Received: 13/03/2025, Accepted: 23/08/2025, Available online: 15/09/2025
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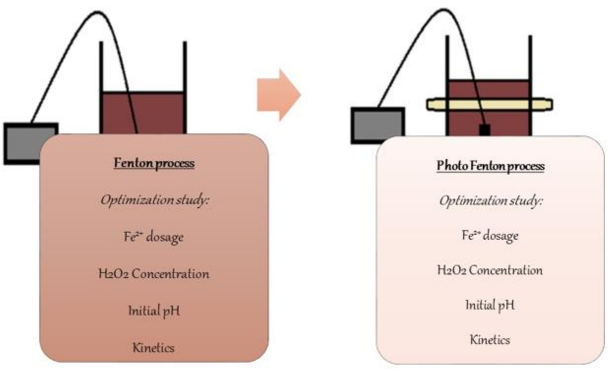
https://doi.org/10.30955/gnj.07452

Graphical abstract



Abstract

This research explores the optimization of the most important parameters (Fe^{2+} dosage, H_2O_2 concentration and pH) in the Fenton and photo-Fenton processes for the treatment of distillery wastewater (DWW). The impact of these parameters on COD removal efficiency was assessed and the findings proved that Fe^{2+} dosage, H_2O_2 concentration and pH have a significant effect on treatment efficiency. The Fenton process achieved a maximum COD removal efficiency of 54.5% under the operational conditions of 1.25 g L^{-1} Fe^{2+}, 1110 mg L^{-1} H_2O_2, and pH 3. In contrast, the photo-Fenton process exhibited an enhanced COD removal efficiency of 59.6% at a lower Fe^{2+} concentration of 0.75 g L^{-1}, the same H_2O_2 concentration of 1110 mg L^{-1}, and pH 3, facilitated by the presence of UV irradiation which accelerates the generation of hydroxyl radicals, thereby increasing the reaction kinetics. Kinetic modelling indicated that the Fenton process was pseudo-first-order and followed second-order kinetics in the photo-Fenton process with UV radiation contributing significantly to enhancing the rate of reaction. ANOVA analysis validated all three parameters as statistically significant with the most significant factor being pH. The research emphasizes that both the Fenton and photo-Fenton processes are efficient for DWW treatment with the photo-Fenton process showing greater efficacy due to the catalytic action of UV light. The results provide useful information for maximizing these processes for industrial wastewater treatment with the possibility of cost-effective and sustainable use in distillery and other industries. Future studies may investigate hybrid oxidation technologies and other UV sources to further enhance process efficiency and sustainability.

Keywords: Distillery wastewater, comparative study, Fenton process, Photo-Fenton process, COD removal, Advanced oxidation processes, Kinetic analysis

1. Introduction

Distillery industry is reported to be very water-intensive (Saha *et al.* 2005) and is directly associated with the requirement of alcoholic drinks (Kharayat 2012). Alcohol is a major constituent in many products including medicines, cosmetics, drinks and perfumes and has also become significant in gasoline blending and hand sanitizers as a result of the Covid-19 pandemic (Drury *et al.* 2021). Its demand is also growing as a renewable source of energy (Mohana *et al.* 2009; Robak and Balcerek 2020). In India, nearly 60% of ethanol is manufactured from sugarcane molasses, a sugar manufacturing by-product (Anand *et al.* 2021). Molasses have residual sugars, organic compounds and minerals (Kumar *et al.* 2022). During the process of alcohol production, fermentation takes place and alcohol is removed and the rest of the material becomes spent wash (Dubey *et al.* 2024). More ethanol production leads to more volumes of distillery wastewater (DWW) with about 10-15 L of DWW being generated per L of ethanol. DWW is marked by the presence of high organics (Chemical oxygen demand or COD: ~80-180 g L^{-1}) particularly in molasses distilleries, generating wastewater with exceptionally high COD (~130-180 g L^{-1}) and comprising different pollutants such as melanoidins, phenolic compounds and inorganic ions (Johnson *et al.* 2023).

Advanced oxidation processes (AOPs) are often employed for industrial wastewater treatment because they can destroy organic contaminants and decolorize (Ilhan *et al.* 2019; Minnalkodi Senguttuvan *et al.* 2024). Fenton oxidation, an efficient AOP can efficiently degrade recalcitrant substances without the need for costly reagents or specific apparatus (Ribeiro and Nunes 2021). But the reduction in the regeneration rate of ferrous (Fe^{2+}) ions in Fenton oxidation decreases its efficiency (Guimaraes *et al.* 2019). Photo-Fenton enhances the efficiency of Fenton oxidation using ultraviolet radiation (UV) to regenerate Fe^{2+} enhancing hydroxyl radical (OH•) production and oxidation efficiency (Mohadesi and Shokri 2019). This process has been well researched to be effective in degrading organic pollutants, stripping toxic metals such as lead and arsenic and disinfecting bacterial pathogens (Ortega-Gómez *et al.* 2014; Wahyuni *et al.* 2019, 2021). In this study, the treatability of DWW using Fenton and photo-Fenton oxidation processes is assessed, the efficiencies of their removal were compared and kinetic behaviour of the processes under ideal conditions was analyzed.

