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Radiant Remedies – Maximizing Wastewater Treatment Efficiency with Optimized Photo-Fenton Techniques

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ABSTRACT

This study presents a comprehensive investigation into the efficacy of advanced oxidation treatment methods, focusing on the photo-Fenton process for removing organic pollutants from wastewater. Despite prior research, significant knowledge gaps persist regarding the optimal operational conditions for maximizing pollutant removal efficiency. This manuscript fills those gaps through extensive batch experiments, meticulously evaluating the impacts of irradiation time, pH levels, and ferrous sulfate and hydrogen peroxide concentrations on treatment outcomes. Our results indicate that an irradiation time of 140 minutes and a pH of 3.1 are critical for achieving remarkable pollutant removal efficiencies: 91.57% for color, 85.14% for chemical oxygen demand (COD), and 79.87% for total organic carbon (TOC) over a 180-minute treatment period with optimal dosages. To further enhance understanding, we employed predictive models utilizing response surface methodology (RSM) and central composite design (CCD), rigorously assessing their statistical performance. The models demonstrated strong alignment with experimental data and existing literature, showcasing their reliability. This research not only provides novel insights into optimizing wastewater treatment processes but also holds significant practical value for industries aiming to implement effective strategies for mitigating organic pollution. By addressing critical knowledge gaps, this study lays a foundation for improved environmental remediation practices, offering a vital framework for industries committed to sustainable wastewater management.

Keywords: environmental remediation, organic pollutants, Photo-Fenton process, predictive modeling, wastewater treatment.

INTRODUCTION

The Photo-Fenton process, renowned for its exceptional efficiency in advanced oxidation reactions, is widely recognized for its effectiveness in treating synthetic municipal wastewater (Ashgar et al., 2019). In this process, ferrous salts undergo a reaction with hydrogen peroxide under light radiation, leading to the production of a significant quantity of hydroxyl radical (OH) radicals that are primarily utilized to react with various organic compounds (Boczkaj et al., 2018). The Photo-Fenton process is a highly efficient and environmentally friendly technique for wastewater treatment, especially for the removal of organic substances owing to its outstanding chemical stability (Vilar et al., 2017). As illustrated in Table 1, a comparative overview of four main wastewater treatment technologies: photo-Fenton, biological treatment, chemical oxidation, and membrane filtration is introduced by Zhang et al. (2021); Hussain and Sulaiman, (2020).

Each method is evaluated based on its advantages, disadvantages, and most convenient application fields. The photo-Fenton process is noted for its high efficacy in degrading organic pollutants but requires stringent control of operational parameters. Biological treatment, while cost-effective for biodegradable waste, tends to be slower and less effective for non-biodegradable contaminants. Chemical oxidation offers rapid treatment but may produce harmful by-products, and membrane filtration excels in removing suspended solids but faces challenges with operational costs and maintenance. This comparison highlights the need to select appropriate technologies based on specific wastewater characteristics and treatment goals (Zhang et al., 2021; Hussain and Sulaiman, 2020).

Several studies have shown that reducing the pH can enhance the oxidation capacity, particularly in the Fenton process, which is typically carried out at a solution pH of 3.2 (Rodriguez et al., 2019). The rate of the Fenton reaction is primarily influenced by optimizing key factors such as pH, hydrogen peroxide dosage, ferrous salts dosage, and radiation exposure time (Pulgarin et al., 2017). An experimental investigation was conducted to determine the optimal operating conditions for wastewater treatment. The progress of the experiment was monitored using parameters such as COD, TOC, and color removal. The findings revealed that photocatalytic oxidation improved the biodegradability of the dye-containing wastewater, establishing a correlation between decolonization and biodegradability (Haseneder et al., 2009). Additionally, researchers in the literature have proposed optimization guidelines for treating dye wastewater by manipulating various photo Fenton operating variables (AL-Khateeb et al., 2022). In batch experiments, the treatability of raw textile wastewater was examined using the Fenton process and compared with chemical coagulation. The optimization results confirmed that the Fenton process can achieve distinct removal efficiencies of 82.8% for COD, 96.2% for color, and 75.6% for TOC (Kurt et al., 2019). The objective of this study is to assess the effectiveness of the photo Fenton oxidation process, a sophisticated chemical technology technique, in eliminating residual colors, COD, and TOC from wastewater. Additionally, we aim to determine the optimal operational conditions that result in the highest uptake of target environmental pollutants in wastewater. To achieve this, an extensive batch experimental program was conducted, monitoring various parameters including irradiation time, pH levels, and initial concentrations of ferrous sulfate and hydrogen peroxide. The findings from this study will provide valuable data for the development of predictive models to enhance removal efficiency.

