Optimization Approach to Evaluate the Solar, UV and LED Visible Light Fenton Processes for Pollutant Degradation in Landfill Leachate

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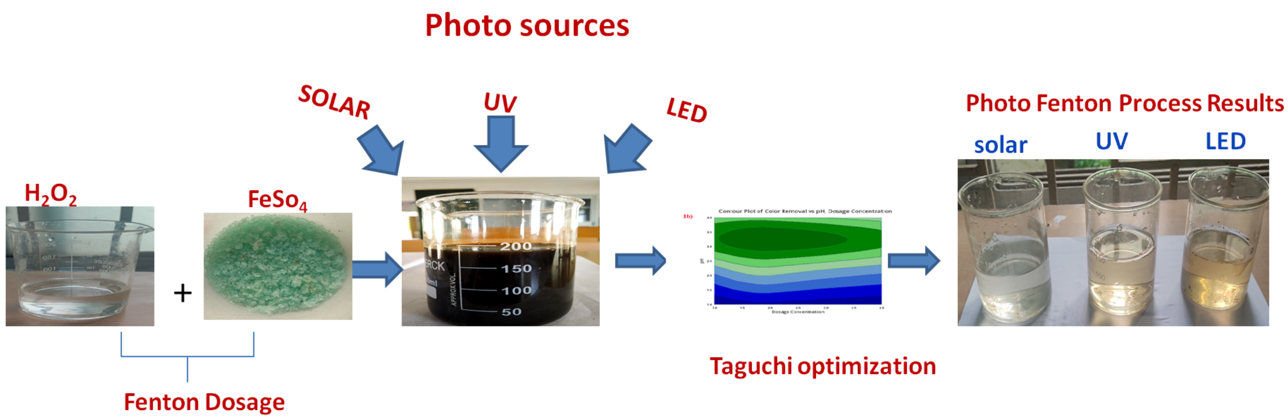
GRAPHICAL ABSTRACT



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Abstract

In the current study, three different photo-assisted sources were used to evaluate the photo-Fenton oxidation process for the pollutant degradation of mature landfill leachate. Solar, UV, and LED visible light photo sources were adopted in this Fenton process. Fenton dosages ($FeSO_4$:H_2O_2) 1:30, 1.5:30, 2:30, and 2.5:30g/L were used in the investigation, which was conducted under a variety of pH settings (2 to 3.5) and at experimental reaction duration of 30, 60, 90, and 120 minutes. To analyze and compare the efficiency of the solar, UV, and LED visible light photo

Fenton processes for pollutant degradation, Taguchi experimental design orthogonal arrays (L16) was employed. To analyse the significance of this experimental design for landfill leachate treatment, Larger the Better was selected. The highest levels of pollutant degradation in the Solar Photo Fenton method was identified when compared to UV, and LED visible light photo Fenton processes. The maximum removal of 95% color, 83% COD, 89% TSS, 94% Cr, 86% Cd, and 93% Cu was achieved in Solar Photo Fenton process at pH-3, Fenton dosage 1.5:30 g/L and reaction period 60 minutes.

Key words: Landfill leachate, UV, LED visible light photo Fenton process, Solar, Taguchi method.

1. Introduction

The production of wastewater was mostly a result of human activity in the earlier days, it was not considered as a serious issue. However, as urbanisation and population grew, these wastewaters later had a significant negative impact on the environment (Giusti, 2009). The increase in trash output on both developed and developing countries caused serious environmental, economic, and social issues (Dharmarathne and Gunatilake, 2013). Solid wastes in India have emerged as the major environmental issue because of its high population density. The landfill leachates were regarded as a significant environmental concern since they have a major impact on soil, surface and ground water (Mohan and Gokul, 2022). Leachate wastewater is highly contaminated, foul-smelling, dark-brown colored liquids that are formed when rainwater seeps through landfill layers and when organic wastes decompose (Ghaffariraad and Ghanbarzadeh Lak, 2021). The environment and aquatic organisms are harmed by the different organic chemicals, heavy metals, ammonia nitrogen, soluble salts, BODs, CODs, suspended particles, etc. that are present in landfill leachate (Christensen et al., 2001). The extremely concentrated ammonia nitrogen concentration of leachates creates a variety of issues, including rapid eutrophication, algae growth, and dissolved oxygen depletion (Niza et al., 2021). Landfill age, kind of trash disposed of, percolation, climatic conditions, and other variables all influence the composition of the leachate. Based on their age leachate from landfills are divided into three categories: young (5 years), intermediate (5–10 years), and mature or stable leachates (>10 years) (Amor et al., 2015).

Treatment of leachate is necessary to control the ground water pollution, soil pollution and air pollution; however it is challenging because of leachate's intricate structure. The numerous available procedures for the treatment of landfill leachates include biological treatment methods, membrane processes, coagulation, flocculation, and AOP (Avsar et al., 2007). Biological treatments were considered as an efficient method for treating young leachates because of its higher BOD_5/COD ratio. However, it was not preferred for treating mature leachate (Li et al.,2017) since it contains high molecular weight contaminants, higher concentration of N_2 and other organic matter (Klein et al., 2017) which are not easily biodegradable. One of the efficient methods to treat mature leachates was the physicochemical treatment process. Among the various physicochemical processes, AOP method was most preferred since it was cost effective and has good removal efficiency. Biodegradability of mature leachate was improved by AOP (Deng and Englehardt, 2008). AOP uses Reactive Oxygen Species (ROS) for the mineralization of organic contaminants (Ma et al., 2021). By using reactive chemicals species like hydroxyl radicals (OH^-), the most recalcitrant molecules were degraded into bio-degradable compounds (Gogate and Pandit, 2004). The various technologies of AOP include photo catalytic oxidation, Fenton and Fenton-like oxidation, ozonation, electrochemical oxidation and SR-AOPs. In general, combined AOP technologies were preferred over individual AOP because it exhibits higher oxidation efficiency.