2. Materials and Methodology

2.1. Materials

A distillation plant close to Chengalpattu, Tamil Nadu, India provided the distillery wastewater sample used in this investigation. After being gathered in a high-density polyethylene container, the sample was sent straight to the lab and kept at 4°C until additional examination. Sodium hydroxide (NaOH; 97% purity, RANKEM, India), hydrogen peroxide (H_2O_2; 30% w/w, RANKEM, India) and sulfuric acid (H_2SO_4; 98% w/w, MERCK, Germany) were the reagents utilized in the Fenton and photo-Fenton processes. The following reagents were used to determine COD: ammonium iron (II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$; 99% purity, Sigma Aldrich, U.S.), potassium dichromate ($K_2Cr_2O_7$; > 99% purity, MERCK, Germany), silver sulfate (Ag_2SO_4; ≥ 98% purity, RANKEM, India) and mercuric sulfate ($HgSO_4$; ≥ 99% purity, RANKEM, India). The photo-Fenton apparatus had a 16 W UVC germicidal light (254 nm, INDETOUCH, India) and continuous aeration was provided using a fish tank aerator (Model 108, Gujarat, India).

2.2. Experimental Setup

2.2.1. Fenton Process

Fenton process was conducted in a 1 L cylindrical glass reactor. About 600 mL of distillery wastewater was used for each batch. A fish tank aerator was utilized to provide a continuous flow of oxygen as depicted in **Figure 1a**. Initial H_2O_2 concentration was adjusted at 555 mg L-1 and Fe^{2+} dosage was kept at 0.5 g L-1. Reaction was initially done at the native pH of DWW, with subsequent optimization under different experimental conditions. The reaction was performed for 1.5 h and 5 mL samples were drawn at 10 min intervals and analyzed.

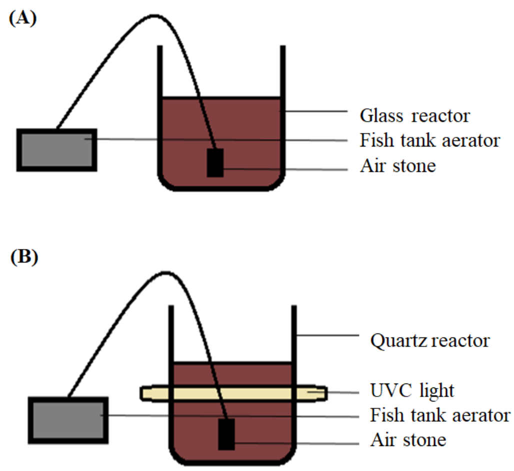


Figure 1. Schematic representation of the (a) Fenton and (b) Photo-Fenton processes

2.2.2. Photo-Fenton Process

For the photo-Fenton process the reactor configuration was identical, but for quartz glass the reactor was constructed to allow UV light to pass through as presented in **Figure 1b**. A UVC lamp of 16 W was placed at the back of the reactor to improve the photo-activation of the Fenton reaction.

2.3. Optimization of Process Parameters

To enhance the conditions for maximum COD removal efficiency, batch experiments were carried out by changing the pH of DWW, Fe^{2+} dosage and H_2O_2 concentration. pH of the DWW was modified between 2 and 7 using 1 N H_2SO_4 and 1 N NaOH. $FeSO_4$ salt was added in the range of 0.5-1.5 g L^{-1}, while H_2O_2 was used at concentrations between 555-2220 mg L^{-1}. Every parameter was independently changed, while others were maintained constant. These optimization experiments were carried out for the Fenton as well as the photo-Fenton process. The experimental conditions of the Fenton and photo-Fenton processes with varying levels of Fe^{2+} dosage and other parameters applied in this work are listed in **Table 1.**

Table 1. Experimental design for the treatment of DWW

Independent Variable	Unit	1	2	3	4
Fe^{2+} Dosage	g L^{-1}	0.5	1	1.25	1.5
H_2O_2 Dosage	mg L^{-1}	555	1110	1665	2220
Initial pH	-	2	3	4	7