MATERIALS AND METHODS

Wastewater characterization

The physicochemical characteristics of the wastewater collected from the effluent of the industrial plant for textiles located at 6 October City, Giza are summarized in Table 2.

Materials

The experimental process included ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2; 30%) to produce hydroxyl radicals. To halt the oxidation reactions, a quenching solution with potassium iodide (KI; 0.1 M), sodium sulfite (Na_2SO_3; 0.1 M), and sodium hydroxide (NaOH; 0.1 M) was utilized. The pH was adjusted by adding concentrated sulfuric acid (H_2SO_4) to the system.

Experimental procedure

The UV-photo-Fenton trials took place in a laboratory-scale batch reactor with a 1,000 mL volume, featuring a UV system located at the upper part of the reactor, as depicted in Figure 1. The UV lamp

Table 1. Wastewater treatment technologies comparison

Method	Advantages	Disadvantage	Convenient application fields
Photo-Fenton	Highly effective for organic pollutants, has fast reaction rates, and can degrade various contaminants.	Requires careful control of pH, UV light dependency, and potential toxic by-products.	Industrial wastewater, textile effluents, pharmaceuticals, and food processing runoff.
Chemical oxidation	Lower operational costs, effective for biodegradable pollutants, and overall water quality improvement.	Slower reaction times and less effective for non-biodegradable compounds.	Municipal sewage, agricultural wastewater, and landfill leachate treatment.
Membrane filtration	Excellent for suspended solids removal, providing high-quality effluent.	High operational costs, fouling issues, and maintenance requirements.	Drinking water treatment and wastewater reuse, as well as industrial wastewater recycling.

Table 2. Industrial wastewater influent characteristics

Parameters	Values
pH	4.41
COD (mg/l)	2513
TOC(mg/l)	1488
Color	
λ_{436}	0.194
λ_{525}	0.156
λ_{620}	0.147
Abs	0.571

Table 3. Experiment's operational parameters

Parameters	Ranges
X_1: pH	1–6
X_2: Hydrogen peroxide (mg/l)	800–1300
X_3: Irradiation time (minutes)	40–180
X_4: Ferrous sulfate (mg/l)	40–90

(395–400 nm) was warmed up for 15 minutes, after which the reactor was loaded with 500 mL of stillage. Next, the necessary amounts of $FeSO_4 \cdot 7H_2O$ and H_2O_2 were introduced to the mixture, following the prescribed Fe^{2+} and H_2O_2 dosages.

Experimental plan and data analysis

The central composite design (CCD) and response surface methodology (RSM) were utilized to analyze the response surface characteristics in the experimental design and determine the optimal settings for the independent variables. The system's efficiency is quantified by Equation 1, an empirical second-order polynomial model.

$$Y = \beta_o + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_i X_i^2 + + \sum_{i<j}^{K} \sum_{j}^{K} \beta_i X_i X_j + \cdots + e \qquad (1)$$

The response Y is influenced by the variables X_i and X_j, where β_0 serves as a constant coefficient, and β_j, β_{jj}, and β_{ij} represent the interaction coefficients for linear, quadratic, and second-order terms. The study factors, denoted by k, include operating variables such as pH (X_1), hydrogen peroxide (X_2), irradiation time (X_3), and ferrous sulfate (X_4). The removal efficiency percentages Y_{color}, Y_{COD}, and Y_{TOC} for color, COD, and TOC respectively were examined within the ranges outlined in Table 3 (Mojiri et al., 2013).

The levels of the real operational variables were coded as –2, –1, 0, +1 and +2. Codded operation variables involving the Fenton processes are given in Table 4.

RESULTS AND DISCUSSIONS

The subsequent sections offer a detailed analysis of the potential effects of different batch treatment operational parameters such as irradiation duration, pH levels, and initial concentrations of ferrous sulfate and hydrogen peroxide on the removal efficiencies of wastewater pollutants.