The ROS was efficiently generated by different AOP combinations that include TiO_2/UV, H_2O_2/ UV, UV/Fe^{2+}/H_2O_2, UV/O_3, Fenton/ Photo Fenton, Fenton/ Electro Fenton and so on (Abdelhaleem and Chu, 2020; Rocha et al., 2011). Henry J. Fenton was discovered the Fenton process in 1894 (Vorontsov, 2019). One of the efficient technologies used in AOP is the Photo Fenton method. The Fenton technique was frequently enhanced by using a variety of photo sources. Based on the applied photo sources, the Photo Fenton process is classified as Solar photo Fenton, Visible light photo Fenton and UV light photo Fenton. Hydroxyl radicals are used as the main oxidizing agent in this process. The combination of ferrous ions and H_2O_2 forms the Fenton reagent. The Fenton's reagent always uses a catalyst for the reaction process. The effective removal of contaminants was achieved by combining high concentrated H_2O_2 and low concentrated ferrous ions. However, it cannot be directly applied to the contaminated surface since it kills the surface microorganisms (Hartmann et al., 2010). The regeneration of ferrous ions and exhibiting of more hydroxyl radicals in the Photo Fenton process Eq.(1) and (2) highly enhances the degradation of organic contaminants when compared to any other conventional Fenton methods (Primo et al., 2008 and Bautitz et al., 2007). To produce the hydroxyl radicals, Hydrogen peroxide was being decomposed by ferric ions under the presence of UV irradiation and under acidic conditions (Poblete and Perez 2020).

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

$$Fe^{3+}+H_2O+hv \rightarrow Fe^{2+}+{}^{\bullet}OH+H^{+} \qquad (2)$$

In these reaction cycles complexes and hydroxides of iron ions were the major contributors. This reaction can be driven by visible and UV light because of the broad absorption bands of these complexes. Generally, Design of experiments (DOE) was used to examine the association of multiple input factors and key output responses. There are several methods available to analyze the design in DOE. The most commonly used methods are Response Surface Methodology and Taguchi OA method of analysis. The orthogonal array experimental optimisation design was put forwarded by Taguchi. In this design the effect of various factors on the performance characteristic were examined in a condensed set of experiments. The parameters which affects a process and the levels at which these factors should be fluctuated can be found by Taguchi method. Selection of the proper orthogonal array was the most important process in TOA methodology. It was selected by number of parameters and their levels (Fraley et al., 2006). Compared with other DOE methods, Taguchi was quiet easy and convenient to use. Results obtained from Taguchi analysis closely match the actual values. Taguchi analysis was performed using many software's like design expert and Minitab. However, Minitab statistical software has many graphical outputs and user friendly tools to analyze. Data transformation, analysis of variance, correspondence analysis, regression analysis, multivariate analysis of variance, analysis of covariance, factor analysis, neural network, correlation was also done by minitab software (Okagbue et al., 2021). The present study focusses on solar, UV, and LED visible light photo Fenton processes used to treat landfill leachate. It also compares and examines the pollutant degradation effects of each process by using Taguchi statistical experimental method in Minitab software (Version 21.1.0).

2. Material and Methods

2.1. Materials

2.1.1. Raw leachate wastewater collection and chemicals used

The matured landfill leachate samples were obtained from a dumpsite in Dindigul, Tamil Nadu, at various time periods between the months of March and April at same point of source. In order to stop the material from decomposing, it was kept at 4°C. Every chemical utilised in analytical grade was acquired from Merck. Chemicals utilised in this study included diluted HCl (1.0 N), sodium chloride solution (0.1 N), Ferrous sulphate powder ($FeSO_4 \cdot 7H_2O$=278.01), buffer solution, hydrogen peroxide (30% W/V), and NaOH (1.0 N). Treated supernatant wastewater samples were filter through Wattman filter paper No.40 and pollutant concentrations in leachate samples before and after treatment were determined, and the effectiveness of the three methods (Solar Photo Fenton, UV Photo Fenton and LED visible Fenton process) for removing pollutants was compared.

2.1.2 Analytical procedures

Physico-chemical characteristics of collected leachate sample were studied before and after treatment according to the guild lines of standard methods (APHA, 2013). Turbidity was measured using Portable turbidity meter (model: 331, make: Deep Vision) and values were recorded in nephelometric turbidity units (NTU). pH meter(model:111120306,make:Deep vision) used to measure and also adjust the pH value, UV-visible spectrophotometer(Model: DR6000, make: HACH, CO., USA) was used to calculate color removal, gravimetrical method to determine total solids, total suspended solids and total dissolved solids, Heavy metal concentration in before and after the treatment of leachate sample was studied using Atomic absorption spectroscopy (AAS) (model name – Shimadzu Atomic Absorption Spectrophotometer AA6300;ROM version-1.03)