2.4. Kinetic Modelling and Data Analysis

The speed of chemical reactions is conventionally measured through kinetic models, which outline the relationship between the concentration of reactants and the rate of reaction (Qiu *et al.* 2015). In this research, the kinetics of the Fenton and photo-Fenton processes were measured through a number of kinetic models such as the zero-order, first-order, second-order and pseudo-first-order models under the best experimental conditions. These models were:

a) Zero-order kinetics

$[C] - [C_o] = -kt$, where [C] is the concentration of the contaminant at time t, $[C_o]$ is the initial concentration and k is the rate constant.

b) First-order kinetics

$\log_e[C] - \log_e[C]_o = -kt$, where k is the rate constant for first-order reaction.

c) Second-order kinetics

$1/[C]-1/[C_o] = kt$, where k is the rate constant for second-order reaction.

d) Pseudo-first-order kinetics

$\ln (C_o/C) = kt$, where k is the rate constant for pseudo-first-order reaction.

The experimental data were linearized via these equations in order to calculate the rate constants. The linear regression technique was utilized to estimate the rate constants (k) and identify the goodness of fit for the individual models. The coefficient of determination (R^2) was employed in measuring the best-fitting model of the data. The reaction rate constants were derived from the slope of the corresponding linearized plots.

2.5. Statistical Analysis

Analysis of Variance (ANOVA) was utilized to determine the factors' significance such as Fe^{2+} dosage, H_2O_2 dosage and initial pH towards the removal efficiency of COD in DWW. ANOVA was also utilized to determine the interactions among the factors and how they influence the treatment performance. Data analysis was carried out using Minitab version 22.1 software.

3. Results and Discussion

3.1. Results

3.1.1. Fe^{2+} Dosage Optimization

Effect of Fe^{2+} concentration on COD elimination was prominent for both the Fenton and photo-Fenton systems with a very distinct correlation between the concentration of Fe^{2+} and elimination efficiency. In the Fenton process as indicated in **Figure 2a**, at 0.5 g L^{-1} Fe^{2+}, COD elimination was 15.8%. Upon increasing the concentration of Fe^{2+} to 0.75 g L^{-1}, elimination efficiency of COD notably enhanced to 24.3%. But at 1.25 g L^{-1} Fe^{2+}, COD removal further rose to 25.7%. When the concentration was increased to 1.5 g L^{-1}, the efficiency fell to 17%. This implies that Fe^{2+} which is crucial for catalysis of H_2O_2 to OH• causes the precipitation of iron hydroxides [$Fe(OH)_2$ and $Fe(OH)_3$] in excess and thereby decreases the availability of Fe^{2+} to catalyze, lowering the formation of OH• and oxidation capacity (Ahile *et al.* 2020; De Luca *et al.* 2014; Wahyuni *et al.* 2024).

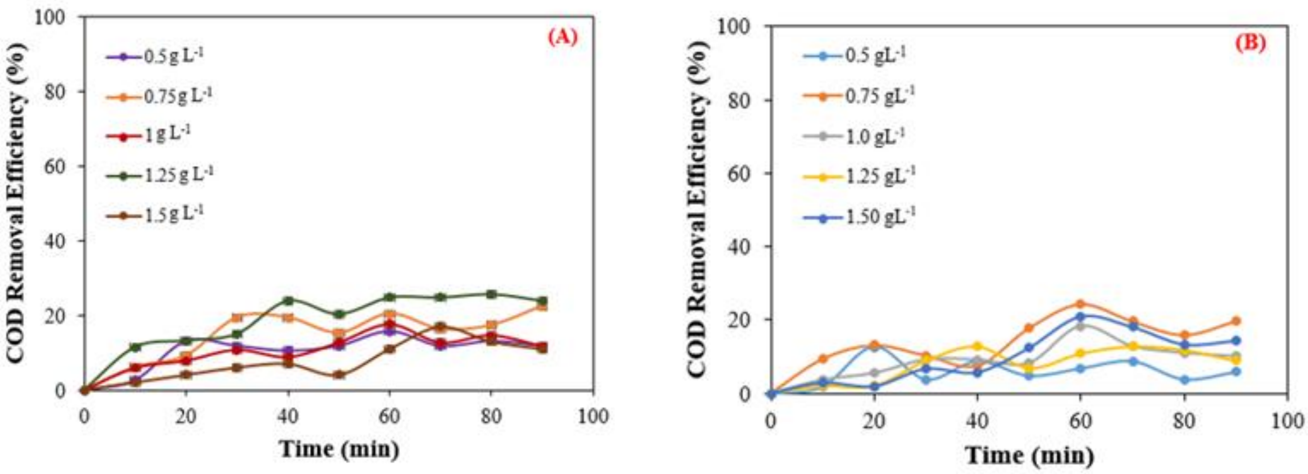


Figure 2. Effect of Fe^{2+} dosage on COD removal efficiency in the (a)Fenton and (b) photo-Fenton processes

