Evaluating a solar photo-Fenton method in COD/organic matter removal from sewage wastewater.

Dheeaa al deen Atallah Aljuboury*[1], Fatehah Mohd Omar [2]

[1]Department of Civil Engineering, College of Engineering, AL Noor University, Mosul, Iraq.

[2]School of Civil Engineering, Universiti Sains Malaysia, Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

*Corresponding author at: Department of Civil Engineering, College of Engineering, AL Noor University, Iraq. dr.dheeaa@yahoo.com

ABSTRACT

Aquatic organisms and human health face threats from hazardous pollutants that enter the aquatic environment via wastewater. The characteristics of wastewater differ from location to location, depending on the sources of pollution. This study aimed to analyse organic matter in wastewater samples from the engineering campus of Universiti Sains Malaysia (USM) by employing a solar photo-Fenton method within a central composite design (CCD) framework that utilizes response surface methodology (RSM). In a 60-day study, the independent variables (factors) were the initial concentration of organic matter, hydrogen peroxide dosage, ferrous ion dosage, pH, and reaction time, while the dependent variable (response) was the removal of chemical oxygen demand (COD). The findings indicated that the ideal conditions for the removal of organic matter included a hydrogen peroxide dosage of 100 mg/L, a ferrous ion dosage of 10 mg/L, a pH level of 4, and a reaction time of 120 minutes. The quadratic models derived from the central composite design (CCD) using response surface methodology (RSM) demonstrated statistical significance. This is evidenced by a coefficient of determination ($R^2 = 0.9093$) and a probability value ($P < 0.0001$), both indicating significant results for the chemical oxygen demand (COD) removal model. An experimental design for a wastewater treatment plant employing the solar photo-Fenton process was investigated to attain optimal efficiency. The plant was engineered to meet the requirements set forth by the Malaysian Environmental Quality Regulations (Wastewater) 2009, Standard B. The results were positive and may inform the design of future treatment units using this method. The experiment demonstrated that the solar photo-Fenton process is a practical and effective method for removing pollutants.

Keywords: Solar Photo-Fenton; sewage wastewater; organic matters removal; Chemical oxygen demand (COD); a central composite design (CCD) with response surface methodology (RSM).

Introduction

Wastewater discharge into the environment is an escalating issue, significantly impacting public health and ecological balance due to pollution from complex organic compounds and petroleum hydrocarbons. Various sources contribute to this pollution, including industrial and municipal wastewater and natural seepage from oil wells. The prevalence of pharmaceuticals, often inadequately treated, leads to their presence in water bodies, raising health and environmental concerns. Studies in Malaysia have shown the contamination of oceans, rivers, and groundwater with heavy metals and carcinogens. The coastal waters of Malaysia are polluted by petroleum hydrocarbons from wastewater, oil spills, and offshore drilling, which increases the environmental risks from complex organic compounds that are hard to treat [67, 68, 69, 70].

Numerous techniques are employed to remove chemical and pharmaceutical compounds from wastewater, but challenges remain due to the inefficacy of traditional municipal treatment processes in eliminating complex organic compounds at low concentrations [1, 2, 3, 54]. Despite the potential of solar energy, its utilisation in tropical areas is limited, and effective solutions for increasing pollutant levels are lacking. Advanced studies are essential to improve wastewater treatment, particularly through optimising operating conditions and developing innovative technologies for complete pollutant removal. Physical treatments such as ultrafiltration, nanofiltration, and reverse osmosis are popular due to their effectiveness and environmental benefits, but membrane pore size selection is critical to ensure efficiency. While reverse osmosis is capable of removing persistent organic pollutants (POPs), it can be complex and costly [67, 68, 69, 70]. Advanced oxidation techniques like photo-Fenton methods show promise for enhancing the removal of these complex organic pollutants and reducing chemical oxygen demand concentrations in wastewater [52, 54].

To tackle the challenge of treating municipal wastewater, there is an increasing focus on sustainable methods that can effectively remove complex organic compounds. Conventional treatment processes often inadequately address resistant chemicals, thus highlighting advanced oxidation processes (AOPs) like the solar photo-Fenton process, which have been extensively researched. AOPs, including the solar photo-Fenton process, generate hydroxyl radicals (OH•) that are highly effective in breaking down various pollutants [1, 2, 10]. These methods not only remove organic compounds but also offer disinfection capabilities. The solar photo-Fenton process, utilising hydrogen peroxide (H_2O_2), iron (Fe^{2+}) and solar energy, proves efficient in tropical climates such as Malaysia's, where solar availability is consistent. While effective in mineralising pollutants into biodegradable compounds, challenges remain, including high costs, the need for multiple chemicals, and potential inefficiencies due to the presence of bicarbonate ions. Continued research is necessary to optimise these processes and evaluate their environmental impacts. In industrial wastewater, the Fenton process was difficult to study because intermediate composites are complex and the reaction speed is high at the beginning in this reaction.

[5, 28]. The mechanism of the Fenton process has three major steps (Equations (1-4)) [22, 51, 52].

I. Creation of hydroxyl radicals (OH•) as shown in Equation (1)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \quad (1)$$

II. Creation of ferrous ions (Fe^{2+}) under solar energy as shown in Equations (2-4).

$$[Fe(OH)]^{+2} \xrightarrow{hv} Fe^{2+} + OH\bullet \quad (2)$$

$$[Fe(COOCR)]^{+2} \xrightarrow{hv} Fe^{2+} + CO_2 + OH\bullet \quad (3)$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + H^+ + OH\bullet \quad (4)$$

Creation of ferrous ions (Fe^{2+}) without solar energy as shown in Equations (5)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OH_2 + H^+ \quad (5)$$

III. Hydroxyl radical (OH•) interaction with organic pollutants (organic matter (OM) removal) as shown in Equation (6):

$$OM + OH\bullet \rightarrow H_2O + CO_2 \quad (6)$$

Cavalheri et al. [4] demonstrated that the solar photo-Fenton process effectively degraded ketoprofen, achieving a removal rate of 95% at pH 6, and improving parameters like COD, BOD_5, and turbidity. Anjali and Shanthakumar [5] reported a maximum degradation of 99% of pollutants from wastewater in just 10 minutes under optimal conditions (15 W UV light, 3 mM H_2O_2, 0.04 mM Fe^{2+}, and 5 mg/L mixed pollutants). Araújo et al. [1] found an 86.8% reduction in COD using H_2O_2 and Fe^{2+} in Fenton wastewater treatment. Yuan et al. [3] highlighted the Fenton process's efficiency in dewatering municipal sewage sludge while removing heavy metals, with rates of 92.3% for Cd, 56.8% for Pb, 88.3% for Cu, and 84.9% for Zn. Ren G et al. [6] indicated that electro-Fenton (EF) is a cost-effective solution for sewage wastewater treatment, achieving complete removal of suspended solids and 90.8% of NH_3-N, facilitating simultaneous treatment without extra processes.

Previous research indicates a significant underutilization of solar-powered applications in tropical climates, despite the abundant availability of solar energy. Additionally, challenges persist in managing the increasing levels of pollutants in wastewater, with a continued lack of effective solutions. Enhancing operational conditions is essential for improving pollutant removal in water treatment systems [35, 36].

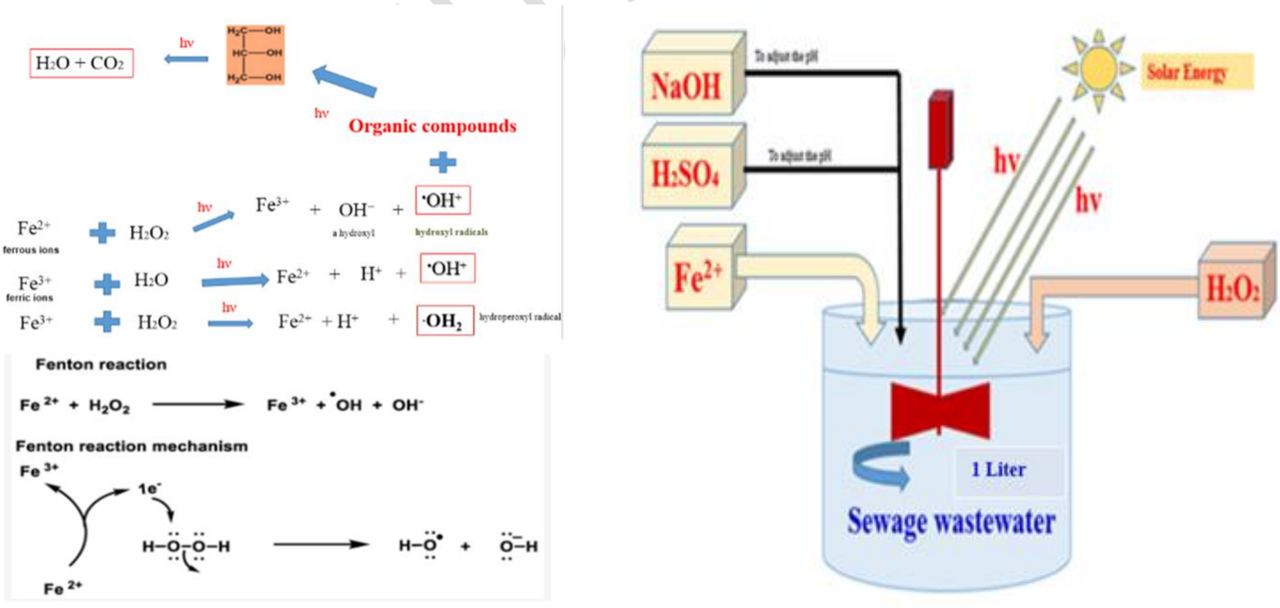
Response surface methodology (RSM) offers a more practical approach to optimisation than traditional methods that examine one factor at a time. By evaluating and optimizing the interaction effects of independent parameters, RSM plays a crucial role in process optimisation and design. Nonetheless, research on central composite design and the application of RSM for optimizing the chemical degradation of organic compounds, as well as for reducing COD concentrations using solar photo-Fenton, remains limited [3, 52, 53].

This research addresses wastewater pollution at the Universiti Sains Malaysia's engineering campus. The study investigates the solar photo-Fenton process, an advanced oxidation technology, for treating significant organic pollutants. Objectives include evaluating the efficiency of the solar photo-Fenton process in reducing pollutant concentrations, comparing the solar photo-Fenton process with the conventional method in chemical oxygen demand (COD) removal, identifying optimal operational conditions, and aligning findings with previous studies. This research aims to enhance sustainable wastewater treatment solutions and mitigate associated environmental and health risks.

