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Photo Fenton oxidation treatment for COD removal in sunflower wastewater

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Abstract

The overall objective of the current study was to investigate the possibilities of using Fenton oxidation (Photo-oxidation) as a mechanism of COD elimination that is available in sunflower wastewater (SWW). It's chiefly appropriate aimed at the handling of organic, and at current, it is one of the most promising advanced oxidation skills. Precisely, rapid Fenton oxidation, which features high elimination competence, thorough reactions, insignificant subordinate contamination, etc., has led to numerous studies on by means of the Fenton reaction toward destroy COD in SWW. In investigational studies, finest experimental limits for example Fenton's reagent, pH, temperature, Irradiation time and light intensity were determined. 98.41% and 78.29 % COD removal for photo-Fenton and Fenton process correspondingly were found. The adding of UV radiation toward the Fenton technique occasioned in improved squalor of COD elimination. Though the best irradiation time of the Fenton process was 150 min, the best reaction time of the photo-Fenton process was 120 min.

Keywords: *Sunflower wastewater, wastewater treatment, advanced oxidation processes (AOPs)*

1. Introduction

Today, water contamination has turned out to be a major danger that facing humans. Progressively, domestic households produce wastewater that can cause pollution of many seas, rivers, groundwater, as well as lakes. This destruction adds for producing various contaminated water which the individuals not using in their daily lives [1]. Furthermore, the harmed water has produced from a wide range of sources including oil refineries, colors, paper, material color, cleansers, surfactants, pesticides, herbicides, bug sprays and pharmaceutical producers [2].Water contaminants can arrive the water environment in numerous ways, also discharged directly from treatment plants that shied away from their duties or industrial wastewaters from various treatment plants, such as petrochemicals , oil refinery , textiles, and tanning [3] . The sunflower oil industry discharges wastewater in large quantities and the discharged wastewater is quite polluted [4]. In the manufacture of sunflower oil, the wastewater from the refining section comprises substantial quantities of chemicals for instance oil, soap, sodium carbonate, sodium hydroxide, sulfuric and phosphoric acids. The release of this wastewater into the environment remains producing countless problems [5]. Mainly in aqueous environments, water cuts in contact with air, plummeting the quantity of oxygen in the water and posing a excessive hazard toward living life [6]. The quantities and characteristics of wastewater differ from one oil manufacturing to another as the characteristics of wastewater are mainly determined by the concentration of the polluted oil and the procedure followed, and its high COD content leads to high organic and inorganic loading [7 and 8].Numerous waste water growths rummage-sale for example coagulation /flocculation, adsorption, ultrafiltration and biological can remain rummage-sale for organic elimination from waste water [9 and 10]. However, these methods are nondestructive, then they only transfer the organic matter into mud, giving increase toward original category of pollution, which necessities extra action [11]. Henceforth there is a vital to grow handling approaches that are additional operative in eliminating organic compound from the industrial wastewater [12]. In new year's care have been attentive on chemical oxidation growths by means of Fenton reagent with UV light aimed at the handling of wastewater [13 and 14]. Fenton oxidation had been originated to be operative in humiliating the headstrong organic contaminants [15]. AOPS have aptitude of fast squalor of intractable pollutants in the water environment [16]. These procedures can completely degrade the pollutants into inoffensive inorganic materials for example CO2 and H2O underneath reasonable conditions [17]. AOPS is built on the cohort of extremely free radicals, which are very robust oxidizing agents [18]. The COD removal from SWW via photo Fenton oxidation is the focus of this paper. First, determine the optimal Fenton's reagent concentration by researching the effects of pH, UV lamps, and exposure time on photo Fenton processes. The second is how temperature affects the photo Fenton technique.

2. Experimental work

2.1. Chemical and analytical analysis

Sunflower wastewater polluted with organic droplets taster was obtained from the discharging of the Al-Rasheed Factory at Baghdad governorate. The sunflower wastewater was preserved at (4°C) in a polypropylene container to be treated by the oxidation technologies. The description of SWW is listed in Table 1. All chemicals used in this work were of analytical grade and used without any additional purification. Hydrogen peroxide (Germany 45% wt./wt.), H2SO4 (SDFCL 98 % purity) and Sodium hydroxide (Thomas baker). At the end of each experiment, collected samples were digested with an oxidizing agent (K2Cr2O7) for 120 min at 150 ^{o}C in (Lovibond COD reactor RD 125). Digested samples cooled down to room temperature then analyzed in a photometer (MD 200 COD VARIO Photometer). The values of pH and conductivity were measured using WTW pH-720 meter. The percentage of COD removal from the treated solution by the photo Fenton treatment was evaluated from equation (1).

$$COD\% = \frac{COD_o - COD}{COD_O} X100 \quad (1)$$

Table 1: Specification of sunflower wastewater used in this study.