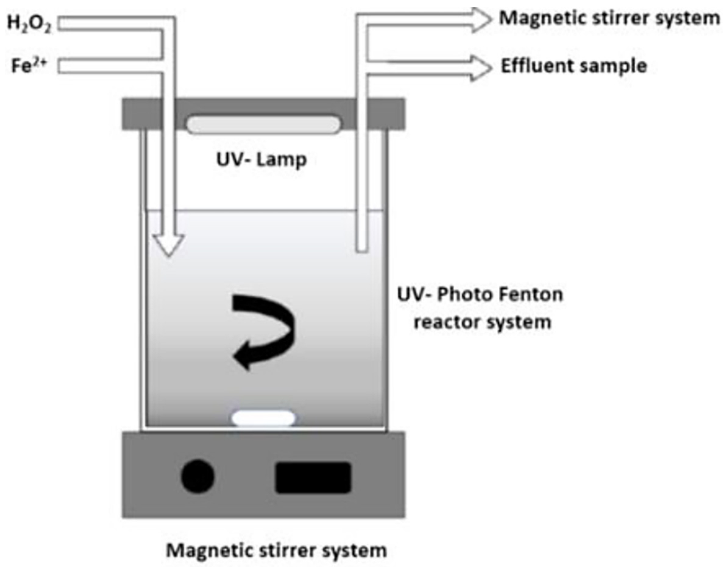

Figure 1. Schematic diagram of UV-photo-Fenton reactor

Table 4. Operation variables codes

Operation variable (X_i)	Coded Variable				
	-2	-1	0	1	2
X_1: pH	1	2.0	3	4.5	6
X_2: Hydrogen peroxide (mg/l)	800	950	1050	1150	1300
X_3: Irradiation time (minutes)	40	80	115	150	180
X_4: Ferrous sulfate (mg/l)	40	52	65	78	90

Effect of pH

Figure 2 presents the pH impact on color, COD, and TOC removal efficiency percentages at an Irradiation time of 80 minutes, Hydrogen peroxide concentration of 900 mg/l, and Ferrous sulfate concentration of 60 mg/l. The pH level plays a crucial role in the generation of -OH radicals, significantly affecting their oxidation potential. The data indicates a sharp increase in pH from 1 to 3, followed by a specific threshold at pH 3.2. Beyond this threshold, there is a noticeable decrease in pollutant removal efficiency as pH values continue to rise. This phenomenon can be attributed to the preference for -OH radicals' generation through H_2O_2 decomposition at acidic pH levels (Okunade et al., 2022). Conversely, at higher pH values, the precipitation of iron as ferric hydroxide occurs, reducing Ferrous sulfate availability (Brillas et al., 2023). The results demonstrate that at the optimal pH of 3.2, removal efficiencies of 90.74%, 84.36%, and 79.74% were achieved for color, COD, and TOC, respectively.

Effect of irradiation times

During a specific irradiation period ranging from 40 to 180 minutes, an investigation was conducted on removing pollutants, maintaining the pH at 3 with hydrogen peroxide at 800 mg/l and Ferrous sulfate at 70 mg/l, as depicted in Figure 3. The data observed indicates that the efficiency of reducing concentrations of various pollutants studied increases with longer irradiation times, reaching equilibrium after 140 minutes with maximum removal efficiencies of 93.13%, 91.05%, and 84.08% for color, COD, and TOC, respectively. This trend can be attributed to the continuous production of hydroxyl radicals for up to 140 minutes. Subsequently, the reaction rate decreased as hydrogen peroxide was depleted, being the main source of hydroxyl radical generation (Çifçi et al., 2023). Our findings align with those Durante et al. (2020) reported regarding removing organic pollutants from wastewater using the photo Fenton reaction on a pilot scale.