For the photo-Fenton process also the same trend was followed as is evident from **Figure 2b**. Increasing the concentration of Fe^{2+} from 0.5 g L^{-1} to 0.75 g L^{-1} increased the COD removal efficiency from 12.6% to 24.3%. But after that there was a decrease in COD removal efficiency since the concentration of Fe^{2+} had gone beyond 0.75 g L^{-1}. At higher concentrations excess Fe^{2+} ions are scavengers for the formed OH• radicals lowering the efficiency of photo-oxidation (Buitrago *et al.* 2020; Ebrahiem *et al.* 2017a). The iron hydroxide precipitation also causes light scattering further inhibiting the photo-oxidation process (O'Dowd & Pillai 2020; Saldaña-Flores *et al.* 2021). These results are in accordance with earlier studies which showed that high Fe^{2+} concentrations may decline the process efficiency (Ting *et al.* 2009; Ribeiro *et al.* 2020; Calik and Cifci 2022; Gamarra-Giiere *et al.* 2022; Wang *et al.* 2023; Wahyuni *et al.* 2019; Wahyuni *et al.* 2021).

3.1.2. H_2O_2 Dosage Optimization

In the Fenton and photo-Fenton processes, H_2O_2 concentration was a key parameter affecting COD removal efficiency. In the Fenton process, with increasing H_2O_2 concentration COD removal efficiency increased with the highest efficiency (34.3%) at 1110 mg L^{-1} H_2O_2 as indicated in **Figure 3a**. But when the concentration of H_2O_2 was raised above this level (to 2220 mg L^{-1}) COD removal efficiency decreased to 28.8%. This reduction is due to the creation of perhydroxy radicals (HO_2•) at elevated H_2O_2 concentrations which are less reactive than OH• and compete with the oxidation of organic contaminants thereby decreasing the overall efficiency of the process (babuponnusami and muthu kumar 2014; Khataee *et al.* 2019; Riberiro and Nunes 2021; Sayin *et al.* 2022; Wang *et al.* 2023). In the photo-Fenton process as depicted in **Figure 3b**, an increase in the concentration of H_2O_2 also increased the rate of photo-oxidation. The peak efficiency was 24.3% at 1110 mg L^{-1}. When the concentration of H_2O_2 was above 1110 mg L^{-1}, a COD removal efficiency decrease was observed. This might be due to the fact that surplus H_2O_2 scavenges OH• radicals generating peroxy radicals (•OOH) which further limit the availability of OH• for oxidation (Ahile *et al.* 2020; O'Dowd & Pillai 2020; Wahyuni *et al.* 2024). The results point toward the need to sustain an optimal level of H_2O_2 concentration for both reactions.

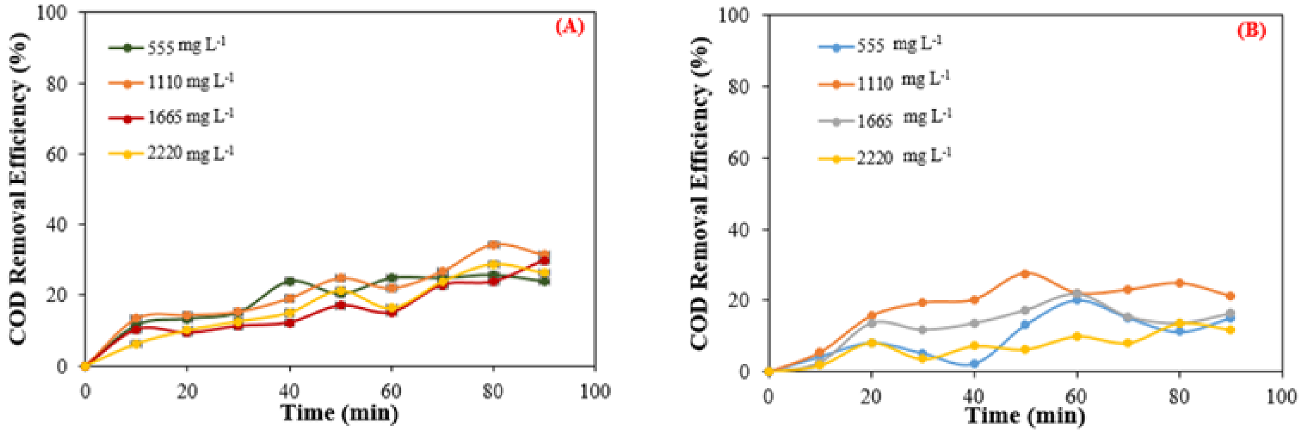


Figure 3. Effect of H_2O_2 dosage on COD removal efficiency in the (a) Fenton and (b) photo-Fenton processes