Processes and materials

The sewage samples (1 liter for each sample) are to measure the COD value, which is a targeted pollutant in the present study. Ferrous sulfate ($FeSO_4$) and Hydrogen peroxide (H_2O_2) (35% (v/v)) are supplied from EMPROVE Exp. Sulfuric acid (H_2SO_4) (95-97%) and sodium hydroxide (NaOH) (50%) are used to adjust the pH to the desired values. COD values using a COD photometer. COD reactor (block digester) to heat COD vial for 2 hours at 150°C. Residual iron was measured in sewage by using an atomic absorption spectrometer.

In the experiments, sewage samples were filtered using medium speed, ashless filter papers (202, 125 mm diameter) to eliminate solid and suspended materials, as well as precipitated iron species. A digital pH meter was used to measure pH levels, and a glass precision beaker (1 L) was employed for stirring to maintain homogeneity. Hydrogen peroxide (H_2O_2) and ferrous sulphate ($FeSO_4$) were added to the samples during the process. as shown in Figure 1.



(a) (b)

Figure 1. (a) Fenton and photo-Fenton process mechanism (b) A set-up of the photo-Fenton process to remove organic matter from sewage wastewater.

In this research, both classical and statistical design approaches were employed to assess the solar photo-Fenton process for treating sewage wastewater. The classical approach involved conducting approximately 100 experiments to evaluate the process's effectiveness and analyse the impact of key operating parameters. Similarly, the statistical design employed a central composite design (CCD) and response surface methodology (RSM) to perform around 50 experiments aimed at determining COD removal efficiency under optimal operating conditions.

Experiments were conducted to determine the optimal pH for the solar photo-Fenton process in sewage treatment, revealing that the optimal pH lies within a strongly acidic range of 2.0-7.0. Additionally, hydrogen peroxide dosages were tested between 10 and 140 mg/L while maintaining a constant ferrous sulfate concentration of 15 mg/L, particularly at pH 4 over 180 minutes, to identify the ideal hydrogen peroxide dosage. The optimal concentration for ferrous iron was also assessed, varying between 5 and 45 mg/L with the hydrogen peroxide dosage fixed at 60 mg/L under the same conditions, to effectively reduce COD levels in sewage.

Experiments utilizing the solar photo-Fenton process examined the impact of varying initial COD concentrations in sewage wastewater samples on removal efficiency over several weeks. Notable differences in initial COD concentrations were observed among samples collected weekly from wastewater ponds at the USM Engineering Campus.

Based on the dose required for the experiment, hydrogen peroxide and ferrous sulfate were weighed using an electronic scale with the Smart Super Hybrid Sensor (SHS). Based on the COD values, the degradation efficiency was calculated by using Equation (9):

$$R = (COD_0 - COD_t)/COD_0 \qquad (9)$$

Where:

R: the COD removal

COD_0: the initial COD concentration.

COD_t: the COD concentration after experiment.

The study measured Chemical Oxygen Demand (COD) in sewage wastewater samples using a COD Photometer and pH levels with a pH meter. A statistical design of 50 experiments was conducted using Design Expert software (version 6.0.7), applying a central composite design (CCD) and response surface methodology (RSM) to optimize various experimental parameters. The independent variables included pH values, hydrogen peroxide dosage, iron dosage, initial COD concentration, and reaction time, with COD removal as the dependent variable. The performance was assessed through COD removal efficiency at varying levels of each independent variable, with samples collected from effluent ponds at the Universiti Sains Malaysia (USM) Engineering Campus.

Sewage wastewater samples.

Several sewage wastewater samples were collected from ponds at the USM Engineering Campus over several weeks and stored at 4°C. The analysis, conducted by USM's Environmental Engineering Laboratory, followed standard methods. The results, summarized in Table 1, show that the samples had a neutral pH (6.5-7.5) and high chemical oxygen demand (COD) levels ranging from 300 to 950 ppm, indicating hazardous organic substance concentrations that exceed Malaysia's discharge limit of 200 ppm. The data highlights the environmental risks associated with this wastewater due to its significant organic content.

Table 1. Wastewater features at USM engineering campus, Malaysia.

No	Parameter	Units	Concentration ranges of parameters	Malaysian discharge standards
1	pH	-	6-8	6 < pH > 9
2	TDS	ppm	600-1100	< 2000
3	COD	ppm	300-950	< 200
4	D.O.	ppm	0.6-2.9	> 5
5	Iron	ppm	<0.01	2
6	Sulfite	ppm	12-15	1.0

The UV-index is calculated as follows

Solar ultraviolet radiation (UV) was measured by a global UV radiometer (model: KIPP & ZONEN, ISO 17166:1999/CIE S007/E-1998). The UV-Index is calculated as follow: The output voltage (v m^{-1}) from the UV-E radiometer transform it to W m^{-2} according to instructions of this radiometer model. The Equations (7 & 8) allows calculating the amount of UV intensity received on any surface in the same position with regard to the sun by UV-Index (UVI):

$$R(W/m^2) = 0.168\ R(v/m) \quad (7)$$

$$UVI = R\ (W/m^2) * 40\ (m^2/W) \quad (8)$$

Where:

UVI is the UV-Index.

R is the reading (R) in UV radiometer by (W/m^2) unit [62].

Experimental setup and procedure

A solar photo-Fenton process for sewage treatment was conducted in a 1 L glass precision beaker under real solar energy exposure. The process involved additive doses of hydrogen peroxide and ferrous sulfate to the raw sewage without dilution, with pH adjustments between 2 and 7. Research assessed various operational parameters like pH, initial COD concentration, and dosages of reagents on COD removal efficiency, using Central Composite Design (CCD) with Response Surface Methodology (RSM) to optimize conditions. The setup utilized a global UV radiometer to ensure high exposure levels, and the impact of process duration and chemical ratios on wastewater treatment efficacy was also evaluated.

In the reactor experiments, each trial lasted two hours under direct midday sunlight, focusing on the removal of excess hydrogen peroxide (H_2O_2) using manganese dioxide (MnO_2) [37]. Continuous agitation occurred until oxygen (O_2) release ceased. Post-reaction, the sample's pH was raised above 8 with sodium hydroxide to inhibit iron precipitation, as outlined in existing literature [63]. The protocol entailed a 30-minute continuous mixing followed by a 30-minute resting phase for effective mixer neutralization. Mixing stopped to allow iron precipitation and H_2O_2 decomposition once organic removal through the solar photo-Fenton process ceased [53]. Millipore Durapore membranes (0.22 micrometres) were utilized to filter out catalysts and iron-containing precipitates.

Analytical methods

All chemical analyses followed standard methods for water and wastewater examination (APHA, 2005), as detailed in Table 2. Dosages of hydrogen peroxide and ferrous sulfate were measured using an electronic scale. pH levels in sewage samples were determined with a digital pH meter. A stirring machine mixed samples to ensure uniformity, while filter paper was used to remove solids and suspended materials. A fume cupboard provided ventilation to protect users from hazardous fumes. Samples were incubated with a strong oxidant at 150°C for two hours in a block digester, and COD levels were measured using a COD photometer.

Table 2. Analytical methods for conventional parameter (APHA, 2005)

NO.	Parameter	Method number
1	COD	5220
3	TDS	2440
5	Fe	3500
6	pH	4500

The study measures chemical oxygen demand (COD) of sewage wastewater samples using a COD photometer. Equation (7) was used to determine COD removal:

$$\text{The COD removal} = \frac{R - [R]t}{R} \qquad (7)$$

Where:

R: the COD of the raw sample

$[R]_t$: the COD of the raw sample after the experiment.

Results and discussion

All experiments were replicated to ensure the reliability of the results, and statistical modelling was used. The average removal percentage was calculated using a central composite design (CCD) with response surface methodology (RSM). Measures of variance (mean ± standard deviation or standard error) were presented, along with many other details detailed in the statistical design methodology results.

Influence of reagent concentrations and Fenton Ratio.

The study on the solar photo-Fenton process for treating sewage wastewater highlights the significance of ferrous iron (Fe^{2+}) dosage. To identify the optimal Fe^{2+} level for Chemical Oxygen Demand (COD) removal, dosages were systematically varied from 5 to 30 mg/L, while maintaining a constant H_2O_2 dosage of 120 mg/L. The results indicated that COD degradation improved with increasing Fe^{2+} up to 10 mg/L, beyond which a decrease in degradation was observed. This suggests that 10 mg/L is the optimal iron concentration for effective treatment. Additionally, it was noted that excessive iron at higher dosages may hinder reaction rates due to the interaction of hydroxyl radicals with additional iron, as indicated by the corresponding reaction dynamics as shown in Equation (8) [9, 33].

$$OH\bullet + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad (8)$$

In addition, the solar photo-Fenton process in wastewater treatment was impeded by the rise in brown turbidity, which obstructed the absorption of sunlight needed for the process [8, 15, 26]. The Fenton process should aim for minimal amounts of Fe^{2+} ions for economic and environmental reasons [4, 27, 38]. In the study, various Fenton ratios (H_2O_2/Fe^{2+}) were evaluated, identifying an optimal ratio of 10 for maximum Chemical Oxygen Demand (COD) removal, which achieved 88% efficacy as evidenced in Table 3. Hydrogen peroxide (H_2O_2) significantly influences this oxidation process by generating hydroxyl radicals (OH•). As H_2O_2 concentration increased, it acted as a free-radical scavenger, interacting with OH• radicals. The study determined the optimal H_2O_2 dosage for sewage wastewater treatment using the solar photo-Fenton process, finding a range of 30 to 140 mg/L while keeping iron (Fe^{2+}) concentration at 10 mg/L. Under conditions of pH 4 and a reaction time of 120 minutes, varying H_2O_2 dosages were examined, revealing that dosages up to 100 mg/L improved COD removal, with efficacy decreasing beyond this point, indicating that 100 mg/L is the optimal dosage under the specified conditions. The overall oxidation capability of the solar photo-Fenton process is enhanced with higher H_2O_2

concentrations, which serve as the primary source of OH• radicals, thereby improving performance. However, the reaction rate diminishes with increased H_2O_2 due to the rapid conversion of Fe^{2+} to Fe^{3+}, which limits the reaction rate of the solar photo-Fenton process. Despite the pivotal roles of H_2O_2 and Fe^{2+} concentrations in oxidation, optimal dosages for effective sewage treatment remain ambiguous. Additionally, H_2O_2 tends to scavenge OH•, converting it into hydroperoxyl radicals (HOO•) when concentrations exceed the optimal threshold, thereby reducing oxidation potential as shown in Equation (9) [4, 8, 13, 20, 21, 22, 23].

$$H_2O_2 + OH^\bullet \rightarrow HOO^\cdot + H_2O \quad (9)$$

During autodecomposition, hydroxyl groups in H_2O_2 decompose into oxygen and water as shown in Equation (10) [8].

$$HOO^\cdot + OH^\bullet \rightarrow O_2 + H_2O \quad (10)$$

Hydroxyl radical (OH•) and hydroperoxyl radical's recombinate more often, as shown in Equations (11) [24].