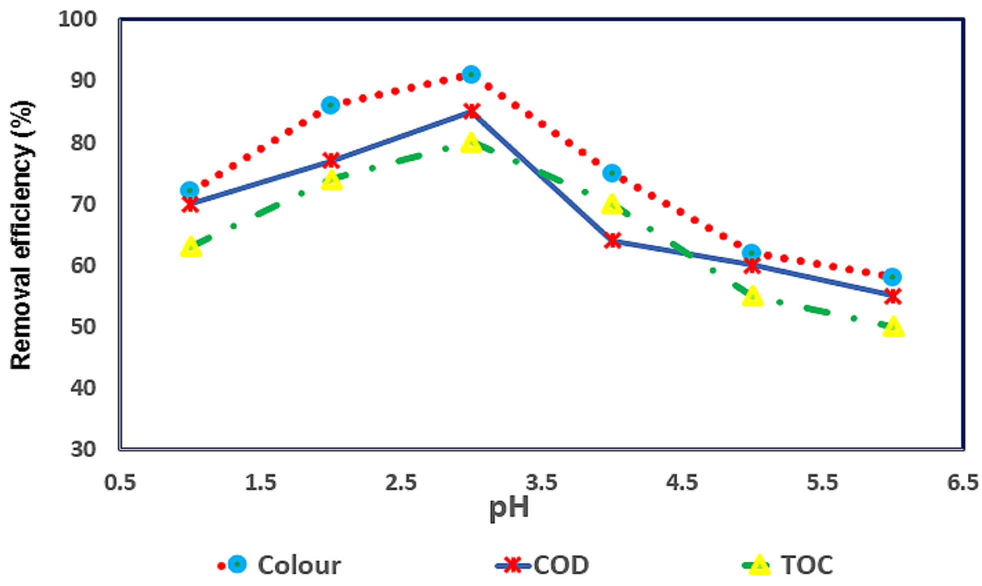

Figure 2. Effect of pH on the pollutant removal efficiency: Irradiation time of 80 minutes, hydrogen peroxide of 900 mg/l, and ferrous sulfate of 60 mg/l

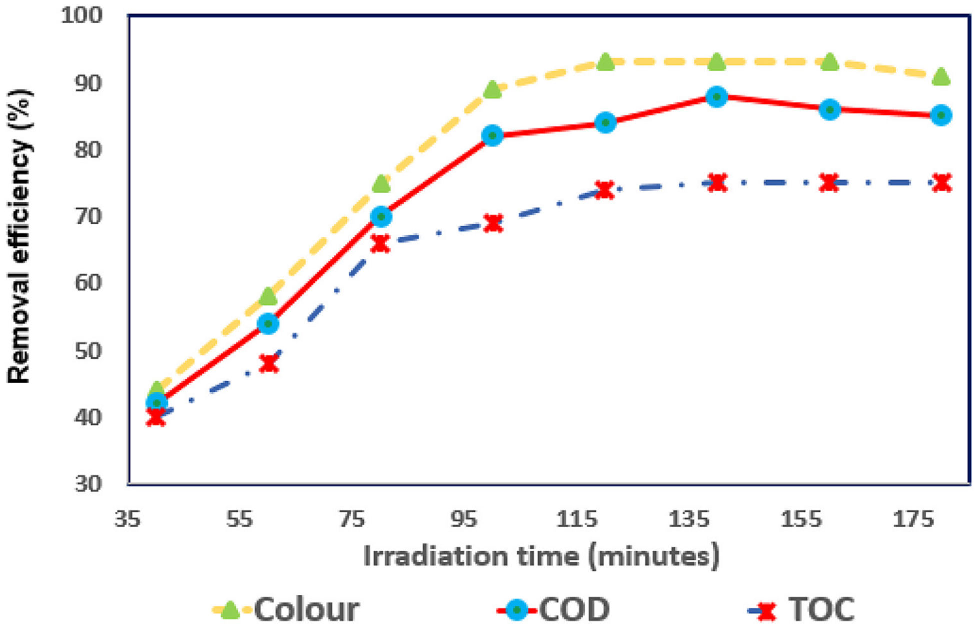

Figure 3. Effect of irradiation time on the pollutant removal efficiency: pH 3, hydrogen peroxide of 800 mg/l, and ferrous sulfate of 70 mg/l

Effect of hydrogen peroxide dosages

Figure 4 depicts the impact of hydrogen peroxide dosage on pollutant removal efficiencies at pH 4 using ferrous sulfate at a concentration of 80 mg/l and an irradiation time of 100 minutes. A dosage of 1000 mg/l is the ideal amount of hydrogen peroxide required to achieve the highest treatment efficiency under the specified experimental conditions. Any further increase in hydrogen peroxide concentration results in a significant decrease in the removal rate. This can be attributed to the auto-decomposition of hydrogen peroxide into oxygen and water, as well as the recombination of OH radicals. Excessive H_2O_2 reacts with OH, competing with organic pollutants and consequently reducing the treatment efficiency. Additionally, H_2O_2 itself contributes to the scavenging capacity of OH radicals. Therefore, at this optimal hydrogen peroxide dosage, significant removal efficiencies of 90.23%, 83.69%, and 79.45% were achieved for