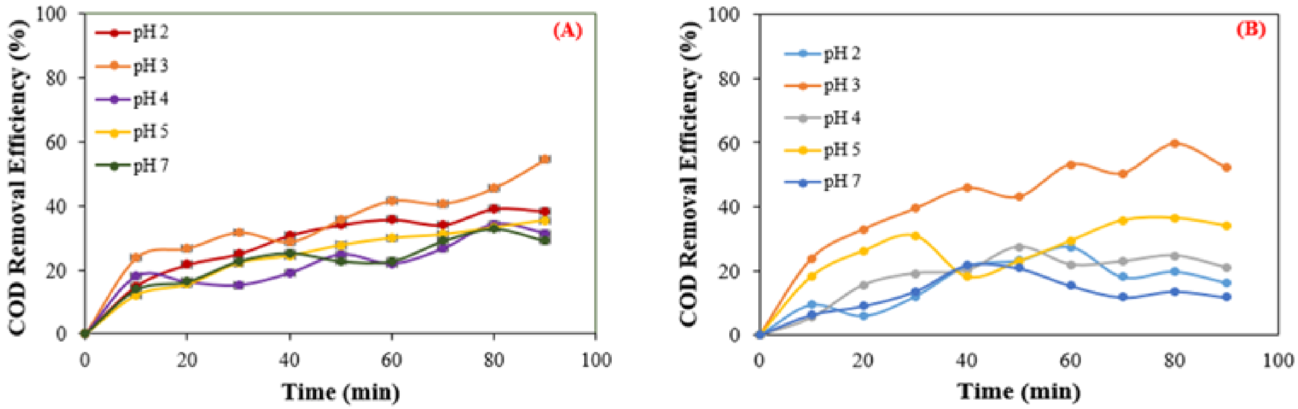


Figure 4. Effect of pH on COD removal efficiency in the (a) Fenton and (b) photo-Fenton processes

3.1.3. pH Optimization

The reaction medium pH was a determining factor affecting the Fenton and photo-Fenton processes as evident from **Figure 4a**. The maximum COD removal efficiency (54.5%) was at pH 3 for the Fenton process. For pH 2, the COD removal was 39.2% while for higher pH levels of 4 and 5 COD removal reduced to 34.3% and 25.7%, respectively. This means that acidic environments favor the Fenton process since pH 2 to 3 increases the solubility of Fe^{2+} ions making them available for the production of OH• (Bokare and Choi 2014). Increasing the pH below 2 reduces the solubility of Fe^{2+} and begins to precipitate the iron hydroxides thus decreasing the available Fe^{2+} for the reaction and inhibiting OH• formation (Umar *et al.* 2010). Likewise, during the photo-Fenton process as indicated by **Figure 4b**, COD removal efficiency was raised from 27.5% to 59.6% upon decreasing the pH from 4 to 3. But decreasing the pH further to 2 reduced the COD removal efficiency to 23.3%. The reduction at extremely low pH levels is because the excess hydrogen (H^+) ions combine with OH• weakening the radicals' oxidation capability. At elevated pH, the solubility of Fe^{2+} reduces and precipitates iron hydroxides and reduces available Fe^{2+} for the catalytic process (Sreeha and Sosamony 2016; Dbira *et al.* 2019; Li *et al.* 2021; Machado *et al.* 2023; Cavalheri *et al.* 2023). Therefore for both the Fenton and Photo-Fenton processes optimum conditions for maximal COD removal exist under acidic pH 2 to 3.

3.1.4. Kinetics of the Fenton Reaction

The kinetic models for the removal of COD in DWW were tested and the results are shown in **Table 2**. The model's regression coefficients (R^2) showed that the pseudo-first-order model was the best fit for the Fenton process with a high R^2 value of 0.898. This indicates that the COD removal rate in the Fenton process is largely dependent on the concentration of the organic pollutants which is typical of a pseudo-first-order reaction. The photo-Fenton process on the other hand had the highest fit with the second-order kinetic model which had a better R^2 value of

0.931. This disparity in the optimal kinetic models between the photo-Fenton and Fenton processes indicates that UV light is involved in changing the reaction mechanism increasing the rate of degradation through the reduction of Fe^{3+} to Fe^{2+} and then further increasing the production of OH• (Wahyuni *et al.* 2019, 2021, 2024). The two rate constants (k) for the two processes were determined as follows: in the Fenton process, k according to the pseudo-first-order model was 0.0067 min^{-1} and for the photo-Fenton process, k using the second-order model was found to be $1E^{-06}$ min^{-1}. Its higher rate constant corresponds to its increased reaction rate versus the traditional Fenton process and indicates the further catalytic impact of UV irradiation in raising the reaction speed (Eddy *et al.* 2023; Vorontsov 2019; Wu *et al.* 2024).