2.2. Experimental setup

2.2.1. Solar Photo Fenton, UV Photo Fenton and LED visible Fenton process

Solar photo Fenton study was carried out in the open sunlight at terrace of main building, University college of Engineering, Dindigul. The study was performed with 1000ml glass beaker with magnetic stirrer to achieve even mixing (Pignatello et al., 2006). 500ml wastewater sample was taken for each study. UV and visible light Fenton process carried out with artificial light sources of Super 395nm UV light (size of UV lamp – 3.5 cm × 8.5 cm) and Wipro LED B22 Bulb Base with 50 lumen coverage. Stable radiation was maintained in UV and LED visible light Fenton process at room temperature in laboratory. pH level was varied from 2 to 3.5, $FeSO_4$ concentration varied from 1 to 2.5 g/L while H_2O_2(30% W/V) concentration was maintained at 30 g/L, reaction times of 30, 60, 90, and 120 were chosen for this study. Based on the findings of the preliminary investigation, the control variable limitations were fixed. Bubbles rising during the advanced oxidation process served as indicators that the oxidation process had begun in a solution. Leachate wastewater sample was combined with prepared Fenton Solution, and then the sample was taken into open atmosphere to conduct solar Photo Fenton experiment. The UV and visible light photo Fenton processes were identical to the solar photo Fenton experiment, but artificial photo sources were used. In place of sunlight, Wipro LED B22 Bulb Base with 50 lumen coverage and Super 395nm UV light (3.5 cm x 8.5 cm in size) were utilised in the UV and LED Visible Light Fenton procedure. Using the following equation, the percentage elimination of the response variables Color, COD, TSS, Cr, Cd, and Cu was computed (3).

Prepared Fenton Solution was mixed with leachate wastewater sample, then the sample was taken out to open place to triggering the oxidation process. UV and visible light photo Fenton process were same as solar photo Fenton process, but UV radiation was artificially used. Super 395nm UV light (size of UV lamp – 3.5 cm × 8.5 cm) and Wipro LED B22 Bulb Base with 50 lumen coverage light sources were used in UV and LED Visible Light Fenton process as a replacement for sun light. The percentage removal of response variables Color, COD, TSS, Cr, Cd and Cu was calculated using the following Eq.(3).

$$R = \frac{(\text{Initial Value of response variable} - \text{Final value of response variable}) \times 100}{(\text{Initial value response variable})} \quad (3)$$

Where,

R(%) - Removal efficiency in percentage

2.2.2. Taguchi experimental design

The experiments were examined and optimized by Taguchi experimental design method. It was an orthogonal array design. It is an efficient method when compared to other design methodologies since it enables desired parameter optimization to be less than or equal to 90%. In this present study three different type of photo Fenton process (Solar, UV, and Visible light) were individually analyzed by Taguchi method. Control factors such as pH, dosage, Time and their levels were fixed in this Taguchi experimental design. It was furnished in Table 1. From the findings of the preliminary one-time classical investigation, each level of the control parameters was fixed.

2.2.3. Signal-to-Noise Ratio S/N

The S/N ratio clearly identifies uncontrollable variables or undesirable noise in the experimental input and output parameters. According to Minitab's S/N ratios there are three types of performance characteristics: Larger the better, smaller the better and nominal the better. To evaluate the experimental design for the treatment of leachate for all three experimental procedures, larger the better choice was selected from Eq(4).

$$S/N = -10 \text{ x } \log (\Sigma (1/Y^2)/n) \qquad (4)$$

Where Y = responses for the given factor level combination

n = number of responses in the factor level combination.

2.2.4. ANOVA

Analysis of variance (ANOVA), which is used to confirm the significance of the model, describes the importance of the experimental modal and provides extensive information on the most influencing factor for this Photo Fenton process. The findings of an ANOVA are widely applied to analyse the interaction behaviour among the control variables and responses. Each factor underwent a qualitative significance analysis using the F and P values. The design is considered significant if the probability value (p value) is less than or equal to 0.05. F value greater than Fcr value for each factor confirm that the adequacy of the modal. The total degrees of freedom (DF), Adjusted mean squares (adj MS) Adjusted sums of squares (adj SS), S value and R^2 value also can obtained from ANOVA; it is easy to predict the significance of the experimental design.

3. Result and Discussion

3.1. Physio-chemical Characteristics of matured landfill leachate wastewater

The obtained matured landfill wastewater samples had the following physio-chemical properties as follows- pH 8.5, dark brown color with high colloidal nature, foul odour, 562 mg/L of BOD_5, 960 NTU of turbidity, 2521 mg/L of COD, 5513 mg/L of Total solids, 4327 mg/L of Total dissolved solid , 1214 mg/L of Total suspended solids, the heavy metal concentration was 1.198 mg/L of chromium, 0.2 mg/L of cadmium, 0.77 mg/L of copper.

3.2 Comparative analysis of Photo Fenton oxidation process: Solar, UV and LED visible light photo

In this present investigation, the control factor levels of the pH, Fenton Dosage, and reaction time were chosen as the same values for solar, UV, and LED visible light photo Fenton experiment. All the three photo Fenton experiments showed the best pollutant reduction efficiency in pH 3. Fenton reaction was often quite active at pH 3 or lower. Solution in an acidic environment (2-4) promotes the formation of more $OH^{\cdot}$ ions, which results in a high rate of oxidation (Pignatello et al., 2006; Silva et al., 2015 and Kavitha et al., 2005). From the study, it was observed that Fenton process heavily depends on the rate of $OH^{\cdot}$ ions scavenged because when pH values greater than 3 demonstrated less pollutant degradation potential. Higher pH causes the reaction between ferric ions and H_2O_2 to produce more ferric hydroxo species, which reduces the effectiveness of pollutant degradation (Karale et al., 2014; Ipek Gulkaya et al., 2006 and Badawy et al., 2006). The pH is a significant factor in molar fraction of iron –inorganic, iron-organic and iron-water species (Silva,et al., 2015), so the effectiveness of pollutant removal was greatly influenced by pH.