Parameters	Values	Parameters	Values
COD	768 (mg/l)	Conductivity	44381.25 μS/cm
BOD	267 (mg/l)	TDS	28404 (mg/l)
pH	6.89	Viscosity	1.0504 m Pa/S
Iron	0.67 (mg/l)	TSS	174 (mg/l)
Specific gravity	0.998	Sulphates	113 (mg/l)

2.2. UV/H2O2 bench-scale batch reactor

The AOPs degradation experiments were conducted in 250 mL glass batch reactor contained 150 mL solution. The sunflower wastewater shaken at an equivalent stirring velocity around 200 rpm at room temperature for 30-150 min in the UV chamber equipped with eight UV each of 18W having a wavelength of 365 nm and it was originated to be 0.5 mW/cm2 using different UV lamp for this work as shown in Figure 1. A magnetic stirrer was rummage-sale to ensure uniform mixing of the solution in the reactor. The pH was adjusted beforehand addition the reagents through adding a dilute NaOH or H2SO4 solution, the pH of solutions was measured by means of WTWpH-720 digital pH meter. The different concentration of Fenton's reagent used in this work.

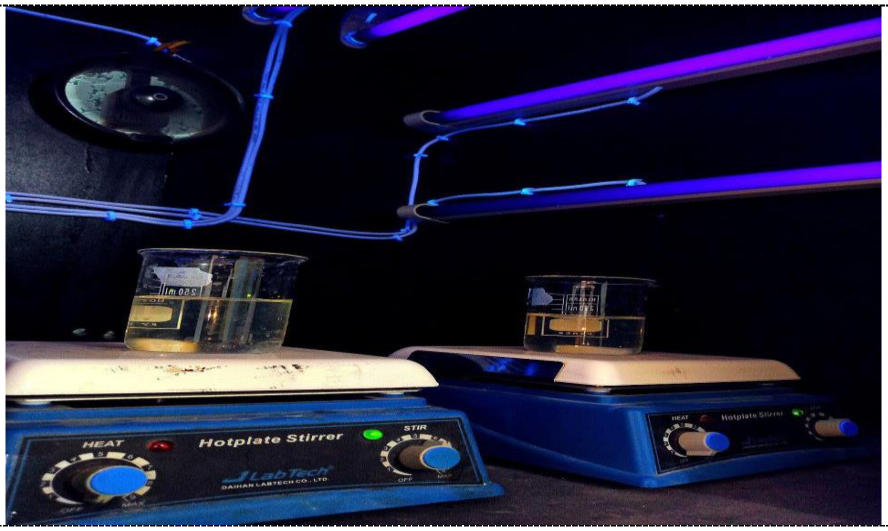

Fig. 1: Photo-Fenton chamber.

3. Results and discussion

3.1. Photo Fenton process

3.1.1. Statistical analysis for these processes

Forty-six statistically developed trials were designed to optimize and test the combined effect of independent variables for specific group of process parameters remained improved by means of the processes of box Behnken design (BBD) below RSM. The independent variables for instance Fenton's reagent, irradiation time, pH, UV Lamps, and temperature on the COD elimination in sunflower wastewater were given in the Table 2.