Table 2. Kinetic model equation and fit for Fenton and photo-Fenton processes

S. No.	Kinetic model	Process	Equation	R^2
1	Zero order kinetics	F	y = -0.0054 x + 0.8925	0.769
		PF	y = -0.0075 x + 0.8855	0.845
2	First order kinetics	F	y = 0.0031 x + 0.0494	0.820
		PF	y = 0.0048 x + 0.05	0.902
3	Second order kinetics	F	y = $1E^{-06}$ x + 0.0002	0.858
		PF	y = $1E^{-06}$ x + 0.0002	**0.931**
4	Pseudo first order kinetics	F	y = 0.0067 x + 0.118	**0.898**
		PF	y = 0.011 x + 0.1152	0.902

F – Fenton process; PF – Photo-Fenton Process

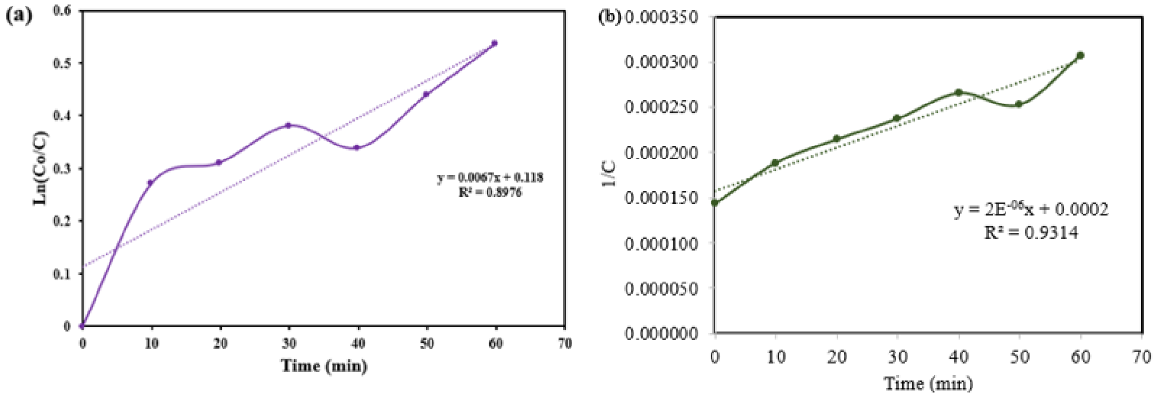


Figure 5. Kinetic Model on COD Removal Efficiency (a) Fenton process (Pseudo-First order model) and (b) photo-Fenton process (Second order model)

Kinetic analysis therefore validated that the Fenton and photo-Fenton processes show different kinetic behaviours with the Fenton process showing pseudo-first-order kinetics while the photo-Fenton process showing closer adherence to second-order kinetics. The enhanced reaction rate in the photo-Fenton process highlights the positive function of UV light in speeding up pollutant degradation, thus it is a more efficient process for DWW treatment (Brillas and Sengura 2020). These findings are in agreement with the findings reported in earlier research by Hasani *et al.* (2020) and Babuponnusami and Muthukumar (2022) validating the strong potential of these treatments for efficient wastewater treatment.

3.1.5. ANOVA Analysis

The ANOVA findings reported in **Table 3** show that Fe^{2+} dosage, H_2O_2 dosage and pH significantly influence COD removal efficiency under both the Fenton and photo-Fenton processes as reflected by p-values of less than 0.05. This emphasizes the need for the regulation of these factors for effective performance. Fe^{2+} dosage specifically contributed the most to COD removal efficiency with p-values of 0.008 in the Fenton process and 0.002 in the photo-Fenton process. These findings show the crucial role of Fe^{2+} during the oxidation process since it produces OH• responsible for degrading organic pollutants. The regression equations for the Fenton and photo-Fenton processes COD removal efficiency are represented by Eq. (1) and (2), respectively as follows:

Fenton process

COD removal Efficiency = 22.8 + 21.2 Fe^{2+} + 2.00 H_2O_2 - 4.56 pH

Photo-Fenton process

COD removal Efficiency = 8.85 + 5.28 Fe^{2+} + 0.01670 H_2O_2 - 1.00 pH (2)