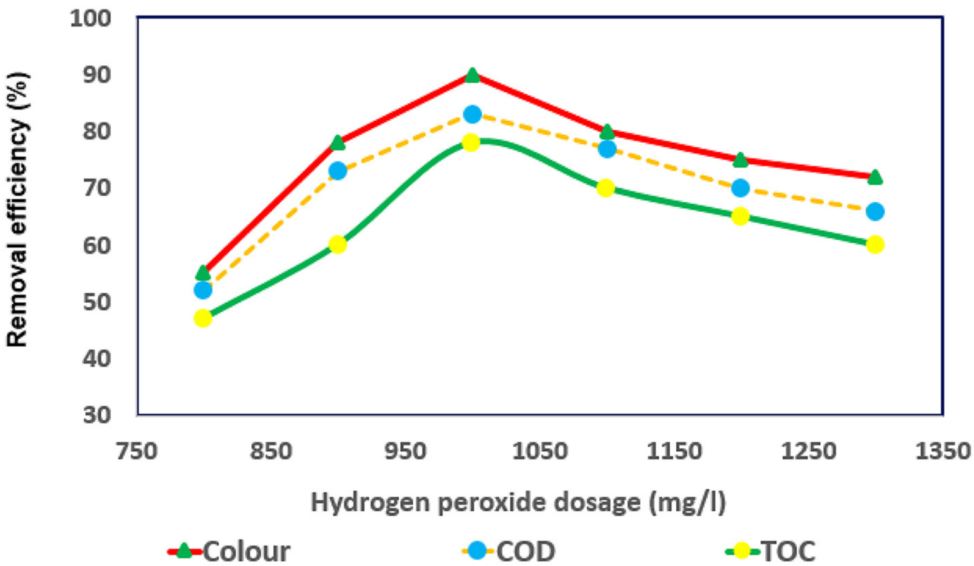

Figure 4. Effect of, hydrogen peroxide dose on pollutant removal efficiency at pH 4 with ferrous sulfate at 80 mg/l, and an irradiation time of 100 minutes

color, COD, and TOC, respectively. These key findings align with those reported by (Akrami et al., 2022).

Effect of ferrous sulfate dosages

The quantity of ferrous iron plays a crucial role in influencing the photo-Fenton processes. In Figure 5, the impact of ferrous sulfate dosage on color, COD, and TOC removal at pH 3 with hydrogen peroxide at 900 mg/l, and an irradiation time of 120 minutes is illustrated. The optimal ferrous sulfate dosage for wastewater treatment using the photo-Fenton process was determined to have a significant effect on color, COD, and TOC removals, with a threshold value of 70 mg/l. However, exceeding ferrous sulfate concentrations beyond 70mg/l did not enhance color, COD, and TOC removal efficiency due to the excess iron reacted with hydroxyl radicals producing compounds (Sirés et al., 2019). It is worth noting that with the optimal ferrous sulfate dosage, the achieved removal efficiency was 91.87% for color, 85.77% for COD, and 78.98% for TOC.

Removal efficiency predictive models developing

It was mentioned earlier that the Photo Fenton batch experiments examined pH and ferrous sulfate and determined the optimal operational conditions for achieving the desired industrial wastewater treatment. Central composite design (CCD) and response surface methodology (RSM) were employed to create predictive models removal efficiency: color, (Y_{color}), COD (Y_{COD}), and TOC (Y_{TOC}) respectively:

$$Y_{color} = 63.17 + 0.842X_4 + 0.328X_1 - 0.0054X_1^2 - 0.00065X_4^2 \quad (2)$$

$$Y_{COD} = 60.24 + 0.751X_4 + 9.28X_1 - 0.0491X_1^2 - 0.0424X_4^2 + 2.383X_3 - 0.0056X_3^2 \quad (3)$$

$$Y_{TOC} = 59.71 + 0.787X_4 + 10.541X_1 - 0.054X_1^2 - 0.0419X_4^2 + 2.198X_3 - 0.0086X_3^2 + 0.0059X_2 \quad (4)$$

Model evaluation statistics

In this study, four standardized statistical performance evaluation measures were selected to assess the effectiveness of the developed models in accurately predicting pollutant removal efficiency.