Table 2: Photo Fenton treatment

Sample	Irradiation Time (min)	pH	Hydrogen peroxide (ppm)	Ferrous Sulphate (ppm)	UV Lamps	COD removal
1	30	3	62.5	12.5	5	78.49
2	150	3	62.5	12.5	5	84.16
3	30	9	62.5	12.5	5	62.41
4	150	9	62.5	12.5	5	66.89
5	90	6	25	5	5	62.11
6	90	6	100	5	5	78.41
7	90	6	25	20	5	67.41
8	90	6	100	20	5	83.66
9	90	3	62.5	12.5	2	87.99
10	90	9	62.5	12.5	2	74.22
11	90	3	62.5	12.5	8	98.41
12	90	9	62.5	12.5	8	81.77
13	30	6	25	12.5	5	69.18
14	150	6	25	12.5	5	77.89
15	30	6	100	12.5	5	83.49
16	150	6	100	12.5	5	88.41
17	90	6	62.5	5	2	84.77
18	90	6	62.5	20	2	87.34
19	90	6	62.5	5	8	85.14
20	90	6	62.5	20	8	89.33
21	90	3	25	12.5	5	84.89
22	90	9	25	12.5	5	77.92
23	90	3	100	12.5	5	94.17
24	90	9	100	12.5	5	83.8
25	30	6	62.5	5	5	75.32
26	150	6	62.5	5	5	78.6
27	30	6	62.5	20	5	80.05
28	150	6	62.5	20	5	83.47
29	90	6	25	12.5	2	75.8
30	90	6	100	12.5	2	81.23
31	90	6	25	12.5	8	81.25
32	90	6	100	12.5	8	85.88
33	30	6	62.5	12.5	2	80.22
34	150	6	62.5	12.5	2	85.29
35	30	6	62.5	12.5	8	84.82
36	150	6	62.5	12.5	8	88.99
37	90	3	62.5	5	5	89.17
38	90	9	62.5	5	5	82.54
39	90	3	62.5	20	5	92.42
40	90	9	62.5	20	5	85.89
41	90	6	62.5	12.5	5	86.17
42	90	6	62.5	12.5	5	85.99
43	90	6	62.5	12.5	5	86.05
44	90	6	62.5	12.5	5	86.77
45	90	6	62.5	12.5	5	87.01
46	90	6	62.5	12.5	5	86.45

Regression equation 2 in uncorded units at room temperature.

$$\text{Removal (Y)} = 38.5 + 0.36x_1 + 0.05x_2 + 0.665x_3 + 1.24x_4 - 0.40x_5 - 0.001541x_1^2 - 0.084x_2^2 - 0.00348x_3^2 - 0.0424x_4^2 + 0.169x_5^2 - 0.0017x_1x_2 + 0.00042x_1x_3 + 0.00008x_1x_4 - 0.0012x_1x_5 - 0.0076x_2x_3 + 0.001x_2x_4 - 0.08x_2x_5 - 0.0000x_3x_4 - 0.0018x_3x_5 + 0.018x_4x_5 \quad (2)$$

The adequacy of the model was determined in ANOVA analysis Table 3 based on F test and P test. A regression equation will display more variance in response if the Fisher value is higher. The competence of the classical in ANOVA inspection remains recognized founded on Fisher F-test and P-test. P-value test is rummage-sale to regulate whether F is high sufficient to suggest statistical meaning (90%). The percent of variability of the model might remain elucidated if the was fewer than 0.05 [19].

Table 3: ANOVA for COD removal for Photo Fenton

Source	DOF	Seq. SS	Adj. MS	Fisher Value	P–test Value
1-Model	20	1785.75	89.288	2.75	0.009
Linear	5	1244.27	248.854	7.66	0.000
X_1	1	98.60	98.60	3.04	0.094
X_2	1	555.31	555.31	17.09	0.000
X_3	1	426.42	426.42	13.13	0.001
X_4	1	70.183	70.183	2.16	0.154
X_5	1	90.75	90.75	2.89	0.102
Square	5	531.56	106.312	3.27	0.021
X_1^2	1	268.50	268.50	8.26	0.008
X_2^2	1	5.02	5.02	0.15	0.698
X_3^2	1	209.11	209.11	6.44	0.018
X_4^2	1	49.61	49.61	1.53	0.228
X_5^2	1	20.10	20.10	0.62	0.439
2-Way Interaction	10	9.92	9.92	0.03	1.000
X_1*X_2	1	0.35	0.35	0.01	0.918
X_1*X_3	1	3.59	3.59	0.11	0.742
X_1*X_4	1	0.00	0.00	0.00	0.990
X_1*X_5	1	0.20	0.20	0.01	0.938
X_2*X_3	1	2.89	2.89	0.09	0.768
X_2*X_4	1	0.00	0.00	0.00	0.993
X_2*X_5	1	2.06	2.06	0.06	0.803
X_3*X_4	1	0.00	0.00	0.00	0.997
X_3*X_5	1	0.16	0.16	0.00	0.945
X_4*X_5	1	0.66	0.656	0.00	0.888
Error	25	812.22	32.489		
Lack-of-Fit	20	811.37	40.568	237.32	0.000
Pure Error	5	0.85	0.171		
Total	45	2597.97			
R^2	95.21				