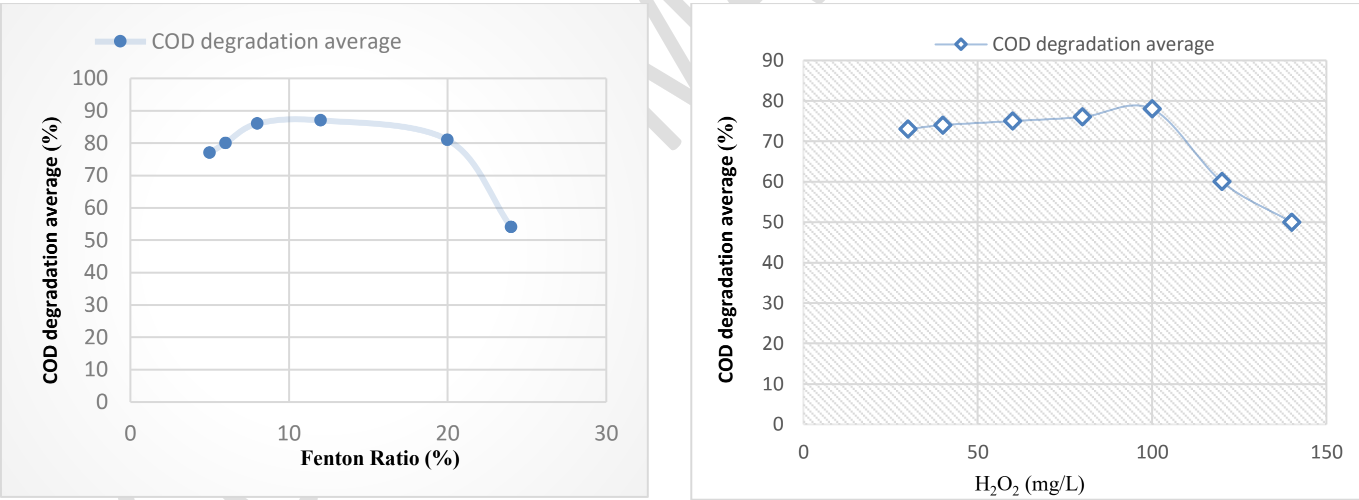
$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \quad (11)$$

In this research, a comparison of the Fenton ratio (H_2O_2/Fe^{2+}) of 10 in a solar photo-Fenton process is made against literature values. Yuan et al. [3] reported a maximum COD removal of 63.9% with a Fenton ratio of 9, while Tony et al. [9] achieved 50% COD removal using a photo-Fenton method with a ratio of 10. Dincer et al. [43] evaluated Fenton processes, noting a favorable ratio of 8.6, and Hasan et al. [64] reached 70% TOC and 98.1% COD reduction with a ratio of 5. Saber et al. [65] reported over 83% COD removal with a ratio of 2.6, and Davarnejad et al. [66] showed around 82% removal at a ratio of 2.75. Variability in the effectiveness of the Fenton ratio across studies is attributed to differences in pollutant types and concentrations, which impact the Fenton reaction and overall treatment efficiency.

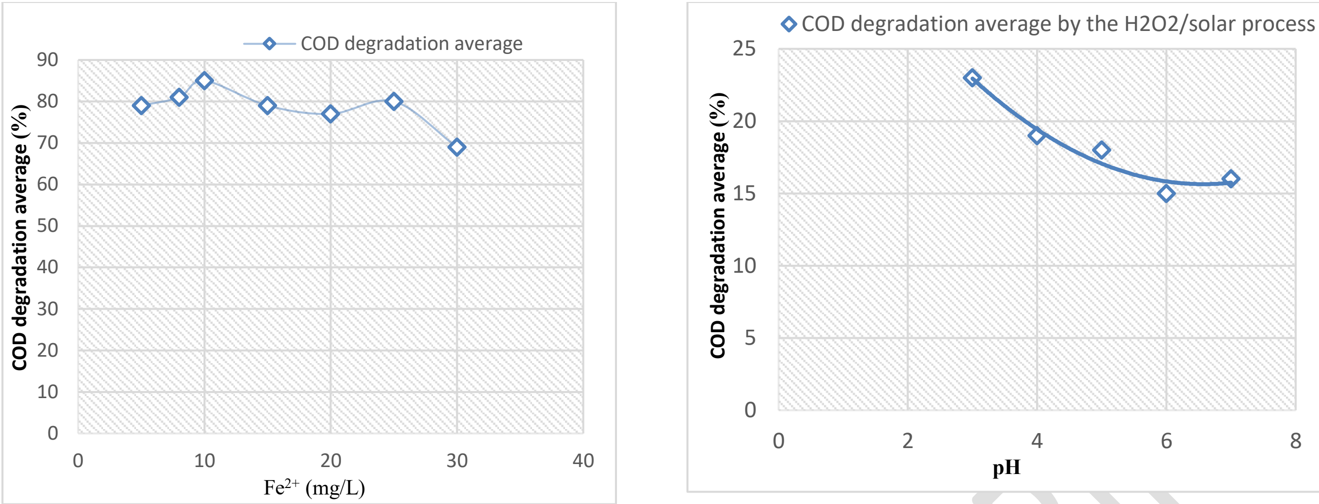
Table 3. The influence of concentrations of H_2O_2 and Fe^{2+} on COD removal by the solar photo-Fenton process.

Iron (mg/L)	$^*COD_{raw}$ (ppm)	$^*COD_t$ (ppm)	$^*COD_R$ (ppm)	Standard Deviation (SD)	Hydrogen peroxide (mg/L)	$^*COD_{raw}$ (ppm)	$^*COD_t$ (ppm)	$^*COD_R$ (ppm)	Standard Deviation (SD)
5	331	70	261	135.0937946	140	343	172	171	99.01683359
8	331	63	268	140.1297018	120	343	138	205	104.5291028
10	331	50	281	149.9010785	100	343	110	233	116.5604278
15	331	69	262	135.8025527	80	343	89	254	128.8810821
20	331	76	255	130.9210958	60	343	76	267	137.5657419
25	331	67	264	137.2309489	40	343	90	253	128.2432584
30	331	102	229	114.7272127	30	343	93	250	126.3579571

$^*COD_{raw}$: concentration of COD before treatment.
$^*COD_t$: concentration of COD after treatment.
$^*COD_R$: amount of COD removal by treatment.



(a) **(b)**

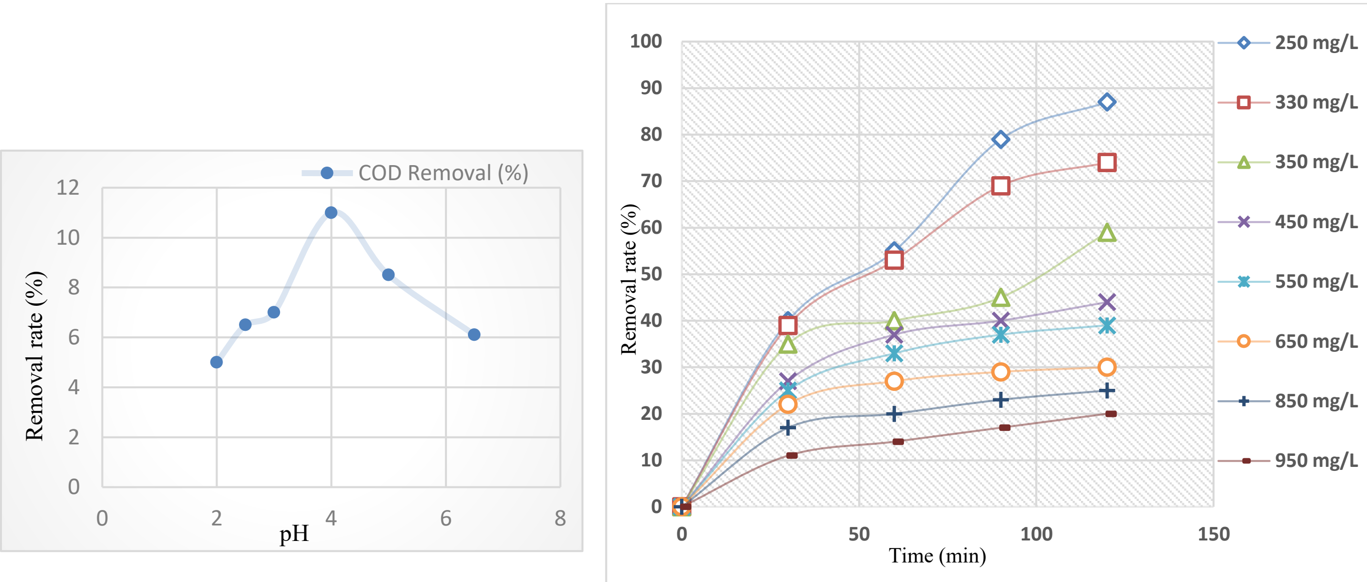


(c) **(d)**

Figure 2. (a) The Fenton ratio influence on the COD removal. **(b)** Hydrogen peroxide dosage influence. **(c)** Iron dosage influence. **(d)** The pH influence.

Effects of pH

In the context of pollutant degradation, the pH level significantly influences oxidation processes. Variations in pH can alter oxidation characteristics, ionization levels, and the activity of oxidants, critically affecting the formation of hydroxyl radicals and the rate of oxidation [5]. Specifically, Fenton's process, which relies on the decomposition of hydrogen peroxide (H_2O_2) catalyzed by ferrous ions, shows optimal performance at a pH of 4, as it enhances H_2O_2 stability and ensures the availability of dissolved ferrous ions [5]. However, as the pH increases above 4, the efficiency of chemical oxygen demand (COD) degradation declines due to reduced oxidation potential from hydroxyl radicals as shown in Figure 3a, resulting in the prevalence of less reactive iron species such as $Fe^{3+}(OH)_2$ [3, 4, 8, 28]. Moreover, the formation of ferric hydroxides and the auto-decomposition of H_2O_2 further impede free iron ion levels, particularly under alkaline conditions, leading to precipitation and diminished reaction effectiveness [5, 31, 34]. Paterlini & Nogueira [34] and Kang & Hwang [35] found that the Fenton reaction is less effective when pH is above 4, with optimal conditions for the photo-Fenton process suggested at pH 2.5-4. Additionally, studies have shown that heavy metal removal through Fenton's approach is best under acidic conditions (1-3), where degradation rates decline rapidly when pH exceeds 3 [28, 32, 33, 49].



(a) (b)

Figure 3. (a) Effects of pH on COD removal. (b) Influence of COD amount in wastewater on COD removal by the solar photo-Fenton process (Conditions: pH: 4, Fe^{2+}: 10 mg/L, H_2O_2: 100 mg/L).