In this solar, UV, and LED visible light Fenton investigation, the dosage concentration of $FeSO_4$ was adjusted from 1 to 2.5 g/L while 30 g/L of H_2O_2 dosage remained constant. Pollutant degradation effectiveness was excellent up to a dosage of 2 g/L, but as the dosage increased, iron precipitation formed, which slowed down the reaction. Higher concentration of $FeSO_4$ dosage induced the self – hindrance of $OH^{\cdot}$ radical which reduce the pollutant degradation efficiency, $OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$ (Du and Qiu 2013), because both H_2O_2 and Fe^{2+} can serve as radical scavengers. Several researches believed that the ideal dosage of these two compounds was crucial to achieving high pollutant degradation efficiency (Tang and Tassos, 1997 ; Kochany and Lugowski, 1998).In the photo Fenton experiment H_2O_2 initiate superior effect in oxidizing organic complexes and producing of more oxygen ions in the presence of Fe^{2+} ion (Panizza and Cerisola, 2001). Fenton experiment is also activated at lower Fe^{2+} ion concentrations, but the removal is inefficient. The photo Fenton method is more preferable than classical Fenton method since it results in less iron sludge formation by decreasing the dosage of catalyst and Solar sources (Solar or UV) increase the utilization of H_2O_2 (Bandala et al., 2009; Giri and Golder, 2014 and Xiao et al., 2014).

There were four different time intervals used for the solar, UV, and LED visible light photo Fenton processes: 30, 60, 90, and 120 minutes. Maximum results for the Solar Fenton procedure at 60 minutes of reaction time were 95% of color, 83% of COD, and 89% of TSS. At 120 minutes of reaction time, the UV and LED visible Fenton processes demonstrated maximum of color 93% and 90%, COD 79% and 81% and TSS 87% and 84% removal efficiencies respectively. In comparison to UV and LED visible Fenton processes, the solar Fenton process demonstrated good removal efficiency in a shorter reaction time. According to (Jyoti Katara and Reshma Patel 2018), the solar Fenton process outperformed the UV Fenton method in terms of pollutant degrading efficiency. Temperature and UV radiation intensity may be to causes for the pollutant's fast deterioration in the solar Fenton reaction. The study was done in the morning at 10:30 am - 12.30 pm, when the outside temperature varied from 34 to 36°C and the inside room temperature was between 31 and 33°C. High temperature boosts the effectiveness of pollutant degradation by increasing $OH^{\bullet}$ production and H_2O_2 consumption (Zazo et al., 2011). The production of more hydroxyl radicals ($OH^{\bullet}$) by the ferrous ions and hydrogen peroxide (H_2O_2) combination in the treatment method, high COD removal was achieved (Lucas et al., 2007 ; Gallard and De Laat 2000). During the Fenton process, hydroxyl radicals convert all the minerals in wastewater into CO_2, water, and inorganic compounds. The study was carried out on Fenton process for landfill leachate using two standard high-pressure mercury-vapor immersion lamps (100 W and 450 W) and a specially made 8 W 365 nm UVA-LED lamp (Tejera et al., 2021). With an 8 W 365 nm UVA-LED lamp, COD could be removed 90%, whereas high pressure mercury vapour immersion lamps demonstrated poor COD removal. UV radiation improves the usage of H_2O_2 concentration and speeds up the photolysis process on each small organic molecule, but the visible light photo Fenton process requires a long processing time and higher energy consumption. Using 14 W UV lamps at 1.1 g/L Fe ion and 5.5 g/L H_2O_2

concentration, 84.43% of COD and 92.54% of total PAHs were removed from landfill leachate wastewater (Singa et al., 2018). The three treatment methods virtually always used the ideal Fenton dose concentration. Optimum Fenton dosage concentration was almost common in the all three treatment method. In comparison to UV radiation from artificial sources, solar sources was higher in pollutant degradation because more active photons from high light wave length of solar induced high reaction rate in comparison to the other two artificial photo sources. In the current investigation, it was found that pH and UV radiation both had a significant impact on the pollutant degradation in landfill leachate wastewater in all three Fenton processes. In comparison to the standard Fenton method, the solar photo Fenton procedure demonstrated greater pollutant degrading efficiency (Vilar et al., 2012).

3.3. Statistical Experimental Result

In Taguchi experimental optimization techniques, OA L16 (4^{3}) was used to optimize the process variables using minitab statistical software (Version 21.1.0). pH, Dosage concentration and Time were taken as a control variables and color, COD, TSS, Cr, Cu and Cd were taken as a responses. All the experimental values were analyzed in three times and average values noted. Experimental results of solar, UV and LED visible light photo Fenton process corresponding to L16 design were presented in Table 2, Table 3 and Table 4 respectively. Totally 16 number of runs were performed for each solar, UV and LED visible light Photo Fenton method. Solar Fenton process achieved maximum amount of color 95%, COD 83%, TSS 89%, Cr 94%, Cd 86% and Cu 93% at control factors level 3 pH (pH 3), level 2 dosage (Dosage 1.5:30 g/L) and level 2 (60 minutes) reaction time. From Table 3 and Table 4 it was observed that UV and Visible light photo Fenton method needed higher reaction time to show the better removal efficiency. Photo Fenton mechanism highly depends on the emission frequency of the light source, availability and absorption rate of photoactive species (Pignatello et al., 2006).