For the Fenton process, the regression equation (Eq. 1) indicates that an increase of 1 unit in Fe^{2+} concentration results in a significant 21.2% increase in COD removal efficiency. Likewise, in the photo-Fenton process, Fe^{2+} dosage was equally effective with the regression equation (Eq. 2) indicating a 5.28% increase in COD removal efficiency for every unit increase in Fe^{2+} concentration. The dose of H_2O_2 was also found to be statistically significant with p-values of 0.018 and 0.042 for the Fenton process and photo-Fenton process, respectively. The regression equation for the Fenton process (Eq. 1) shows that an increase of 1 unit in H_2O_2 causes a 2% increase in COD removal efficiency. In photo-Fenton, the influence of H_2O_2 is relatively more pronounced as the regression equation (Eq. 2) indicates an increase of 1.67% in COD removal efficiency for every unit increase in H_2O_2. This indicates that H_2O_2 concentration is a significant factor specifically in the photo-Fenton process, wherein it co-operates with UV radiation to increase the formation of OH•.

Table 3. ANOVA results for Fenton and photo-Fenton processes

Source	DF		Adj. SS		Adj. MS		F-value		p-Value	
	F	PF	F	PF	F	PF	F	PF	F	PF
Model	3	3	289.13	394.91	96.38	131.64	0.76	52.77	0.087	0.004
Linear	3	3	289.13	394.91	96.38	131.64	0.76	52.77	0.087	0.004
Fe^{2+} dosage	1	1	66.35	230.45	66.35	230.45	0.52	92.38	0.008*	0.002*
H_2O_2 dosage	1	1	8.00	29.01	8.00	29.01	0.06	11.63	0.018*	0.042*
pH	1	1	110.72	16.58	110.72	16.58	0.87	6.65	0.049*	0.082
Error	3	3	381.10	7.483	127.03	2.49				
Total	6	6	670.23	402.40						

**Significant; SS – Sum of squares; MM – Mean Square; F – Fenton process; PF – Photo-Fenton*

The pH factor was also important in the Fenton process where p = 0.049. The regression equation (Eq. 1) indicates that a 1-unit drop in pH results in a decrease of 4.56% in COD removal efficiency which confirms that acidic conditions are best for the Fenton process. But in the photo-Fenton process the influence of pH was not statistically significant (p-value = 0.082) though there was a weak negative trend. The photo-Fenton process regression equation (Eq. 2) shows that for every 1-unit drop in pH, COD removal efficiency drops by 1% which implies that the photo-Fenton process is less sensitive to changes in pH compared to the Fenton process. The predictive accuracy of the models was evaluated using the R^2 values which are presented in **Table 3**. The Fenton process model has a predicted R^2 of 63.91% indicating that the model accounts for a moderate percentage of variation in COD removal efficiency. This implies that the model is fairly accurate for the experimental conditions but may be improved with further optimization. Conversely, the photo-Fenton process model with a higher predicted R^2 of 76.79% indicates that this process can react more uniformly to the factors tested and might provide improved performance upon optimization.

3.2. Discussion

The optimization runs gave pertinent information regarding the effect of Fe^{2+} dosage, H_2O_2 concentration, pH and reaction kinetics on Fenton and photo-Fenton process efficiency for the treatment of DWW. All these parameters are important to the treatment process and their interactions need to be well controlled in order to get the best out of it. These results agree with the literature (Salazar *et al.* 2012; Lee *et al.* 2014; Garcia-Sengura *et al.* 2016) which emphasizes the significance of these parameters in making Fenton-based processes more efficient. Fe^{2+} concentration had a very significant effect on COD removal efficiency consistent with previous research (Brink *et al.* 2017; Rebeiro *et al.* 2022). Firstly, Fe^{2+} dosage increases enhanced COD removal by facilitating the formation of OH• which are highly active and play key roles in the oxidation of organic contaminants (Ribeiro *et al.* 2020; Wang *et al.* 2016). But beyond 1.25 g L^{-1} of Fe^{2+}, an excess of Fe^{2+} formed iron hydroxides which are precipitated from the solution and hence reduce the concentration of Fe^{2+} available for catalysis and the formation of OH•. This effect documented well in the literature (Gunes *et al.* 2019; Li *et al.* 2021; Machado *et al.* 2023) restricts the efficiency of the Fenton reaction and emphasizes the maintenance of a proper Fe^{2+} concentration to prevent undesired precipitation but provide ample Fe^{2+} for the reaction.