Equation 1 it is Regression Equation for COD removal in sunflower wastewater. It is representing the relation between the independent variables (the parameters) and the dependent (the removal efficiency). The values of positive constants exposed that the COD elimination augmented with cumulative factors while negative coefficient values exposed the opposite effect. So that pH, Temperature and has a negative Impact on efficiency of removal, while the irradiation time, hydrogen peroxide concentration, UV Lamps and ferrous Sulphate have a positive effect.

3.1.2. The process parameters:

3.1.2.1. Effect of irradiation time

The effect of irradiation time for COD elimination in SWW was examined within different periods (30 – 150) min. The COD removal was 78.2 % at the 30 min as shown in Figure 2. It is rising with the time of the oxidation process increasing and continue with that until achieved the optimum irradiation time 120 min [20 and 21]. This fast degradation rate is due to advanced oxidation process which hydrolysis of contaminant, and creating the free radical necessitates a sufficient amount of time to complete these stages then, there is a slight increase. Further increasing of irradiation time does not lead to more COD degraded. Figure 2 shows the influence of irradiation time on the elimination. previous studies, the trend of this effect provided Photo-Fenton process was at pH=3 offered the best treatment time [22]. And the summary of the saying. The results show the positive effect of the irradiation time on photo Fenton process, that’s agree with [23].

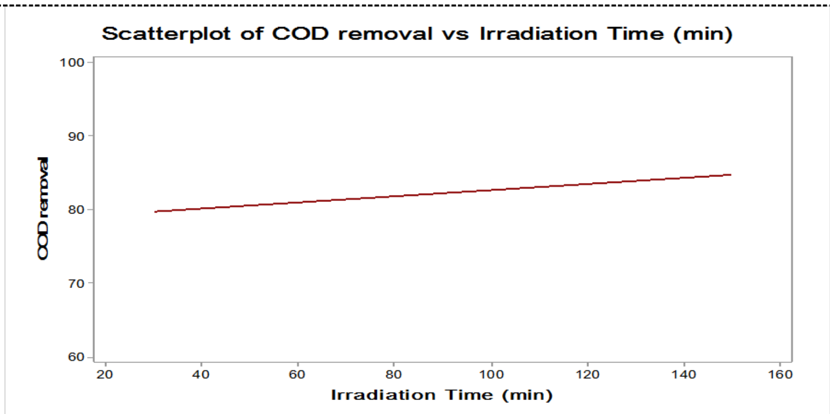

Fig. 2: Effect of irradiation time on COD elimination.

3.1.2.2. Effect of pH

The Fenton reaction remains strongly affected through the pH value due to effects the cohort of hydroxyl radicals and therefore the oxidation competence [24]. The pH value of the solution was varied and adjusted by adding sodium hydroxide or Hydrochloric acid. Figure 3 shows how the pH of the solution affects COD removal in sunflower wastewater. The removal efficiency of pH=3, pH=6, and pH=9, are (88.3, 81.2, and 77.12) %. From these results indicates increasing the pH leads to a decrease in COD elimination. The maximum degradation occurred at pH equal to 3, and the lowest removal efficiency was detected at pH =9. The decreasing in the degradation because of the reaction of Fenton reagent which at high pH value always present in the bulk Fe(III) species precipitate as Fe(OH)3 more rapidly which reducing the amount of fe+2 in the solution and contravention the hydrogen peroxide into oxygen and water [25]. The results appearances, the optimum pH was found equal to 3. The findings agree with Wang, et. al [26] that found, the best pH variety (2-5) in the photo Fenton process.