Figure 1 illustrates the S/N ratio, which describes how each control factors affects each response. The control variables pH, dose concentration (Fe^{2+}/H_2O_2), and reaction time were plotted in the S/N ratio graph's X axis, and each response (Color, COD, TSS, Cr, Cd, and Cu) was plotted in the graph's Y axis. S/N ratio graph clearly demonstrate that pH played a major role in the elimination of color, COD, TSS, Cr, Cd, and Cu in all three of the treatment processes—solar, UV, and LED.

Tables 5 and 6 display the ANOVA results for the solar, UV, and LED visible light photo Fenton processes. For all three processes (Solar, UV, and LED Fenton process), almost all of the p values were less than 0.05, and larger F values indicate that the designs were significant. In the ANOVA results, pH had a very high SN value, demonstrating that pH was an important factor in the breakdown of pollutants throughout all treatment stages. Table 7 gives the detailed summary report of Taguchi experimental design results of these three types of Fenton process. From Table.7, it was observed that R value more than 99% for all the control variables for all the three methods, it is evident that the good correlation between the each responses and each operating variables. Almost all the methods achieved more 97% of adj R^2 value; it also confirms the significance of this design. Less residual error (less than 50%) in total run indicates the results to be reliable (Pourjafar et al., 2013 and Reyhani, et al., 2015). F value should be greater than Fcr value otherwise the design was not significant (Sousa, et al., 2020). In this robust design DF value for each factor is 3 a residual error is 6 so the confidence level is more than 95% for all the factors in these three methods. Fcr < F, it confirms that this design is significant.

Figures 2 and 3 illustrated interaction effect of pH and dosage concentration on color and Cr removal in 2D Contour plots. The well-conditioned elliptical form is strong indication that the pH and dose concentration for the elimination of color and Cr interact more. Solar Fenton technology removed up to 95% of the color and 94% of the Cr, UV Fenton technology removed up to 93% of both the color and Cr, and LED visible light technology removed up to 90% of the color and 91% of the Cr. In this study the heavy metals concentration of before and after the treatment was analysed with AAS. The Fenton process was a suitable choice for removing phenol, cyanide, and Cr (VI).

Compared to TiO2/UV, the H_2O_2/UV method demonstrated a quicker decrease of chromium (Golbaz et.al., 2013). Municipal wastewater can be successfully treated with the solar photo Fenton technique to remove heavy metals (Cr 92%, Pb 100%, Cu 72.4%, Cd 100%, Ni 36%, Fe 94%, Zn 58%) (Chaudhary et.al., 2012 and Barwal et.al., 2015).

Figure.4 a, b and c furnished the probability plot of removal efficiency of Solar, UV and LED visible light Fenton process. It is confirmed that all of the control variables and responses had a positive interaction impact on one another because all of the anticipated and observed values are followed in a straight line and the 95% confidence limit is displayed. Solar photo Fenton technology has been described as being both affordable and appropriate for complex industrial wastewater (Malato et al., 2013).

4. Conclusion

According to the findings of this investigation, with one hour of reaction time at an acidic pH, the solar-assisted Fenton process successfully removed color, COD, TSS, Cr, Cu, and Cd from landfill leachate wastewater, whereas the other two methods required longer reaction times. Using the Taguchi technique, the most accurate data and relationships between controls and responses may be gathered and analysed with the fewest number of experimental designs. The findings of this experiment demonstrate that generation and rate of scavenging of hydroxyl radicals in the process highly depends on pH and UV radiation. The three techniques' R^2 values were greater than 99%, which demonstrated the model's good suitability. The solar, UV, and LED visible light Fenton processes are all effective at removing pollutants from landfill leachate wastewater while generating a less amount of sludge as compared with other Physico- chemical methods. However, solar photo Fenton process has higher removal efficiency and uses a naturally occurring energy source in comparison to the other two artificial photo sources. Organic pollutant and heavy metal reduction in landfill leachate wastewater can be accomplished using the competitive and promising solar photo Fenton process.

Future directions

Economical contribution of these three processes has to be investigated. There have also been other studies done on the efficiency of micro pollutant degradation. Investigating various UV sources and wave lengths may improve the efficiency of pollutant degradation.

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Conflict of Interest

The authors declare that there are no competing interests associated with this research work.

Author contributions

First author collected wastewater samples, conducted all the experimental studies, analysed the results and prepared the manuscript.

Second author analysed the result finding, validated the results and reviewed the manuscript

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Figure 1. S/N ratio Plot for color removal with each control factors for Solar (a), UV (b) and LED visible light (c)