In the same fashion, optimization of H_2O_2 concentration displayed trends as experienced in previous literature. The initial increase in concentration of H_2O_2 boosted COD removal efficiency but thereafter efficiency decreased upon increased concentration levels. This deterioration can be due to competition of OH• with HO_2• radicals a less reactive ion that inhibits the oxidation reaction (babuponnusami and muthu kumar 2014; Riberiro and Nunes 2021). This effect has been reported in earlier research which points out that surplus H_2O_2 is also capable of scavenging OH• radicals during the photo-Fenton process making them less available for oxidation. These results are in line with current literature, highlight the importance of precise control of H_2O_2 concentration to prevent the generation of competing radicals and ensure optimal oxidation efficiency (Ahmadzadeh and Dolatabadi 2018; Hasani *et al.* 2020; Zhang *et al.* 2019). The pH role in the Fenton and photo-Fenton processes was also in line with previous studies (Liu *et al.* 2020). Acidic pH levels (pH 2-3) were optimal because they preserve the solubility of Fe^{2+} which is required to produce OH• radicals. Increasing pH values result in decreasing Fe^{2+} solubility which causes iron hydroxide precipitation, thus reducing the availability of Fe^{2+} and compromising the efficiency of the reaction. This conclusion is supported by earlier research (Al-Raad and Hanafiah 2021; Bokare and Choi 2014) that highlights the necessity of acidic pH in ensuring optimal Fenton reaction. Nevertheless, photo-Fenton process was also efficient at low pH levels, efficiency reduced drastically at very low pH (pH 2) possibly because of excessive H^+ ion interference with OH• radicals (Umar *et al.* 2010). Such a finding is further in accordance with literature evidence against the side effects of high acidity on OH• production (Zhou *et al.* 2019; Liu *et al.* 2020).

Kinetic analysis showed that both Fenton and photo-Fenton processes obeyed pseudo-first-order kinetics with photo-Fenton process having a greater reaction rate constant. This result is consistent with previous research that documents increased degradation rates in the photo-Fenton process due to the regeneration of Fe^{2+} from Fe^{3+} under UV irradiation which increases OH• radical formation (Ahile *et al.* 2020; De Luca *et al.* 2014; popova *et al.* 2021; Wahyuni *et al.* 2024). The enhanced rate of reaction in the photo-Fenton process also reinforces the literature indicating that UV light can be very effective in improving the efficiency of the Fenton process especially in the treatment of wastewater containing high levels of organic pollutants or compounds that are recalcitrant to degradation under normal conditions (Ahile *et al.* 2020; De Luca *et al.* 2014; Verma *et al.* 2015; Wahyuni *et al.*,2019). The ANOVA test verified that Fe^{2+} dose, H_2O_2 concentration and pH are statistically significant parameters influencing the COD removal efficiency and that pH was the most significant parameter. This is in agreement with previous research which often highlights the key role of pH in the Fenton and photo-Fenton processes (Calus–Makowska *et al.* 2025; Guo *et al.* 2021; Wahyuni *et al.* 2024). Nevertheless, the comparatively low estimated R^2 indicates that the model might not yet capture all the intricacies of the system, which has also been reported in comparable studies wherein other variables like temperature and reaction time were found to have an impact on treatment efficacy (Behrouzeh *et al.* 2022; Calus–Makowska *et al.* 2025; Guo *et al.* 2021; Wahyuni *et al.* 2024).

4. Conclusion

Maximizing the efficiency of Fenton and photo-Fenton processes for the treatment of DWW is dependent on the optimization of crucial parameters like Fe^{2+} dosage, concentration of H_2O_2 and pH. The photo-Fenton process with an enhanced catalytic effect of UV light proved more efficient compared to the traditional Fenton process as reported by earlier studies and in line with the benefits of UV integration. Fenton's optimum condition was established to be Fe^{2+} of 1.25 g L^{-1}, H_2O_2 of 1110 mg L^{-1} and pH of 3 for the greatest amount of OH• formation and minimizing the risk of precipitation of hydroxide from iron and attained the maximum COD removal efficiency of 54.5 %. Photo-Fenton reaction by enhancement of kinetics under UV radiation was specifically advantageous in dealing with highly contaminated wastewaters. The optimal conditions for the photo Fenton process were determined to be a concentration of Fe^{2+} at 0.75 g L^{-1}, H_2O_2 at 1110 mg L^{-1}, and a pH level of 3, which collectively achieved the highest observed COD removal efficiency of 59.6 %. These results provide useful lessons for wastewater treatment in industries such as distilleries producing high amounts of organic pollutants and indicating potential to scale up and optimize these reactions for cost-saving sustainable processes. Future work might investigate integration of photo-Fenton with other advanced oxidation processes, different catalysts and UV sources to increase efficiency further, lower operational costs and enhance sustainability. Studies on catalyst regeneration and byproduct recycling can also minimize environmental effects and decrease treatment costs in industrial-scale applications.

Conflict of Interest

The authors have no conflicts of interest to disclose

Funding

No funding was received.

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