Mean absolute percentage error (MAPE)

The MAPE value that provides the best fit when comparing simulated data to observed data is zero. Here is the calculation:

$$MAPE = \left[\frac{1}{n}\sum_{i=1}^{n} |Y_{Observied} - Y_{Simulated}| / Y_{Observied}\right] \quad (5)$$

Percent bias (PBIAS)

According to Kisi, et al. 2020, the ideal value for PBIAS is zero. However, it can be calculated as:

$$PBIAS = 100 \times \frac{\sum_{i=1}^{n}(Y_{Observied} - Y_{Simulated})}{\sum_{i=1}^{n} Y_{Observied}} \quad (6)$$

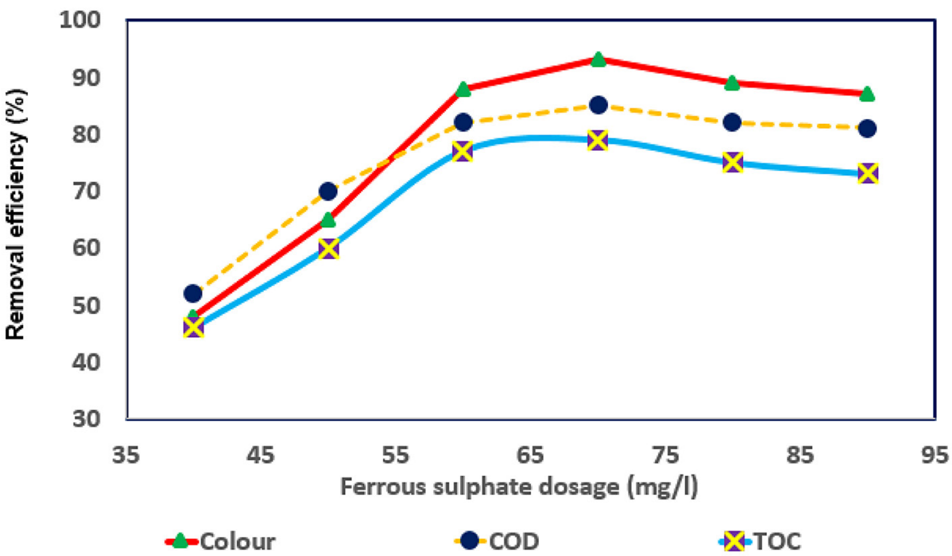

Figure 5. Effect of ferrous sulfate on the pollutant removal efficiency: pH 3, hydrogen peroxide of 900 mg/l, and irradiation time of 120 minutes

Scatter index (SI)

The scatter index can be computed using Equation 7:

$$SI = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(Y_{Observied} - Y_{Simulated})^2 / Y_{Observied}} \quad (7)$$

Relative bias (RE)

The relative bias may be computed by Equation 8 as:

$$RE = \left(\frac{\sum_{i=1}^{N}(Y_{Observied} - Y_{Simulated})^2}{\sum_{i=1}^{N} O_i}\right) \quad (8)$$

Accordingly, the heat map plot in Figure 6 displays the graphical comparison of predictive models based on standardized statistical performance evaluation measures (Friendly et al., 2009). It can be noted that the Y_{COD} model (light green) demonstrates superior prediction performance in comparison to other models. Conversely, the Y_{TOC} (dark green) model exhibits