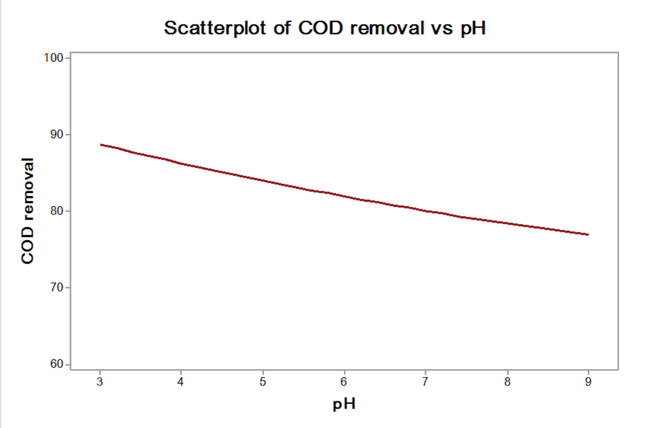

Fig. 3: Effect of pH on COD elimination.

3.1.2.3. Effect of hydrogen peroxide

Another significant parameter in getting the maximum percentage removal as well as uptake capacity in the Fenton process is the H_2O_2 concentration [27]. Hydrogen peroxide is a source of OH radicals and oxygen in the UV/H_2O_2/Fe^{+2} process, the amounts of H_2O_2 in this test were varied (25-100) ppm. In this process, the quantity of OH radicals formed be contingent on the concentration of H2O2. The results of this effect provided a common trend as represented in Figure 4 depict the effect of peroxide hydrogen on COD elimination from polluted water. The clearance rises in direct proportion to the quantity of H_2O_2 because more free radicals (HO*) are created, resulting in more pollutant recovery. This effect would succeed if the initial concentration of hydrogen peroxide continues to increase as equations 3 and 4, competing for the free radicals made by the presence of the COD in the wastewater solution [28] to achieve the highest possible value at (84.5ppm). After that, efficiency removal declines gradually with increasing amount of H_2O_2. That agree with Haider. et. al [29]. The raising of concentration of H_2O_2 above the optimum might have a negative impact on the process due to scavenging H_2O_2 by OH.

$$H_2O_2 + hv \rightarrow 2OH^* \quad (3)$$

$$H_2O_2 + OH^* \rightarrow H_2O + OH_2^* \rightarrow O_2^{*-} + H^+ \quad (4)$$

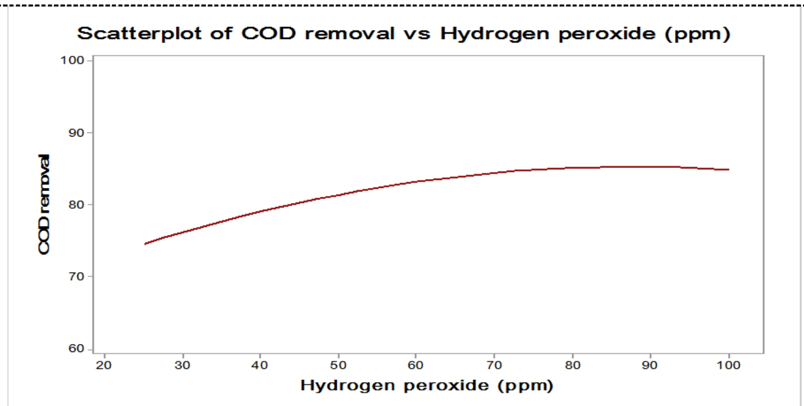

Fig. 4: Effect of hydrogen peroxide on the COD removal.

3.1.2.4. Effect of ferrous Sulphate

The ferrous Sulphate concentration is an important factor that affecting in photo Fenton processes [29]. To explore this effect on the degradation rate, various amounts of Fe+2 was tested in this study (5, 10, 15, 20) ppm, the efficiency removal was (78.76, 81.33, 84.78, 86.53) %. Figure 5 shows the practical effect of Fe+2 concentration on elimination. In this graph where notice the ferrous Sulphate Fe+2 concentration was increased, the elimination rate increases directly, to reach the optimum concentration of ferrous Sulphate at 20 ppm. Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions, they are having strong oxidizing properties. In this reaction ferrous ion initiates and the catalysis decay of hydrogen peroxide subsequent in the generation of hydroxyl radicals are made through a radical mechanism [30]. Also, it was notice Xiao, Y. et. al [31], increasing the Fe+2 content improvements the efficiency for the Fenton oxidation process have been achieved by introducing UV light.

