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Comparative analysis of the treatment of Reactive Azo dye using Fenton and photo Fenton treatment

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ABSTRACT

Reactive azo dye has serious implications of the health of human beings. Therefore, its use has been banned in many countries. However, due to its versatile applicability and cheaper production cost no other dye could replace Reactive azo dye. Numerous efforts have been made to find an efficient treatment technology for azo dye contaminated waters among which treatment using Advanced Oxidation Processes (AOPs) have become most renowned. In this study also, a comparative analysis has been done to treat the Reactive azo dye contaminated wastewater. Efficiency of Fenton and photo Fenton treatment process was assessed and optimization of process parameters (i.e., pH, concentration of H_2O_2 and $FeSO_4.7H_2O$) was done using Box Behnken Design along with Response Surface Methodology (RSM). After 2 h of reaction time, at the optimal conditions, pH =2.9, H_2O_2 = 952.32 mg/L and Fe^{2+} = 358.66 mg/L the % degradation of dye in Fenton process was 68.68%. On the other hand, % degradation of dye obtained using photo Fenton process at the optimal conditions, pH=2.95, H_2O_2 = 1282.22 mg/L, Fe^{2+} = 371.82 mg/L was 75.9%.

Keywords: Advanced Oxidation Process, Fenton and photo Fenton treatment, Box Behnken Approach, Response Surface Methodoloy, Reactive azo dye.

1.0. INTRODUCTION

After oil, water is the most important commodity in the world. In fact, since it is a basic necessity for life itself, one would be inclined to believe that it is more important than oil or money. By 2010, water shortage in many developing countries is recognized as one of the most serious political and social issues. Steps should be taken for recycling wastewater of the various industries as water has now become a key symbol of protest around the world and is seen as the most serious social and political issue of this generation.

A large number of organic substances are nowadays introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulation authorities around the world. The wastewater from textile mills causes serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, chemicals which are dark in color leading to turbidity in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems.

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove color from dye contaminated wastewaters in order to cost effectively meet environmental regulatory requirements. Chemical and biological treatments have been conventionally followed till now but these treatment methods have their own disadvantages. The aerobic treatment process is associated with production and disposal of large amounts of biological sludge, while wastewater treated by anaerobic treatment method does not bring down the pollution parameters to the satisfactory level and activated charcoal adsorption and air stripping methods simply transfer the pollutants from one medium to another. They either transfer it to the atmosphere, which causes air pollution, or to a solid which is often disposed off in landfills or must be treated in an energy-intensive regeneration process. Merely transferring toxic materials from one medium to another is not a long term solution to the problem of hazardous waste loading on the environment. The recent developments in water decontamination processes are concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade more number of recalcitrant molecules into biodegradable compounds and are called advanced oxidation processes (AOP's) (Glaze, et al. 1997; Deng et al., 2006). From different types of AOPs, Fenton based treatment has emerged as an efficient water treatment technology because of its ambient operation conditions, non-toxicity and inexpensiveness (Pekakis, et al., 2006).

Fenton and photo Fenton processes can degrade a vast variety of xenobiotic compounds because of the high oxidation potential of OH radical produced during the treatment process. Studies have shown that they can efficiently degrade toxic compounds like BTEX (benzene, toluene, ethyl benzene and xylenes), naphthalene, pesticides, organic and inorganic dyes (Gandhi et al., 2016; Tony et al., 2015; Salazar et al., 2011). However, the composition of the leachate is not only dependent on the type of waste but also on the duration of disposal activities done on a particular landfill site (Ehrig, 1984). Deng et al, (2006) reported inconsistencies in the results from the studies on pre-treatment of dye contaminated wastewater using Fenton process. Therefore, in this study, optimization of operating parameters for pre-treatment of azo dye contaminated water, using Fenton and photo Fenton process, was attempted using a multivariate statistical approach of Box-Behnken design (BBD) along with response surface methodology (RSM). Various parameters were optimized including concentration of H_2O_2, concentration of Fe^{2+} and initial pH.

2.0. MATERIALS AND METHODS

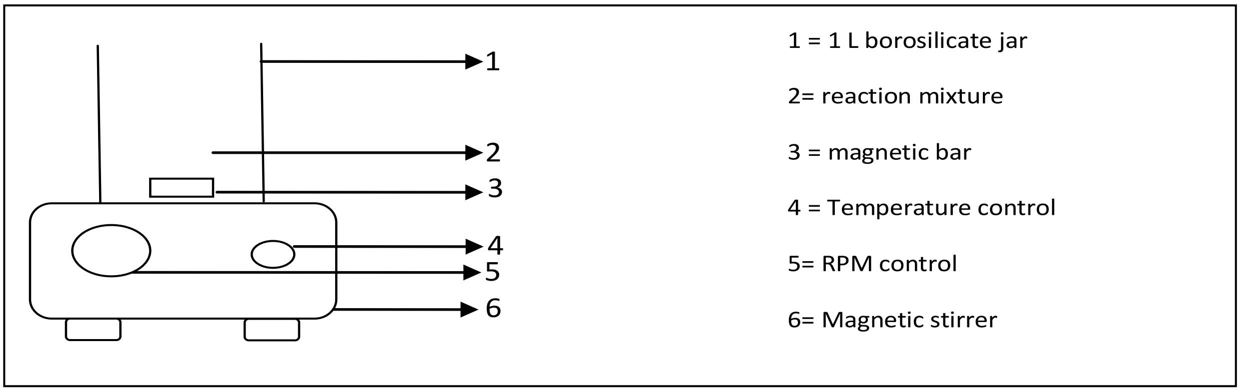
2.1. Chemicals and reagents

In this study, Hydrogen peroxide (30% w/v), ferrous sulphatehepta-hydrate, hydrochloric acid and sodium hydroxide were supplied by Sigma-Aldrich, India. All these chemicals and reagents were of analytical grade purchased from Fischer Scientific, India.