Influence of COD Concentration

Experiments were conducted to assess the impact of varying chemical oxygen demand (COD) levels in sewage samples over a period of 120 minutes, utilizing optimal conditions of 100 mg/L hydrogen peroxide and 10 mg/L Fe^{2+} at pH 4 as shown in Figure 3b. Results indicated that COD removal rates exhibited an inverse correlation with COD levels; specifically, an 87% removal efficiency was achieved at the lowest concentration of 250 mg/L COD. The study highlighted that higher levels of contamination resulted in a reduced formation of reactive oxygen species (ROS) due to the competition between primary and intermediate reactants for available ROS, which affects the overall performance of the Fenton process [5, 50]. The role of hydrogen peroxide, although crucial as a reactive intermediate, also limits further ROS production due to its consumption in competing reactions, thus diminishing the efficiency of pollutant degradation as intermediates can outpace primary reactants in utilizing oxidizing agents. This highlights the kinetics involved in the Fenton reaction, illustrating the need for balance in managing both primary and intermediate reactants to enhance degradation efficiency [5, 50, 53].

Effects of reaction time

The Fenton process for sewage wastewater treatment demonstrated an increased COD degradation rate with prolonged reaction time, stabilizing after approximately 120 minutes as shown in Figure 3b. Hydroxyl radical production peaked at this point, then stabilized due to H_2O_2 depletion. The presence of difficult organic contaminants and high molecular weight compounds in sewage prolongs the photo-Fenton process [8, 9, 22, 37, 41]. The stabilization after 120 minutes indicates a significant consumption of hydroxyl radicals (OH•) and Fenton reagent, leading to reduced efficiency in the process thereafter.

Results of statistical design approach for solar photo-Fenton processes:

ANOVA results and adequacy of the quadratic model for solar photo-Fenton processes.

The study explores the solar photo-Fenton process for degrading Chemical Oxygen Demand (COD) in sewage wastewater, focusing on five independent variables: pH, H_2O_2 dosage, Fe^{2+} dosage, initial COD concentration, and reaction time. Variable levels were chosen based on preliminary experiments and existing literature. The model's adequacy was evaluated under optimal conditions utilizing Central Composite Design (CCD) and Response Surface Methodology (RSM) for experimental design and data analysis. The face-centered CCD approach varied each variable across three levels (-1, 0, and +1), detailed in Table 4. The main objectives were to identify optimal operating conditions, compare results with previous studies, and assess the effectiveness of CCD and RSM in employing the solar photo-Fenton process for COD degradation, alongside examining the statistical relationships between operating variables and COD removal efficiencies. Performance was evaluated using COD removal efficiency analysis, with Tables 5 and 6 displaying ANOVA results and regression coefficients for second-order polynomial models describing COD removal. The results indicated significant interactions between responses and process factors, confirming that all five variables influenced COD degradation through the solar photo-Fenton treatment.

Table 4. Central composite design (CCD) independent variables in the solar photo-Fenton process.

The actual factors	Unit	The coded factors	Factor ranges (Level of value)		
			-1	0	1
pH	-	A	2	4	6
H_2O_2	(mg/L)	B	50	100	150
Fe^{2+}	(mg/L)	C	5	10	15
Reaction time	(min)	D	60	90	120
COD_{in}	(mg/L)	E	250	600	950

The total number of experiments conducted for the five factors according to Equations (12):

$$\text{No. of Experiments} = 2^k + 2k + 8 \qquad (12)$$

Where:

K: the number of factors.

The design included 2^k factorial points, supplemented by 2k axial points and eight replications for a center point. In this study, the total number of experiments conducted was 50, comprising 2^5 (32 factorial) points, 2x5 (10) axial points, and eight replications, aimed at assessing the pure error and obtaining a reliable estimate. The response measured during this process was the COD removal. Performance was evaluated by analyzing the COD removal efficiencies, as presented in Table 5.

Table 5. Central composite design for the solar photo-Fenton process

Run	Factor 1 A:pH	Factor 2 B:H_2O_2 mg/L	Factor 3 C:Fe^{2+} mg/L	Factor 4 D:RT min	Factor 5 E:CODin mg/L	COD removal
1	4.00	100.00	10.00	90.00	600.00	78
2	2.00	50.00	15.00	60.00	950.00	29
3	6.00	150.00	15.00	60.00	250.00	38
4	4.00	100.00	15.00	90.00	600.00	71
5	6.00	50.00	15.00	120.00	250.00	34
6	2.00	150.00	5.00	120.00	950.00	34
7	2.00	100.00	10.00	90.00	600.00	31
8	4.00	100.00	10.00	90.00	600.00	78

9	2.00	50.00	5.00	60.00	950.00	25
10	6.00	150.00	15.00	120.00	950.00	22
11	4.00	100.00	10.00	60.00	600.00	59
12	2.00	50.00	15.00	120.00	250.00	45
13	6.00	50.00	5.00	60.00	950.00	11
14	2.00	150.00	15.00	60.00	250.00	47
15	6.00	150.00	15.00	120.00	250.00	31
16	6.00	150.00	5.00	120.00	950.00	23
17	6.00	50.00	15.00	60.00	950.00	10
18	2.00	50.00	15.00	120.00	950.00	33
19	2.00	150.00	5.00	120.00	250.00	48
20	6.00	150.00	5.00	60.00	250.00	24
21	6.00	150.00	15.00	60.00	950.00	13
22	4.00	100.00	10.00	90.00	600.00	78
23	4.00	100.00	10.00	90.00	600.00	78
24	6.00	100.00	10.00	90.00	600.00	18
25	2.00	150.00	5.00	60.00	950.00	23
26	6.00	150.00	5.00	120.00	250.00	33
27	6.00	50.00	5.00	60.00	250.00	26
28	4.00	100.00	10.00	90.00	600.00	78
29	2.00	150.00	15.00	60.00	950.00	26
30	4.00	100.00	10.00	90.00	600.00	78
31	2.00	50.00	5.00	120.00	250.00	43
32	2.00	50.00	5.00	60.00	250.00	41
33	4.00	100.00	10.00	90.00	950.00	58
34	6.00	50.00	5.00	120.00	950.00	16
35	4.00	100.00	10.00	90.00	250.00	87
36	2.00	50.00	5.00	120.00	950.00	28
37	6.00	50.00	15.00	120.00	950.00	19
38	4.00	100.00	10.00	120.00	600.00	65
39	6.00	150.00	5.00	60.00	950.00	21
40	6.00	50.00	5.00	120.00	250.00	29
41	6.00	50.00	15.00	60.00	250.00	24
42	2.00	150.00	5.00	60.00	250.00	43
43	4.00	50.00	10.00	90.00	600.00	34
44	2.00	50.00	15.00	60.00	250.00	38
45	4.00	100.00	5.00	90.00	600.00	51
46	2.00	150.00	15.00	120.00	250.00	47
47	2.00	150.00	15.00	120.00	950.00	36
48	4.00	150.00	10.00	90.00	600.00	39
49	4.00	100.00	10.00	90.00	600.00	78
50	4.00	100.00	10.00	90.00	600.00	78

Table 6. ANOVA results and adequacy of the quadratic model for COD removal efficiency by the solar photo-Fenton process.

	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob > F
COD	Model	21156.41	13	1474.72	27.17	< 0.0001
	A	1488.97	1	1488.97	24.86	< 0.0001
	B	116.74	1	116.74	1.95	< 0.0001
	C	56.94	1	56.94	0.95	< 0.0001
	D	227.76	1	227.76	3.8	0.0005
	E	1852.97	1	1852.97	30.93	< 0.0001
	A^2	3187.85	1	3187.85	53.22	< 0.0001
	B^2	1298.17	1	1298.17	21.67	< 0.0001
	E^2	638.24	1	638.24	10.65	0.0024
	AB	6.13	1	6.13	0.10	< 0.0001
	AC	2.00	1	2.00	0.033	0.8560
	AE	6.13	1	6.13	0.10	0.7510
	BC	0.13	1	0.13	0.000003	0.9630
	DE	18.00	1	18.00	0.308	0.0.587
	Residual	256.5173	36	59.9		
	Lack of Fit	113.3089	15	7.553929	0.49561	0.8658
	Pure Error	76.20833	5	15.24167		
	Cor Total	13462	29			

The ANOVA and multiple regression coefficients of the second-order polynomial model describing the COD removal are summarized in Table 6. The ANOVA was used for graphical analysis of data to obtain the interactions between the process variables and the responses. It indicated that all five variables were significant and played important roles in the degradation of COD by the solar photo-Fenton process. The significance of each coefficient was determined by F-value and P-value. A model F-value of 27.17 and low probability values (prob < 0.0001) imply the model was significant for COD removals. There was only a 0.01% chance that a model F-value could occur due to noise. All of the response surfaces' quadratic models for parameters in this table were significant since the probability values ($p < 0.0001$) were less than 0.05. Corresponding probability values suggested that, among the test variables used in this study, A, B, C, D, E, A^2, B^2, E^2, AB, AC, AD, BD and DE were significant model terms for COD removal. If the model terms have the probabilities exceeding 0.05, they are considered limited in influence. Thus, they must be excluded from the study to improve the models. The model of COD removal was considered significant using the *F*-test at a 5% significance level. In order to simplify the model, these model terms (C^2, D^2, AE, AC, BD, and BE) were eliminated. A high correlation coefficient (R^2) value ensures a satisfactory adjustment of the quadratic model to the experimental data, illustrates good agreement between the calculated and observed results and shows a desirable and reasonable agreement with the adjusted correlation coefficient (adj. R^2) according to literature [53]. The correlation coefficients (R^2) for the COD removal rate in this process were 0.9093, which was greater than the cut-off (0.8) for a model with a good fit. The predicted models, according to results, could be used to navigate the space defined by the CCD because the value of the adequate precision ratio (AP ratio) was 33.47, which was considered adequate due to the fact that they were above 4 according to literature [54]. To improve the models in this study, all insignificant model terms were excluded because of their limited influence. According to the results of models, the constructs of response surface models were reasonable for predicting COD removal efficiency. The extremely high degree of precision and good degree of reliability of the experimental values were demonstrated by the low value of the coefficient of variation (CV), which was 18.45%. The optimisation technique was assessed using the actual and anticipated values of the COD removal rates. They were compared as shown in Figure 4. The replies' actual values and the model's anticipated values matched up nicely. Consequently, these plots indicated an adequate agreement between the real data and the data obtained from the model.