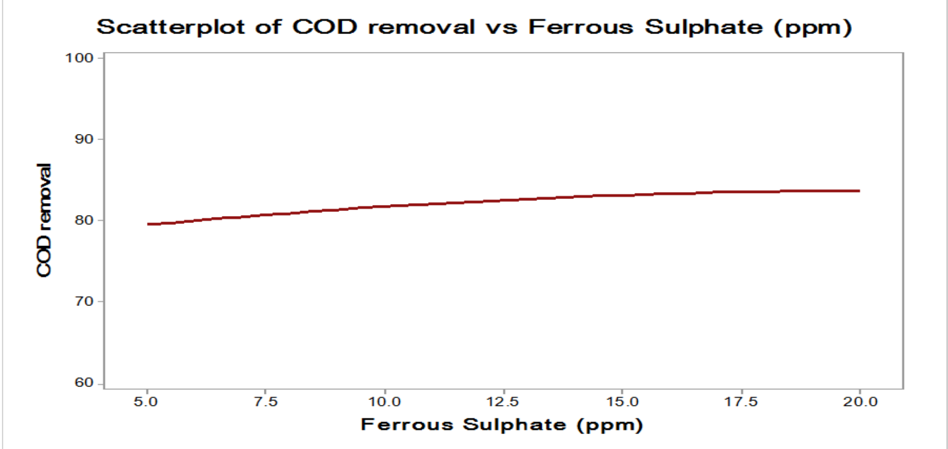

Fig. 5: Effect of ferrous Sulphate on COD elimination.

3.1.2.5. Effect of UV Lamps on the COD removal

The occurrence of light intensity remained expectable toward be one of the rate-controlling limits. The result of UV Lamp on the photo-Fenton competence of H_2O_2 concentration was deliberate through variable the UV Lamp number [32]. The result of the number of UV lamps (2-8) on photo Fenton process was experienced toward designate the number of UV lamps obligatory to competence of COD elimination and keeping the other limits and quantity constant. Figure 6 demonstrations the result of the number of lamps on the COD elimination in sunflower wastewater. The competence augmented with cumulative UV-A lamp changing from 2 to 8 UV lamp. This is reliable with Jelena mitrović et. al, 2012 [33].

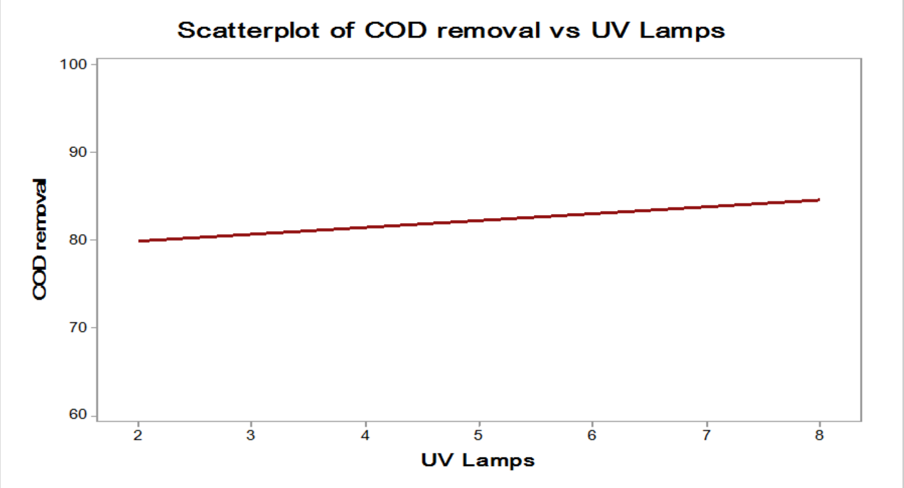

Fig. 6: Effect of UV Lamps on the COD removal.

3.1.3. Effect of Temperature

The effect of temperature on COD removal in sunflower wastewater was studied using different temperatures was between (25-60) ˚C. While, other parameters were kept. Figure 7 shown an increase in temperature was associated with a decrease in COD clearance rate, as depicted the removal was 85.42% at the initial temperature of 25ºC, the removal efficiency rapidly declines once the temperatures rose to 20ºC to 60ºC where it was reached 52.22%. This behavior continually at high temperature due to the hydrogen peroxide may be decomposition before its reaction with ferrous ion hence do not generate the hydroxyl radicals therefore [34]. The temperature of 25 ºC was chosen to further prediction of the degradation rate performance, which agrees with E. C. Catalkaya, et .al [35] that found Fenton's reagent experiments were accepted out at room temperature (25–28 ºC).