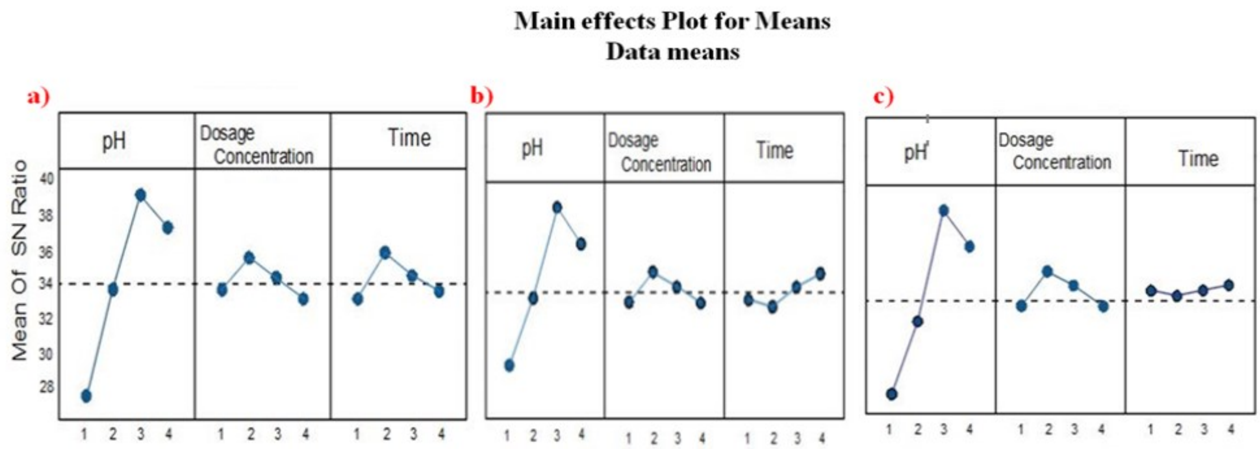
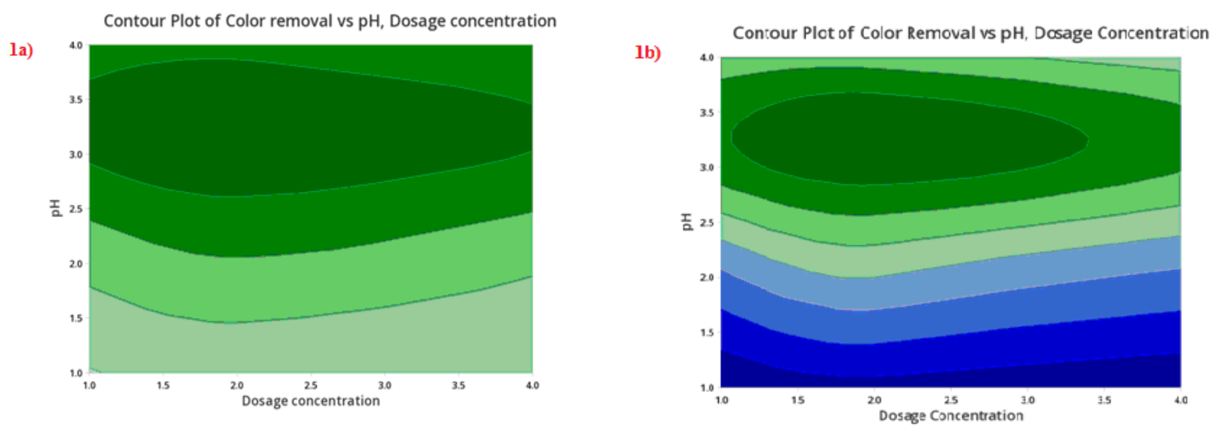


Figure 2. 2D Contour plot for removal of color by using Solar (1a), UV (1b) and LED visible light photo Fenton (1c)



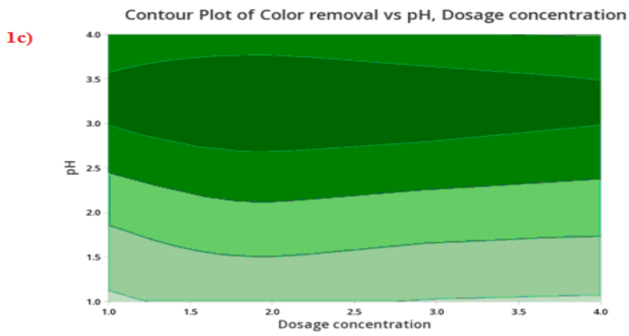


Figure 3. 2D Contour plot for removal of Cr by Solar (2a) , UV (2b) and LED visible light photo Fenton (2c)