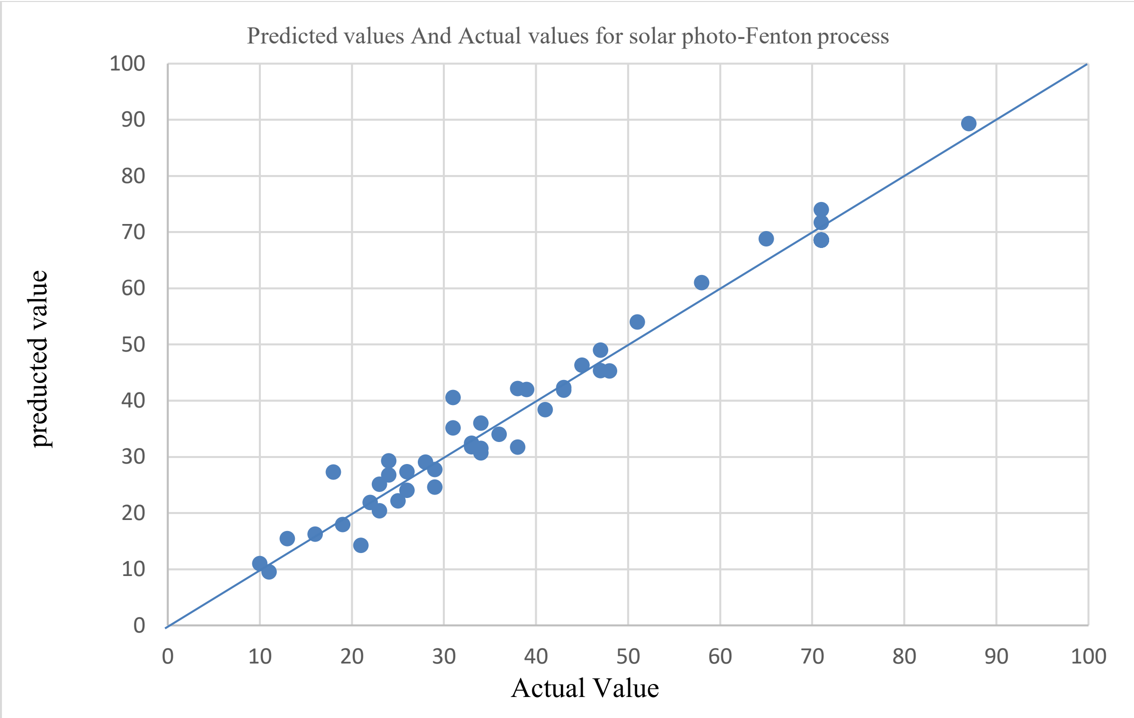


Figure 4. Diagnostics plots for predicted versus actual values for the COD removal rates by the solar photo-Fenton process.

The following polynomial equation (12) provided empirical connections between the variables and COD removal efficiency after removing unimportant coefficients.

$$\text{COD removal (\%)} = 68.8 - 6.6A + 1.8B + 1.3C + 2.6D - 7.4E - 33A^2 - 21B^2 + 14.8E^2 + 0.4AB - 0.2AC + 0.4AE - 0.06BC + 0.7DE \quad (12)$$

Where:

A: a coded factor of pH.

B: the coded factor of hydrogen peroxide dosage (mg/L).

C: the coded factor of ferrous sulphate dosage (mg/L).

D: reaction time (min).

E: initial concentration of COD (mg/L).

The variables and their interactions had a considerable impact on the COD removal efficiencies, as indicated by the coefficients in Equation (12). The variables pH (A) and hydrogen peroxide concentration (B) have a significant impact on the COD removals.

Final equations in terms of actual factors were presented by the following Equation (13):

$$COD\ removal\ (\%) = -87 + 6.2pH + 1.7H_2O_2 + 0.4Fe - 0.2COD_{in} - 8.3pH^2 - 8.5(H_2O_2)^2 + 1.2(COD_{in})^2 + 4.3pH*H_2O_2 + 6.3pH*COD_{in} - 2.5H_2O_2*FE + 7RT*COD_{in} \quad (13)$$

Figure 5 shows that the normalized coefficients effectively demonstrate the impact of model terms on COD removal efficiency. The main contributors to COD removal are the first- and second-order effects of various parameters, ranked as follows: second-order effect of hydrogen peroxide dosage (8.5), second-order effect of pH (8.3), pH (6.6), interaction between pH and CODin (6.3), interaction between pH and hydrogen peroxide dosage (4.3), interaction between hydrogen peroxide dosage and ferrous sulphate dosage (2.5), hydrogen peroxide dosage (1.7), and ferrous sulphate dosage (0.4).

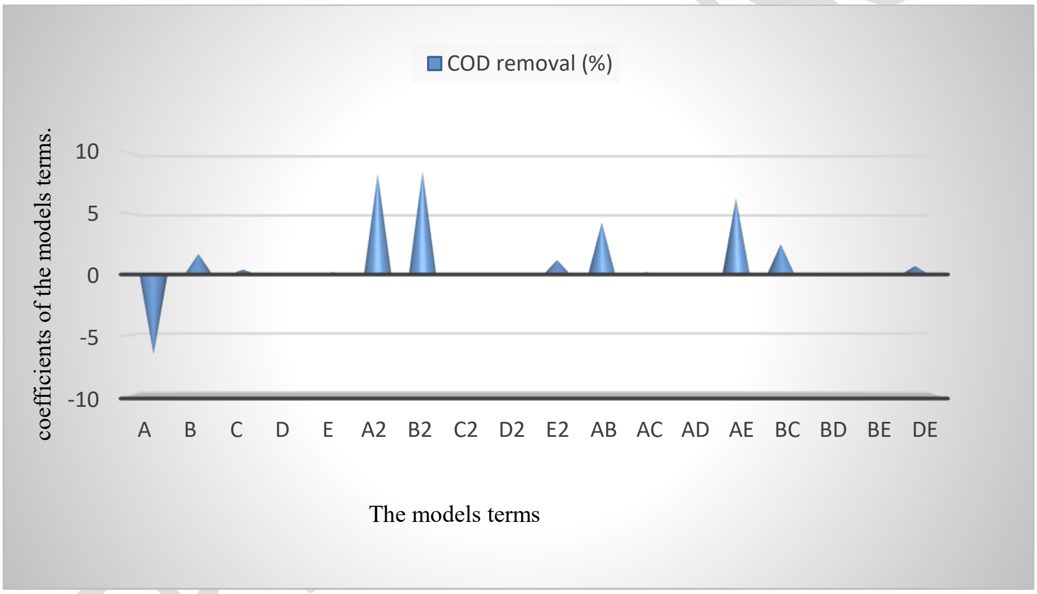


Figure 5. Normalized coefficients of the models for COD removal by the solar photo-Fenton process

Normal probability plots for the solar photo-Fenton process.

To evaluate the models' accuracy in reflecting the real system, Design Expert 6.0.7 software generated plots of studentized residuals for the solar photo-Fenton process as shown in Figure 6. The analysis revealed that the residuals exhibited a normal distribution with a standard deviation aligning with predicted and actual values. Key diagnostic plots indicated that, while some data points showed typical scattering, the residual analysis suggested a generally normal distribution. Factors such as pH significantly influence the degradation of organic compounds in sewage, affected by charges, solubility, and hydrophobicity [55, 56].

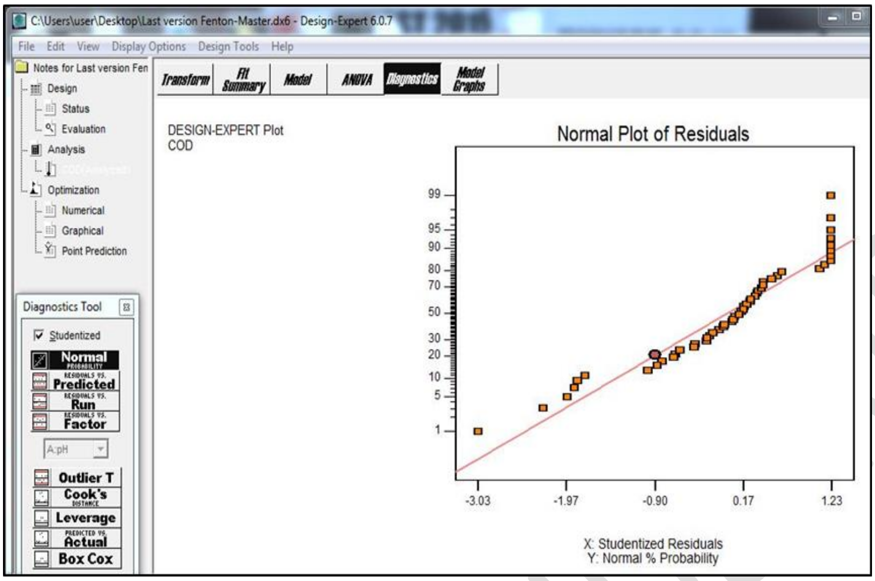
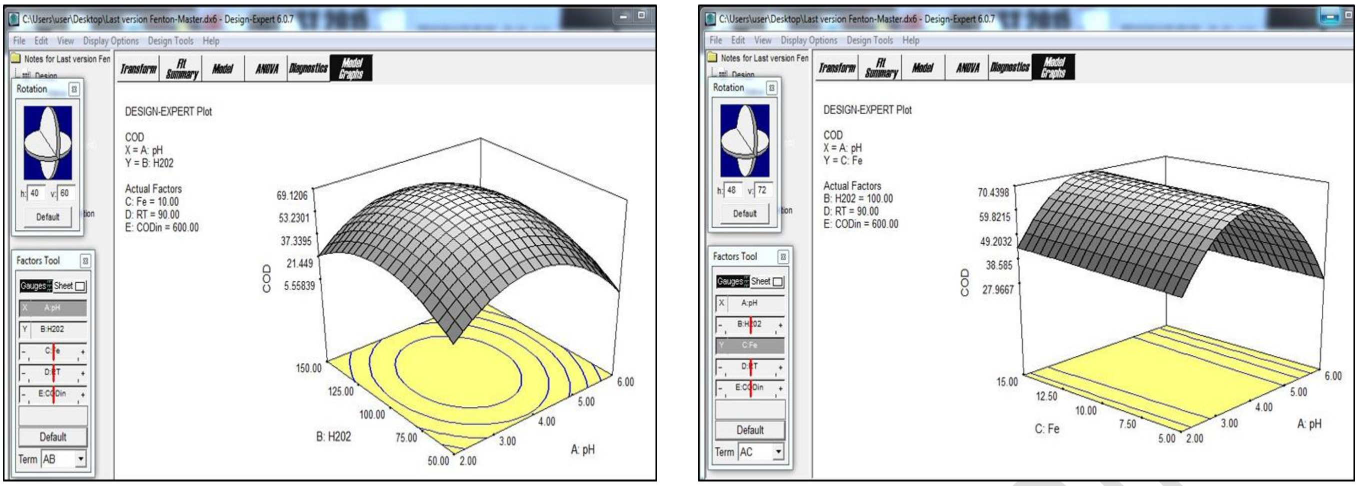


Figure 6. Normal probability plots of the studentized residuals for COD removal by the solar photo-Fenton process

The response surfaces plots for the solar photo-Fenton process.