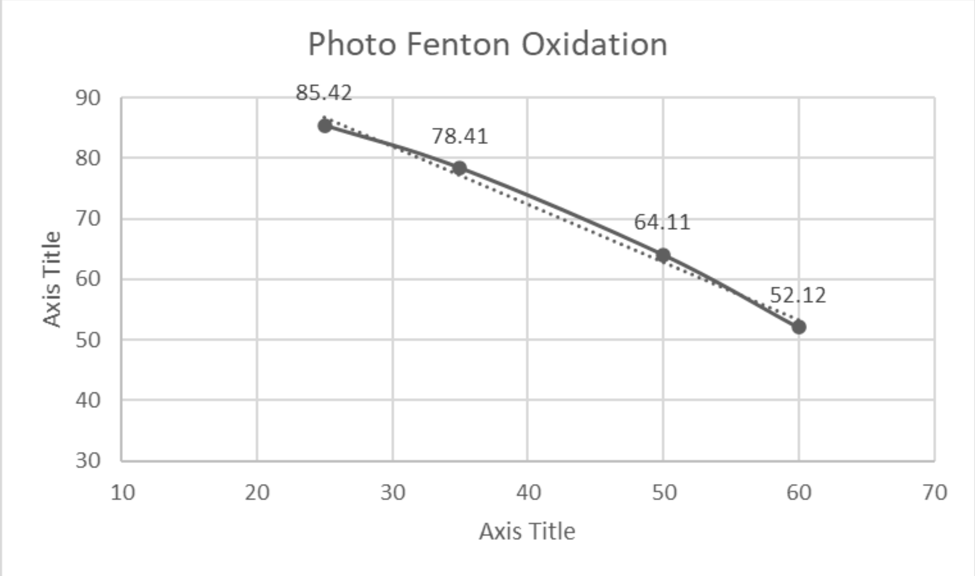

Fig. 7: Effect of temperature on the COD removal.

3.1.4. Improving the working variables

Finest values of working variables for example hydrogen peroxide, pH, irradiation time, ferrous Sulphate and UV lamps remained got using Minitab-17. Figure 8 labels the measurements significances of the D-optimization. The COD removal more than 98%.

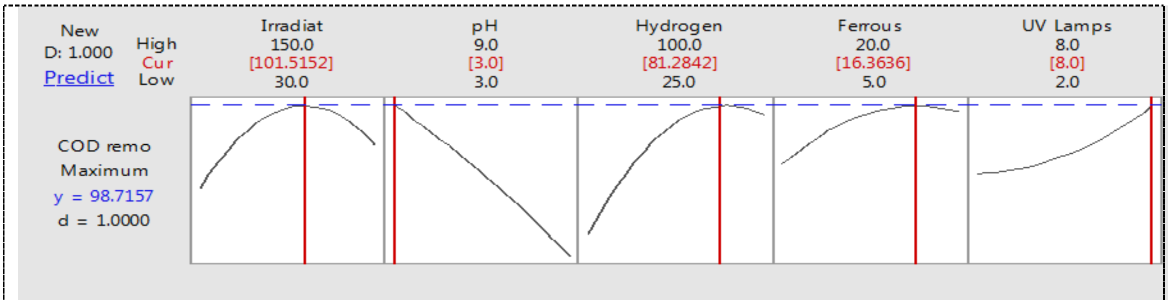

Fig. 8: Finest employed variables and the validated deliberate replies.

4. Conclusions

The photo-Fenton action knowledge has been exposed toward remain very active aimed at higher COD elimination from sunflower wastewater Behavior presentation remains a function of working circumstances for instance hydrogen peroxide concentration, Ferrous Sulphate, pH, UV Lamps and Irradiation time. Of these, the contaminating load appears toward play a decisive role by way of photo Fenton and, indeed, other progressive oxidation skills, are suitable to treat COD and reduce the organic in the sunflower wastewater. COD elimination competence was the lowermost in the case of the Fenton reagent action procedure alone associated to the combination procedure of Fenton reagent and UV. The finest elimination condition of 98 % had achieved by means of the photo-Fenton processes compared to the Fenton processes.

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