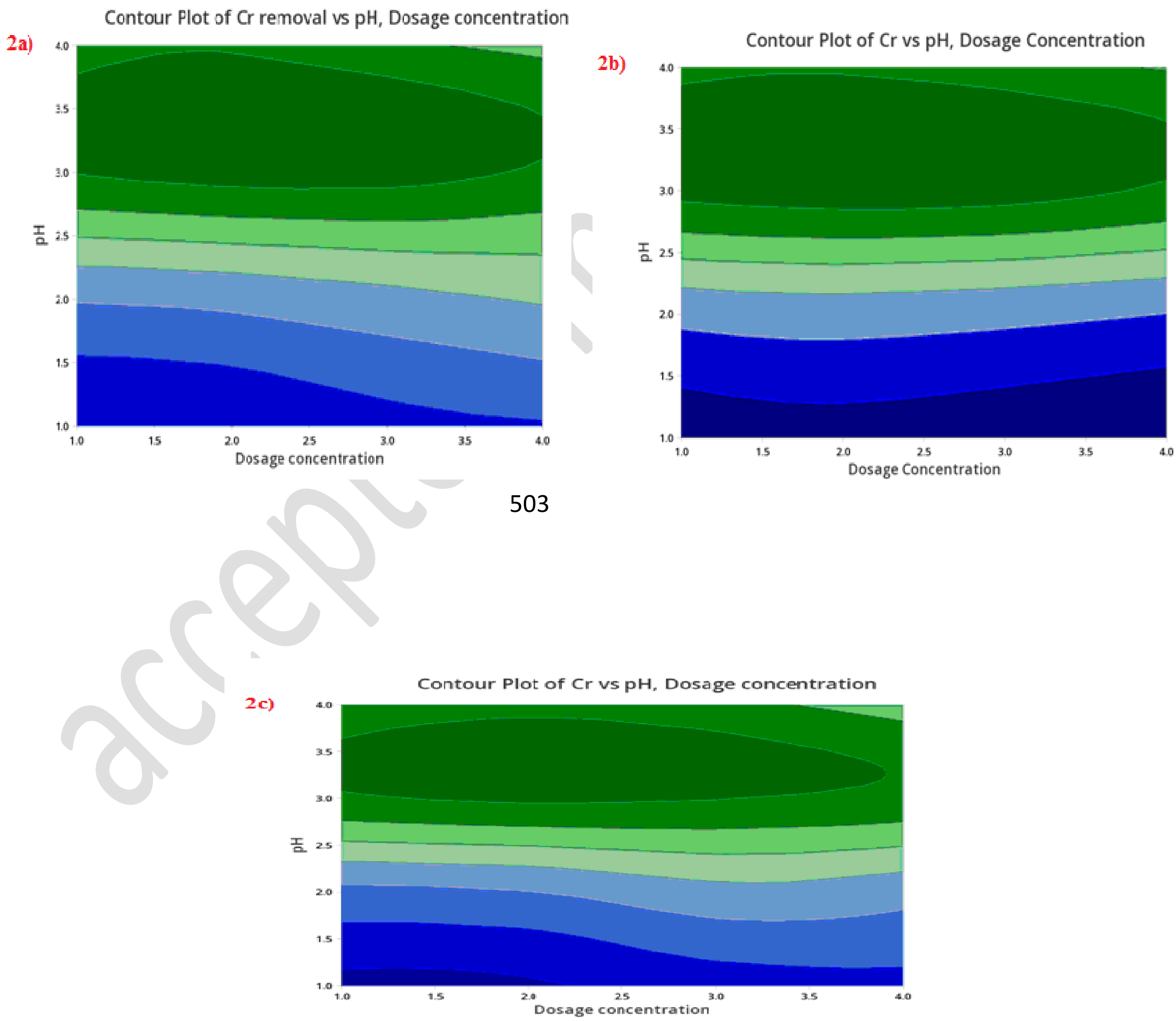


Figure 4. Probability plot for removal Efficiency of Solar (a), UV (b) and LED visible light (c) Fenton process

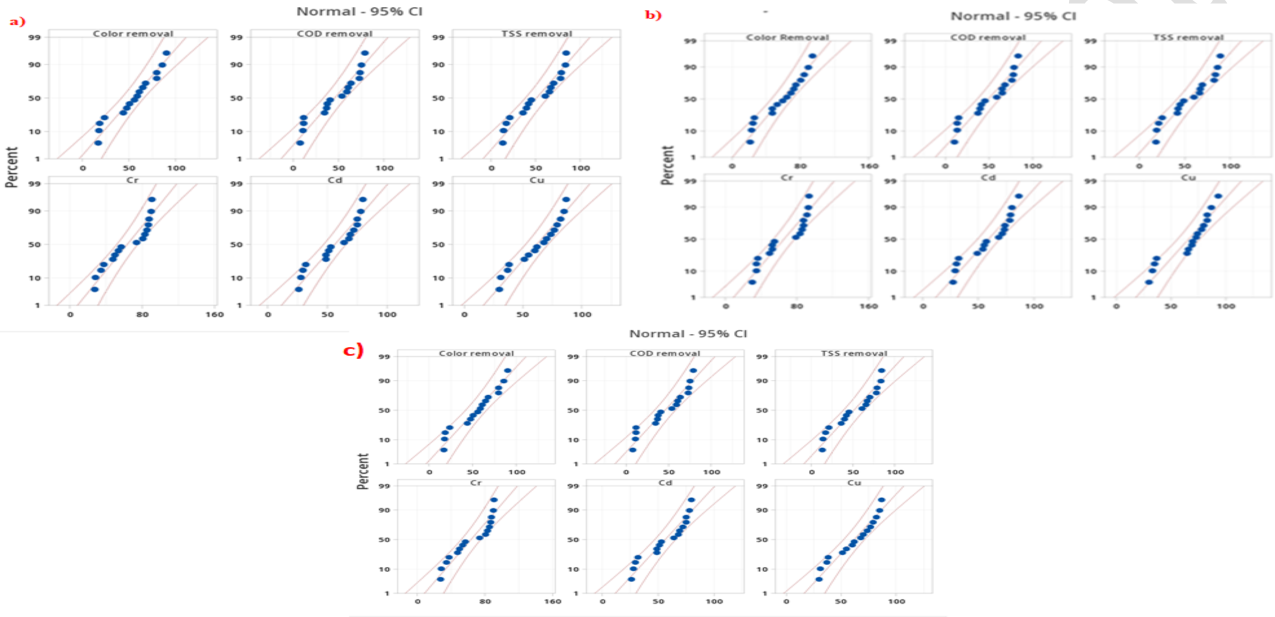


Table 1. Operating factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
pH	2	2.5	3	3.5
Dosage(g/L) ($FeSO_4$: H_2O_2)	1:30	1.5:30	2:30	2.5:30
Time (min)	30	60	90	120

Table 2. Experimental results corresponding to L 16 design of solar Photo Fenton process

Run	pH (Level)	Dosage (Level)	Time (Level)	Color (%)	COD (%)	Total Suspended Solids (%)	Cr (%)	Cd (%)	Cu (%)
1	1	1	1	22	13	19	35	30	35
2	1	2	2	27	15	25	37	32	37
3	1	3	3	25	13	21	35	29	33
4	1	4	4	23	10	18	31	27	30
5	2	1	2	60	45	49	58	57	73
6	2	2	1	48	37	43	55	54	69
7	2	3	4	53	40	45	50	49	70
8	2	4	3	46	39	43	53	55	68
9	3	1	3	85	76	82	92	84	85
10	3	2	4	87	79	87	90	82	83
11	3	3	1	72	70	86	90	80	88
12	3	2	2	95	83	89	94	86	93
13	4	1	4	75	65	67	86	70	68
14	4	2	3	73	63	69	88	73	70
15	4	3	2	78	68	69	88	74	74