In a study of the solar photo-Fenton process for COD removal, response surface plots indicated that pH, hydrogen peroxide, and ferrous sulphate dosages significantly influence removal efficiency, achieving up to 89% COD removal at optimal conditions as shown in Figure 7. Excess hydrogen peroxide and ferrous sulphate can adversely affect degradation efficiency due to hydroxyl radical scavenging and iron sludge production. The ideal hydrogen peroxide dosage is capped at 100 mg/L to maintain oxidation capacity, while ferrous sulphate doses should not exceed 6.5 mg/L. The process is highly sensitive to pH levels, with lower pH (at least 2) promoting better COD removal, and a drop in efficiency beyond pH 4 due to reduced iron solubility. Effective COD removal depends on precise dosages of ferrous iron and hydrogen peroxide to overcome the contaminant load in sewage.



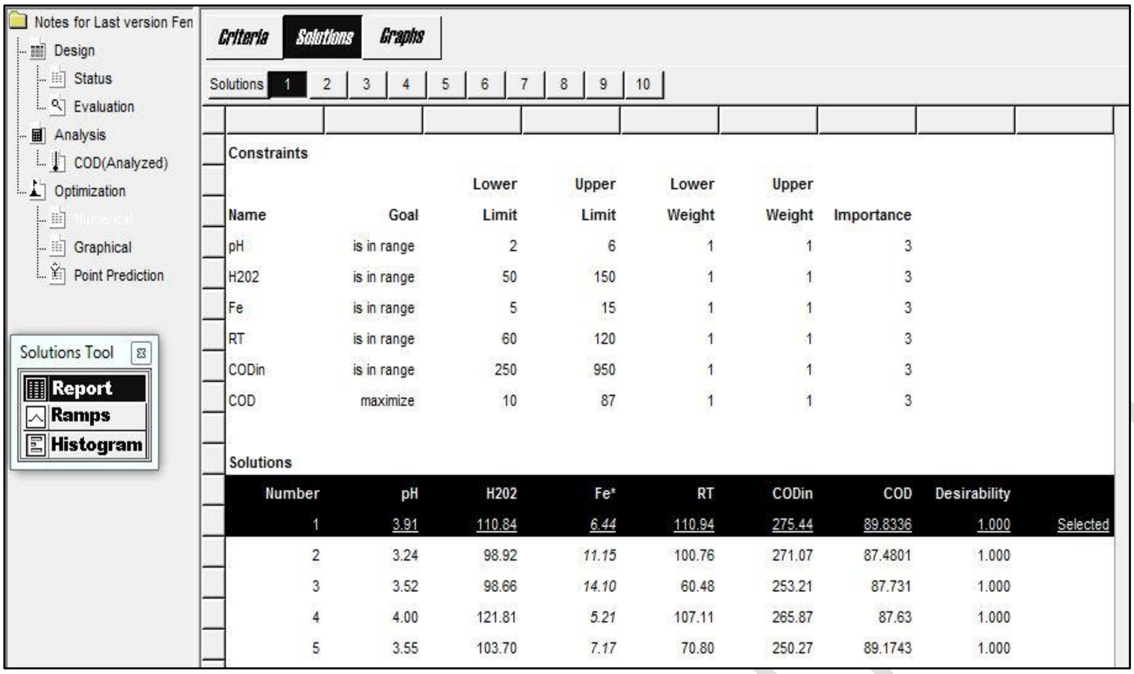
(a) Interaction between the pH and H_2O_2 dosage (b) Interaction between the pH and Fe^{2+} dosage

Figure 7. Response surface models (a) and (b) for COD removal by the solar photo-Fenton process

The optimization of COD removal efficiency for the solar photo-Fenton process

The Design Expert 6.0.7 was used to optimize COD removal efficiency by adjusting parameters such as pH, reaction duration, and dosages of hydrogen peroxide and ferrous sulphate. The optimal conditions showed a rapid COD degradation for up to 110 minutes as shown in Table 7, attributed to high hydroxyl radical concentrations [58]. Beyond 110 minutes, the effectiveness declined as ferrous sulphate and hydrogen peroxide concentrations decreased. The models predicted an 89.83% COD removal rate as shown in Table 7, and experimental outcomes confirmed the model's reliability. Maximum removal was achieved at 110 minutes, with no further improvement beyond this point, indicating potential complete consumption of hydrogen peroxide.

Table 7. The prediction of models for maximum COD removal rate and a desirability function under optimal operating conditions for the solar photo-Fenton



The perturbation plots for the solar photo-Fenton process

The perturbation plots in Figure 8 show that the cooperatives of pH dosage (A) and hydrogen peroxide dosage (B) were highly sensitive to COD removal efficiencies when oxidizing sewage using the solar photo-Fenton process, whereas the cooperatives of ferrous sulphate dosage (C), reaction time (D), and initial COD concentration (E) were less sensitive to them.

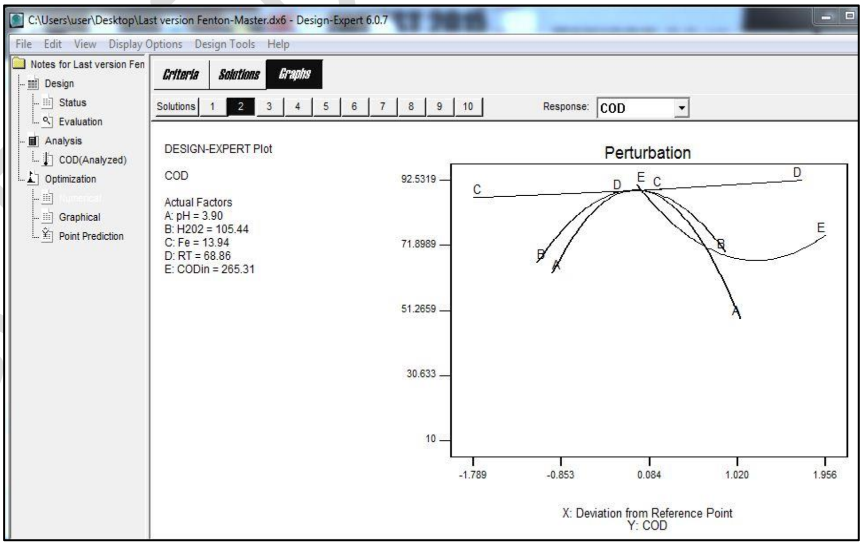


Figure 8. Perturbation plots for COD removals by the solar photo-Fenton process

Assessment the results with previous studies

The study compares various findings related to the Fenton method for wastewater treatment as summarized in Table 8. Anjali and Shanthakumar [5] reported a 99% pollutant degradation from hospital sewage using the photo-Fenton process under specific conditions. Araújo et al. [1] demonstrated an 86.8% reduction in organic matter, while Yuan et al. [3] noted effective heavy metal removal. Da Rocha et al. [36] achieved significant hydrocarbon removal from petrol wastewater, and Tony et al. [9] highlighted Fenton application removing 61% COD at pH 4. Overall, the mineralization potential and efficiency of the Fenton process for different waste types align with existing literature, indicating optimal performance under acidic conditions [42, 43, 46].

Table 8. Recent developments in the Fenton application

Item	The Fenton application	Water kind	Removed material	Elimination effectiveness (%)	Researchers
1	H_2O_2/Fe^{2+}/Solar	sewage wastewater	ketoprofen (KET)	95	[4]
			COD	86.1	
2	H_2O_2/Fe^{2+}/UV	Hospital sewage	Pharmaceutical pollutants	98	[5]
3	H_2O_2/Fe^{2+}/Solar	Municipal sewage	Contaminants of Emerging Concern (CECs)	50	[7]
4	H_2O_2/Fe^{2+}	sewage wastewater	COD	86.8%	[1]
5	H_2O_2/Fe^{2+}	Municipal sewage	heavy metal	88.3	[3]
6	Electro-(H_2O_2/Fe^{2+})	sewage wastewater	TP	97.6	[6]
			NH3-N	90.8	
			Suspended solids	100	
7	H_2O_2/Fe^{2+}	Wastewater	CFVP	96	[39]
8	H_2O_2/Fe^{2+}	The fish canning industrial wastewater.	DOC	63	[44]
9	H_2O_2/Fe^{2+}	Wastewater	DB71 dye	94	[42]
			COD	50.7	
10	H_2O_2/Fe^{2+}	Active pharmaceutical wastewaters.	COD	54	[45]
11	Solar/H_2O_2/Fe^{2+}	Wastewater	COD	54	[36]
12	H_2O_2/Fe^{2+}/UV	sewage wastewater	COD	92	[9]
#	H_2O_2/Fe^{2+}/Solar	Sewage wastewater	COD	89	This study

The experiments on the photolytic process indicated that under sunlight, the method achieved only 9% COD removal in acidic conditions. In contrast, using hydrogen peroxide (H_2O_2) at 750 mg/L led to a 23% reduction in COD due to photochemical cleavage by solar light, enhancing hydroxyl radical generation. The conventional Fenton process without solar energy resulted in 61% COD removal. However, the solar photo-Fenton process significantly improved treatment, achieving 89% COD removal in sewage wastewater under optimal conditions after 120 minutes at pH 4, attributed to increased hydroxyl radical production as shown in Figure 9.

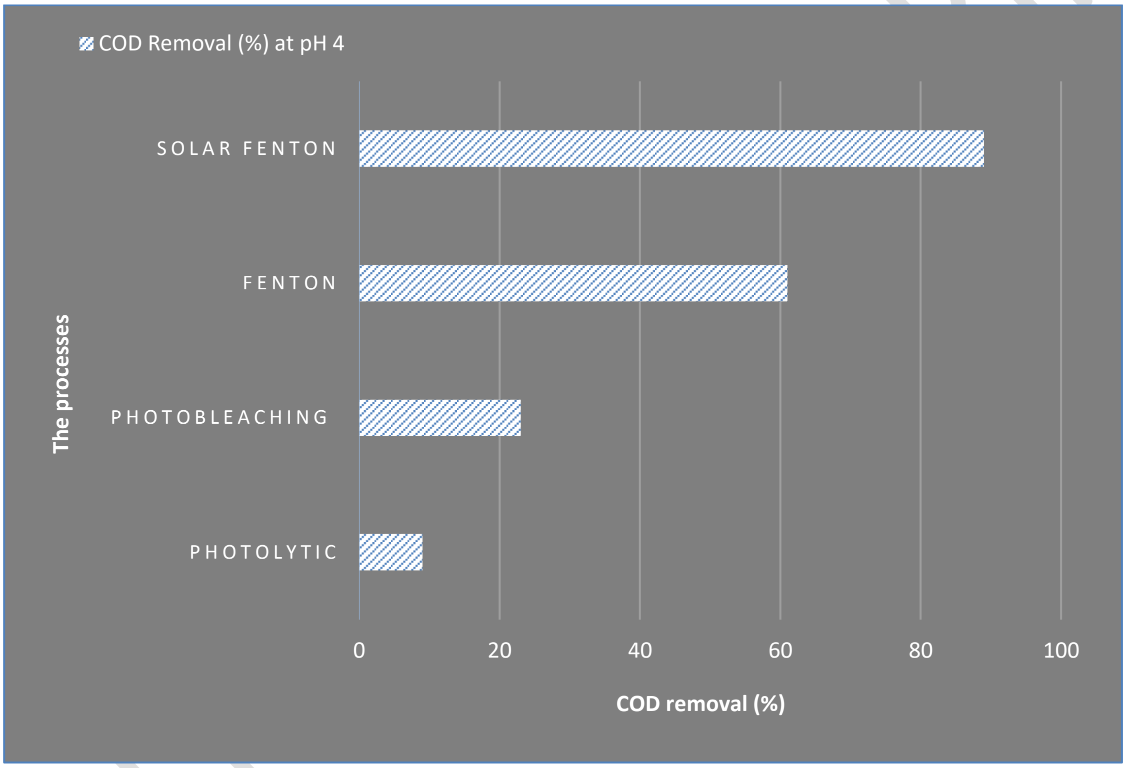


Figure 9. Elimination of COD by several methods from sewage

Establishment of a speculative design for a sewage wastewater treatment plant using solar photo-Fenton technology.