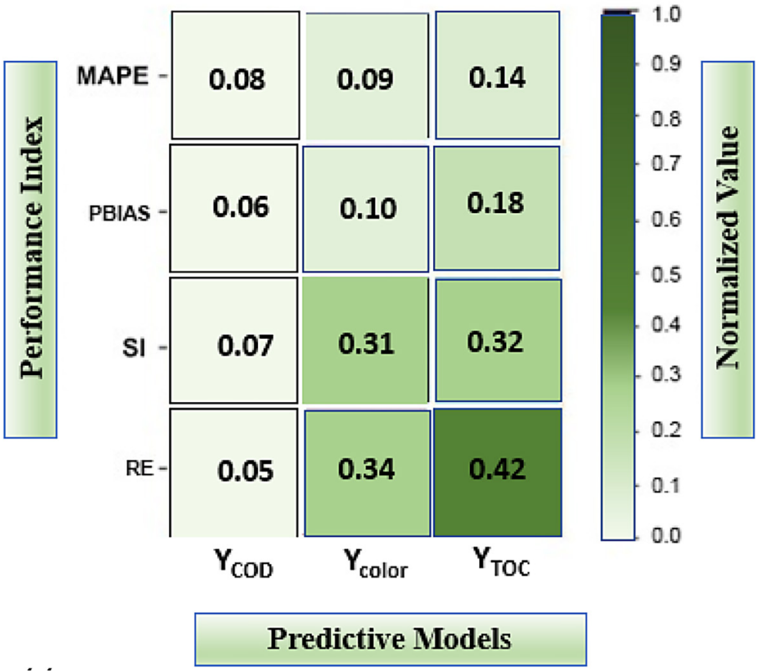

Figure 6. Heat plot of the observed and the predicted pollutant removal efficiency values

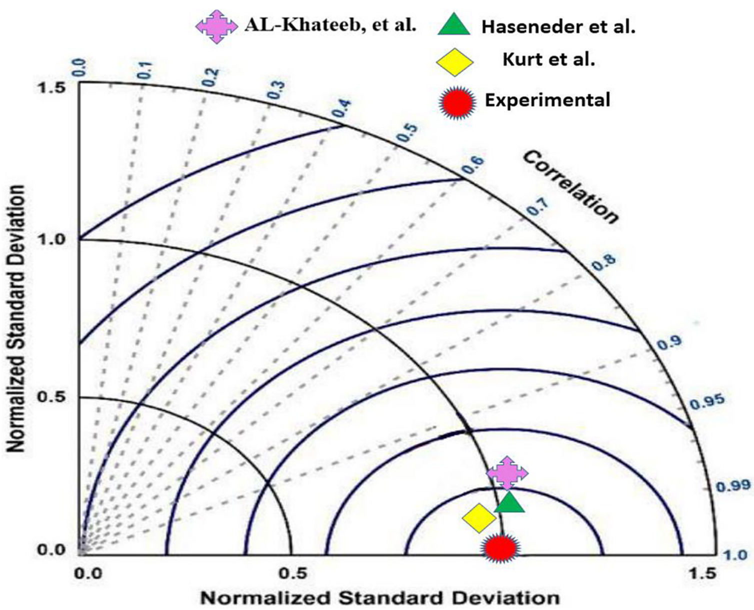

Figure 7. Taylor diagram of the previous studies and experimental values (Taylor, 2001)

the lowest performance in forecasting pollutant removal efficiency during Photo Fenton batch experiments.

Comparing with previous studies

The current study's pollutant removal efficiency model was evaluated for accuracy by utilizing a Taylor diagram, a commonly used graphical tool, to compare it with results from previous studies, Figure 7. The correlation coefficient and normalized standard deviation were considered for this evaluation. The accuracy of the model was assessed by comparing the distance between the model's predictions and the corresponding experimental (Taylor, 2001). The data presented in the diagram indicates that the findings put forth by Kurt et al. (2022) closely resemble the experimental results, making it a more reliable model. On the other hand, the model proposed by AL-Khateeb et al. (2022) is considered the least accurate among the others, albeit with a slightly larger deviation. In general, it can be inferred that all three models, when compared to the current study, demonstrate satisfactory predictive capabilities.

CONCLUSIONS

This research paper presents the key findings of utilizing photo-Fenton oxidation reactors. In the case of the batch system, the most significant impact on the optimization of the Fenton process was determined to be pH (3), ferrous sulfate concentration (70 mg/l), hydrogen peroxide concentration (1000 mg/l), and irradiation time (140 minutes). These systems achieved impressive removal efficiencies of 91.57% for color, 85.14% for COD, and 79.87% for TOC. To develop predictive models for pollutant removal efficiencies, response surface methodology (RSM) was employed, and the central composite design (CCD) was successfully utilized to evaluate these models. Statistical criteria confirmed the agreement between the developed models and the experimental results. The developed models exhibited satisfactory agreement with previous research, as evidenced by the employed statistical performance metrics.

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