Table 3. Experimental results corresponding to L 16 design of UV Photo Fenton process

Run	pH (Level)	Dosage (Level)	Time (Level)	Color (%)	COD (%)	Total Suspended Solids (%)	Cr (%)	Cd (%)	Cu (%)
1	1	1	1	19	11	16	30	28	33
2	1	2	2	25	14	23	32	30	33
3	1	3	3	21	14	19	37	33	38
4	1	4	4	20	10	15	39	34	40
5	2	1	2	46	39	39	51	51	64
6	2	2	1	58	43	47	53	55	71
7	2	3	4	53	40	45	57	61	73
8	2	4	3	43	37	43	61	65	79
9	3	1	3	82	76	80	90	77	81
10	3	2	4	93	81	87	93	82	91
11	3	3	1	88	75	86	93	80	87
12	3	4	2	79	70	78	88	77	85
13	4	1	4	69	62	65	84	71	77
14	4	2	3	73	65	68	88	74	76
15	4	3	2	65	60	63	82	71	70
16	4	4	1	61	59	60	77	66	65

Table 4. Experimental results corresponding to L 16 design of LED Visible light Photo Fenton

Run	pH (level)	Dosage (level)	Time (level)	Color (%)	COD (%)	Total Suspended Solids (%)	Cr (%)	Cd (%)	Cu (%)
1	1	1	1	17	11	14	28	26	30
2	1	2	2	24	12	21	29	28	31
3	1	3	3	19	12	17	35	30	37
4	1	4	4	18	8	13	38	32	38
5	2	1	2	44	37	36	48	49	62
6	2	2	1	56	41	45	50	53	68
7	2	3	4	51	38	42	57	51	55
8	2	4	3	48	35	40	54	49	51
9	3	1	3	80	74	78	88	75	79
10	3	2	4	90	79	84	91	80	87
11	3	3	1	86	75	83	90	78	85
12	3	4	2	80	73	79	87	75	82
13	4	1	4	65	61	67	81	69	74
14	4	2	3	68	64	70	86	72	77
15	4	3	2	61	59	65	83	68	70
16	4	4	1	59	54	61	74	64	66

Table 5. ANOVA for SN ratios of Color removal by Solar, UV, and LED Visible light Photo Fenton process

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Analysis of Variance for SN ratios of Color removal by solar photo Fenton						
pH	3	835.506	835.506	311.835	460.7	0.000
Dosage	3	7.704	7.704	2.568	3.79	0.039
Time	3	2.831	2.831	0.944	1.39	0.033
Residual Error	6	6.061	6.061	0.677		
Total	15	852.102				
Analysis of Variance for SN ratios of Color removal by UV photo Fenton						
pH	3	345.799	345.799	181.933	207.2	0.000
Dosage	3	9.459	9.459	3.153	3.59	0.036
Time	3	1.701	1.701	0.567	0.65	0.013
Residual Error	6	7.267	7.267	0.878		
Total	15	364.226				

Analysis of Variance for SN ratios of Color removal by LED Visible Light photo Fenton						
pH	3	307.833	307.833	69.2777	1303.20	0.000
Dosage	3	3.877	3.877	1.2924	24.31	0.001
Time	3	1.368	1.368	0.4559	8.58	0.014
Residual Error	6	0.319	0.319	0.0532		
Total	15	313.397				

Table 6. ANOVA for SN ratios of Cr removal by Solar, UV, and LED Visible light Photo Fenton

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Analysis of Variance for SN ratios of Cr removal by Solar Photo Fenton						
pH	3	338.724	338.724	79.5745	834.96	0.000
Dosage	3	4.135	4.135	1.3783	14.46	0.004
Time	3	1.773	1.773	0.5909	6.20	0.029
Residual Error	6	0.189	0.189	0.0630		
Total	15	344.821				
Analysis of Variance for SN ratios of Cr by UV photo Fenton						
pH	3	407.833	407.833	69.2777	1303.20	0.000
Dosage	3	3.877	3.877	1.2924	24.31	0.001
Time	3	1.368	1.368	0.4559	8.58	0.014
Residual Error	6	0.319	0.319	0.0532		
Total	15	413.397				
Analysis of Variance for SN ratios of Cr by Visible light photo Fenton						
pH	3	216.536	216.536	58.8453	708.87	0.000
Dosage	3	2.821	2.821	0.9403	11.33	0.007

Time	3	0.524	0.524	0.1747	2.10	0.021
Residual Error	6	0.498	0.498	0.0830		
Total	15	220.379				

Table 7. Summary of contribution of each factor for Solar, UV and LED visible light Fenton process.

Treatment Method	**Solar**			**UV light**			**LED visible light**		
Performance Criteria	S	R-sq (%)	R-sq Adj (%)	S	R-sq (%)	R-sq Adj (%)	S	R-sq (%)	R-sq Adj (%)
Color	0.1652	99.90	99.69	0.9752	99.30	98.99	0.9752	99.30	98.99
COD	0.6854	99.29	98.67	0.4754	99.56	99.27	0.4754	99.56	99.27
TSS	0.3140	99.55	97.75	0.5240	99.45	99.07	0.5240	99.45	99.07
Cr	0.2511	99.92	99.60	0.2313	99.82	99.65	0.2313	99.82	99.65
Cd	0.7196	99.18	98.90	0.9186	99.00	98.47	0.9186	99.00	98.47
Cu	0.3464	99.80	99.00	0.3534	99.85	99.26	0.3534	99.85	99.26