This speculative design presents a scientific framework for sewage treatment rather than a definitive blueprint for a treatment plant. It refrains from providing specifics about reactor size, hydraulic retention time (HRT), sludge production, or chemical consumption. The design advocates for a solar photo-Fenton process applicable for complete sewage wastewater treatment, compliant with the Malaysian

Environmental Quality (Sewage) Regulations 2009, Standard B, particularly highlighting COD removal and iron residual effluent characteristics. The proposed solar photo-Fenton sewage treatment plant has a volume of 100 m³, operating under conditions of pH 4, 100 mg/L hydrogen peroxide (H2O2) concentration, and 10 mg/L ferrous (Fe^{2+}) concentration. It is equipped to manage an organic loading of 56 kg COD, influenced by the sewage wastewater's quality and quantity. The optimal Fenton reagent dosage, determined to be 84 L of hydrogen peroxide and 1 kg of ferrous sulphate, achieves an impressive expected removal of 89% of the organic matter (COD) from the 100 m³ sewage after a 120-minute reaction time at the specified acidic pH. To mitigate iron sludge settling, it is recommended to immediately withdraw the treated sewage wastewater from the reactor post-treatment. A subsequent settling process can then occur for 30 minutes at a higher pH exceeding 8 [37].

Table 9. The experimental operational conditions for suggested sewage treatment plant at the USM engineering campus.

No.	*pH*	*Hydrogen peroxide (mg/L)*	*Iron (mg/ L)*	*Time* (min)	COD			
					COD_{raw}	COD_t	< 200 ppm (S.D.L)*	*COD removal, (%)*
1	4	100	10	90	337	308		9
2	2	150	5	120	337	199	Acceptable	41
3	6	150	15	120	505	493		3
4	6	50	15	120	505	375		26
5	4	100	10	90	337	265		21
6	4	100	10	90	337	292		14
7	4	150	10	90	337	336		1
8	4	50	10	90	337	295		13
9	6	100	10	90	505	397		22
10	2	150	15	60	337	176	Acceptable	48
11	6	50	15	60	505	381		25
12	6	50	5	120	505	362		29
13	4	100	10	120	337	332		2
14	4	100	10	90	337	334		1
15	2	50	5	60	337	160	Acceptable	53
16	2	100	10	90	337	108	Acceptable	68
17	6	150	5	120	505	414		18
18	6	50	5	60	505	366		28
19	6	150	15	60	669	369		45
20	4	100	5	90	337	296		13
21	4	100	10	60	669	361		46
22	2	150	5	60	337	197	Acceptable	42

23	4	100	10	90	669	345		49
24	2	50	5	120	337	159	Acceptable	53
25	6	150	5	60	669	387		43
26	2	50	15	60	337	41	Acceptable	88
27	2	50	15	120	337	128	Acceptable	63
28	4	100	10	90	669	331		51
29	4	100	15	90	669	337		50
30	2	150	15	120	337	70	Acceptable	80

*Malaysian Environmental Quality (Sewage) Regulations 2009, Standard B

Table 10. Comprehensive information for the suggested sewage treatment plant.

Amounts and features of sewage						
Sewage volume (m^3)		COD concentration				
			mg/L		Sludge Kg/m^3	
100			510		0.51	
Treatment resources						
H_2O_2 dosage, (0.2 L/kg COD)			Fe^{2+}dosage, (0.002 mg/kg COD)			
L/100 m^3			Kg/100 m^3			
84			1			
Working circumstances			practice			
Time (min)	pH		Settling time (min)		pH	
120	4		30		>8	
effluent quality after treatment						
COD				Residual iron		
mg/L	< 200 ppm (S.D.L)		Removal (%)	mg/L		< 0.001 ppm (S.D.L)
Max. Initial	final			Max. Initial	final	
510	199	OK	89	0.00001	<0.001	ok

Conclusions

- The study examines the solar photo-Fenton method's effectiveness in reducing COD in sewage wastewater at the USM engineering campus. Results show that the optimal conditions for removing chemical oxygen demand (COD) involve a 100 mg/L hydrogen peroxide dose, a 10 mg/L ferrous ions dose, a pH 4, and a reaction time of 120 minutes, achieving an 89% removal rate. Additionally, quadratic models derived from CCD with RSM reveal statistical significance, indicating that optimization strategies can improve the process further.

- Results show that Fenton is a viable treatment method, successfully removing pollutants in adherence to Malaysian Environmental Quality (Sewage) Regulations 2009, Standard B.
- A pivotal focus of this research is the potential for applying this method on an industrial scale. To explore this, a feasibility study was undertaken to establish a comprehensive treatment plant designed to operate under optimal conditions for maximum efficiency. Findings from the study indicate that the practical application of this process is viable; however, challenges often arise when attempting to translate high laboratory efficiencies to industrial scales. The results underscore the importance of addressing these challenges in order to fully leverage the advantages of the Fenton process in industrial settings.
- Fenton reaction-based treatment process has been shown to be highly effective in the degradation of various persistent micro-pollutants, a conclusion supported by extensive research. The significance of this treatment method underscores the urgent need for continued and intensive efforts to advance its development.

Declarations

Ethical Approval

Not applicable.

Funding

There was no Funding.

Availability of data and materials

Not applicable.

References

[1] Araújo J. L., Jaceguai S. da Silva, Fábio A. S. Santos, Cenira M. de Carvalho, José Leandro S. Duarte, Josealdo Tonholo & Carmem L. P. S. (2022) Decontamination of real urban sewage—comparison between Fenton and electrochemical oxidation. Environ. Sci. and P. Res. 29, 35061-35072.

[2] Machado F., Teixeira A. C. S. C., Ruotolo L. A. M. (2023) Critical review of Fenton and photo-Fenton wastewater treatment processes over the last two decades. Inter. J. Environ. Sci. Tech. 20, 13995-14032.

[3] Yuan J., Weining Z., Zhihua X., Xihong Z., Qingru Z. (2020) Efficient dewatering and heavy-metal removal in municipal sewage using oxidants. Chem. Eng. J. 388, 124298.

[4] Cavalheri P. S., Beatriz S. M., Thalita Ferreira da Silva, Jo˜ao Pedro Baza Garcia Rodrigues, Fabio G., Fernando J., Rodrigo Pereira C., Silvio C., Amilcar M. (2023) Optimization of a combined system of vertical flow constructed wetland and solar photo-Fenton for ketoprofen removal in sewage and landfill leachate. Chem. Eng. J. 475, 146282.

[5] Anjali R., Shanthakumar S. (2023) Synergistic effects on the degradation of a mixture of pharmaceutical pollutants in aqueous solution, raw sewage, and hospital wastewater using UV light-assisted Fenton process. J. Water Pro. Eng. 54, 104025.

[6] Rena G, Minghua Z., Qizhan Z., Xin X., Yanchun L., Pei S. (2020) A novel stacked flow-through electro-Fenton reactor as decentralized system for the simultaneous removal of pollutants (COD, NH3-N and TP) and disinfection from domestic sewage containing chloride ions. Chemical Engineering Journal 387, 124037.

[7] Alonso E., Pichel N., Soriano-Molina P., E. Olivares-Ligero, F.X. Cadena-Aponte, A. Agüera, J.A. S´anchez P´erez, J.L. Casas L. (2023) Continuous solar photo-Fenton for wastewater reclamation in operational environment at demonstration scale. Journal of Hazardous Materials 459, 132101.

[8] Prates M. P, Suzana Maria de Oliveira Loures M., Karine B., Danyelle M., Carlos A., Arizeu L., José E. (2023) Fenton: A Systematic Review of Its Application in Wastewater Treatment. Processes. 11, 2466.

[9] Tony, M.A., Patrick, J., Purcell, Yaqian, Z. (2012) Oil refinery wastewater treatment using physicochemical, Fenton and Photo-Fenton oxidation processes. J. Environ. Sci. Heal. A. 47, 435-440.

[10] Yeh, C.K.J., Hsu, C.Y., Chiu, C.H., Huang, K.L (2008) Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes. J. Hazard. Mater. 151, 562-569.

[11] Torrades, J., Garcia, M., Garcia, H. J A, Domenech X, Peral, J. (2004) Decolorization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions. Sol. Energy 77, 573-581.

[12] Kositzia, M., Poulios, I., Malato, S., Caceres, J., Campos, A. (2004) Solar photocatalytic treatment of synthetic municipal wastewater. J. Water Res. 38, 1147-1154.

[13] De Morais, J.L., Zamora, P.P. (2005) Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. J. Hazard. Mater.123, 181-186.

[14] Coelho, A., Castro, A.V., Dezotti, M., Anna, G., Jr., L.S. (2006) Treatment of petroleum refinery sourwater by advanced oxidation processes. J. Hazard Mater. B 137, 178-184.

[15] Rossiter, O., Rochaa, S., Renato, D.F., Marta, M.M., Duarte, B. (2013) Solar photo-Fenton treatment of petroleum extraction wastewater. J. Des. Water Treat. 51, 5785-5791.

[16] Aljuboury, D.D.A., Senthilkumar, R. (2014) Phenol degradation of industrial wastewater by photocatalysis. J. Innov. Eng. 2(2), 5, 1-10.

[17] Chu, L., Wanga, J., Dong, J., Liu, H., Sun, X. (2012) Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Inter. Chemosphere J. 86, 409-414.

[18] Rahman, M.M., Al-Malack, M.H. (2006) Performance of a cross flow membrane bioreactor (CF–MBR) when treating refinery wastewater. Des.191, 16-26.

[19] Zazouli, M. A., Yousefi, Z., Eslami, A., Ardebilian, M. B. (2012) Municipal solid waste landfill leachate treatment by fenton, photo-fenton and fenton-like processes: Effect of some variables. Iranian J. Environ. Health Sci. Eng. 9(3), 1-9.

[20] Chu, W. (2001) Modeling the quantum yields of herbicide 2, 4-D decay in UV/H_2O_2 process. Chemosphere 44, 935-941.

[21] Chu, W., Wong, C.C. (2004) The photocatalytic degradation of dicamba in TiO_2 suspensions with the help of hydrogen peroxide by different near UV irradiations. Water Res 38, 1037-1043.

[22] Silva, S.S., Chiavone-Filho, O., Neto, E.L.B., Foletto, E.L. (2015) Oil removal from produced water by conjugation of flotation and photo-Fenton processes. J. Environ. Manage. 147, 257-263.

[23] Dionysiou, D.D., Suidan, M.T., Bekou, E., Baudin, I., Lain, J.M. (2000) Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water. Appl. Catal. B: Environ. 26, 153-171.

[24] Neyens, E., Baeyens, J. (2003) A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Hazard. Mater. 98, 33-50.

[25] Tony, M.A., Zhao, Y.Q., Purcell, P.J., El-Sherbiny, M.F. (2009) 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 A 44(5), 488-493.

[26] Rodrigues, C., Madeira, L., Boaventura, R. (2009) Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. J. Hazard. Mater. 164, 987-994.

[27] Ramirez, J.H., Maldonado-Hodar, F.J., Perez-Cadenas, A.F., Moreno-Castilla, C., Costa, C.A., Madeira, L.M. (2007) Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts. Appl. Cataly. B: Environ. 75, 312-323.

[28] Lucas, M.S., Peres, J.A. (2009) Removal of COD from olive mill wastewater by Fenton's reagent: kinetic study. J. Hazard. Mater. 168, 1253-1259.

[29] Rubio-Clemente, A., Chica, E., Penuela, G.A. (2015) Petrochemical wastewater treatment by photo-Fenton process. Water Air Soil Pollut. 226, 61-79.

[30] Badawy M. I., Ali M. (2006) Fenton's per-oxidation and coagulation processes for the treatment of combined industrial and domestic wastewater. J. Hazard. Mater. 136, 961-966.

[31] Batista, A.P.S., Nogueira, R.F.P. (2012) Parameters affecting sulfonamide photo-Fenton degradation iron complexation and substituent group. Journal of Photochemistry and Photobiology A: Chemistry 232(15), 8-13.

[32] Babuponnusami, A., Muthukumar, K. (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Eng. 2,557-572.

[33] Sun, Y., Zhang, Y., Quan, X. (2008a) Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure. Separ. Purific. Tech. 62, 565-570.

[34] Paterlini, W.C., Nogueira, R.F.P. (2005) Multivariate analysis of Photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D. Chemosphere 58, 1107-1116.

[35] Kang, Y. W., Hwang, K. Y., 2000. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Res. 34, 2786-2790.

[36] Da Rocha, O.R.S., Dantas R. F., Duarte, M.M.M.B., Duarte, M. M. L., Da Silva, V.L. (2013) Solar photo-Fenton treatment of petroleum extraction wastewater. Des. Water Treat. 51, 28-30.

[37] Mohajeri, S., Hamidi, A. A., Isa, M. H., Bashir, M. J. K., Mohajeri, L. (2010) Influence of Fenton reagent oxidation on mineralization and decolorization of municipal landfill leachate. J. Environ. Sci. Heal. A 45, 692–698.

[38] Chu, L., Wanga, J., Dong, J., Liu, H., Sun, X. (2012) Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Inter. Chemosphere J. 86, 409-414.

[39] Oliveira, C., Alves, A., Madeira, L. M. (2014) Treatment of water networks (waters and deposits) contaminated with chlorfenvinphos by oxidation with Fenton's reagent. Chem. Eng. J. 241, 190-199.

[40] Karthikeyan, S., Titus, A., Gnanamani, A., Mandal, A. B., Sekaran, G. (2011) Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes. Des. J. 2, 438-445.

[41] Martins, R. C., Rossi, A. F., Rosa, M. (2010) Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement. J. Hazard. Mater. 180, 716-721.

[42] Ertugay, N., Acar, F.N. (2013) Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study. Arab. J. Chem., in press.

[43] Dincer, A.R., Karakaya, N., Gunes, E., Gunes, Y. (2008) Removal of COD from oil recovery industry wastewater by the Advanced Oxidation Processes (AOP) based on H_2O_2. Glob. N. J. 10, 31-38.

[44] Cristovao R. O., Goncalves C., Botelho C. M., Martins R. J. E., Boaventur R. A. R. (2014) Chemical oxidation of fish canning wastewater by Fenton's reagent. J. Environ. Chem. Eng. 2, 4, 2372-2376.

[45] Hussain, S., Shaikh, S., Farooqui, M. (2013) COD reduction of waste water streams of active pharmaceutical ingredient Atenolol manufacturing unit by advanced oxidation-Fenton process. J. S. Chem. Soc. 17, 2, 199-202.

[46] Kang, Y. W., Hwang, K. Y., 2000. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Res. 34, 2786-2790.

[47] Parson, S. (2005) Advanced oxidation processes for water and wastewater treatment. IWA, 86-109.

[48] Oliveira, A., Saggioro, E.M., Moreira, J.C., Ferreira, L.F.V., Pavesi, T. (2012) Solar photochemistry for environmental remediation, Advanced Oxidation Processes for industrial wastewater treatment. INTECH Open Access Publisher.

[49] Babaei A.A., B. Kakavandi, M. Rafiee, F. Kalantarhormizi, I. Purkaram, E. Ahmadi, S. Esmaeili, Comparative treatment of textile wastewater by adsorption, Fenton, UV-Fenton and US-Fenton using magnetic nanoparticles-functionalized carbon (MNPs@C), J. Ind. Eng. Chem. 56 (2017) 163–174,

[50] Ahmadi M., B. Kakavandi, S. Jorfi, M. Azizi, Oxidative degradation of aniline and benzotriazole over PAC@FeIIFe2IIIO4: a recyclable catalyst in a heterogeneous photo-Fenton-like system, J. Photochem. Photobiol. A Chem. 336 (2017) 42–53.

[51] G.R. Rakhshandehroo, M. Salari, M.R. Nikoo, Optimization of degradation of ciprofloxacin antibiotic and assessment of degradation products using full factorial experimental design by Fenton homogenous process, X (2018) 1–9.

[52] Aljuboury D.A.D. and Palaniandy P., Kinetic study of inorganic carbon (IC) removal and COD removal from refinery wastewater by solar Photo-Fenton. Global NEST Journal, Vol 19, No 4, (2017) 641-649.

[53] Abu Amr S. S., Hamidi A A, Mohd N A, Mohammed J K. (2013) Optimization of semi-aerobic stabilized leachate treatment using ozone/Fenton's reagent in the advanced oxidation process. J. Environ. Sci. H., Part A 48, 720–729.

[54] Noordin, V.C., Venkatesh, S., Sharif, S., Elting, A. A. (2004) Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 1045 steel. J. Mater. Pro. Tech. 145, 46-58.

[55] Lee C., Sedlak D.L. (2009) A novel homogeneous Fenton-like system with Fe (III) - phosphotungstate for oxidation of organic compounds at neutral pH values. J. Mol. Catal. A: Chem. 311, 1-6.

[56] Shahrezaei F., Pakravan P., Hemati A.A., Pirsaheb M., Mansouri, A.M. (2015) Preparation of multi-walled carbon nanotubedoped TiO_2 composite and its application in petroleum refinery wastewater treatment. Des. Water Treat. 13, 1-10.

[57] Hasan M., Khalekuzzaman M., Hossain N., Alamgir M. (2021) Anaerobic digested effluent phycoremediation by microalgae co-culture and harvesting by Moringa oleifera as natural coagulant. J. Clean. Prod. 292, 126042.

[58] Machado F., Teixeira A. C. S. C., Ruotolo L. A. M. (2023) Critical review of Fenton and photo-Fenton wastewater treatment processes over the last two decades. Inter. J. Environ. Sci. Tech. 20, 13995-14032.

[59] Mohajeri S, Hamidi A A,, M. A. Zahed, Mohajeri, L., Bashir, M. J. K., Aziz, S. Q., Adlan, M. N., Isa, M. H. (2011) Multiple responses analysis and modeling of Fenton process for treatment of high strength landfill leachate. Water Sci. Tech. 64.8, 1652-1660.

[60] Kwon S., Fan M., Cooper A. T., Yang, H. (2008) Photocatalytic applications of micro- and nano-TiO2 in environmental engineering. Criti. Review. Environ. Sci. Tech. 38, 197-226.

[61] Maciel, R., Sant'Anna, J. G. L., Dezotti, M. (2004) Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions. Chemosphere 57, 711-719.

[62] Aljuboury, D.D.A., Shaik F., (2021) Optimization of the petroleum wastewater treatment process using TiO_2/ Zn photocatalyst. South African Journal of Chem. Eng. 38, 61-69.

[63] Amor, C, Torres-Socias, ED, Peres, JA, Maldonado, MI, Oller, I, Malato S, Lucas M S. (2015) Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes. J. Hazar. Mater. 286, 261-268.

[64] Hasan, D.U.B., Abdul Aziz, A.R., Daud, W.M.A.W. (2012) Oxidative mineralisation of petroleum refinery effluent using Fenton-like process. Chem. Eng. Res. Des. 90(2), 298-307.

[65] Saber, A., Hasheminejad, H., Taebi, A., Ghaffari, G. (2014) Optimization of Fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology. Appl. Water Sci. 4, 283-290.

[66] Davarnejad, R., Pirhadi, M., Mohammadi, M., Arpanahzadeh, S. (2015) Numerical analysis of petroleum refinery wastewater treatment using electro-Fenton process. Chem. Prod. Process Model. 10(1), 11-16.

[67] Sayed K. et al. (2024a) Simultaneous enhanced removal of pharmaceuticals and hormone from wastewaters using series combinations of ultra-violet irradiation, bioremediation, and adsorption technologies. J. Water Pro. Eng. 57, 104589.

[68] Sayed K. et al. (2024b) Removal of pharmaceutical compounds from sewage effluent by the nanofiltration membrane. J. Water Pro. Eng. 68, 106320.

[69] Sayed K. et al. (2024c) Removal of Pharmaceuticals from Municipal Wastewater Using Malaysian Ganoderma Lucidum Fungal Strain. J. Kejuruteraan 36(4), 1467-1476.

[70] Sayed K. et al. (2022) Optimization of palm oil mill effluent final discharge as bio stimulant for biodegradation of tapis light crude petroleum oil in seawater. J. Sea Res.188, 102268.