2.2. Experimental set-up

2.2.1. For Fenton based treatment

Experiments for Fenton treatment of Reactive Azo dye were performed in a laboratory scale setup using borosilicate beaker of 1 L capacity. The experimental setup is shown in figure (1):



evaporation. For proper and fast mixing, Fe^{2+} and hydrogen peroxide (30% w/v) were added under vigorous stirring at 300 rpm, using magnetic stirrer (Product #: Z693448, Sigma Aldrich). Afterwards to prevent the foaming, the setup was kept at 200 rpm for rest of the experimentation time.

2.2.2. For Photo Fenton based treatment

All the experiments were performed in a photo-reactor shown in figure (2):

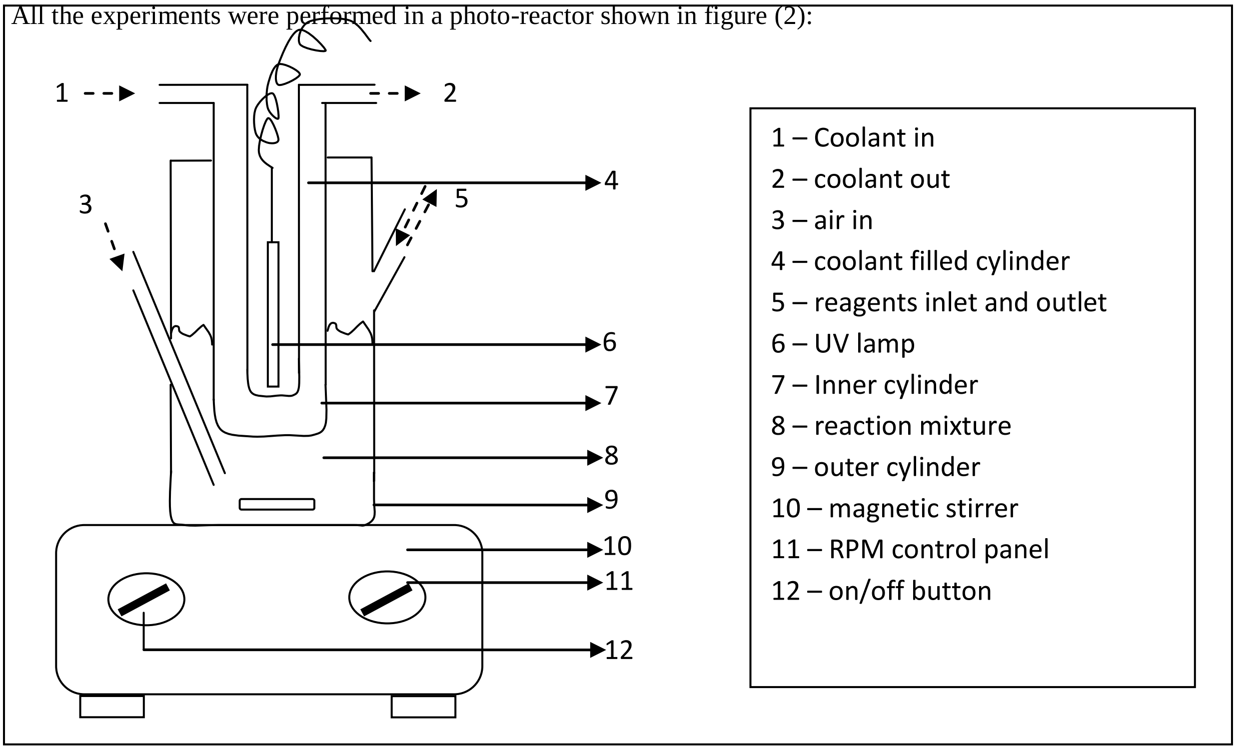


Figure 2. Experimental setup for photo Fenton treatment

This photo-reactor is made up of glass and due to circular bottom of the inner cylinder UV light, produced by a UV lamp placed in an innermost cylinder, is directed towards the outer cylinder where reaction mixture is kept. UV lamp used in this study was a Mercury vapor lamp (60 Watts). This lamp emits radiations in the range of 300-400 nm (Irie, 2007). At outer cylinder openings are provided for air supply and taking out and injecting the reagents. Continuous mixing of reaction mixture was maintained using magnetic stirrer. Inner cylinder is having inlets for coolant (i.e. water) required for maintaining the temperature of the reaction mixture.

All the experiments were performed for two hours, at three levels of the operation parameters i.e. low level (-1), middle level (0) and high level (+1). After completion of every experiment, the reaction mixture was allowed to settle and the supernatant was collected for further analysis. The aliquots were treated with 3 M NaOH to neutralize remaining H_2O_2, so that no interference is caused during COD analysis (Lee, 2004). COD was analyzed using closed reflux titrimetric method, as per *Standard Methods*, using DRS 800 (HACH, USA) digester.

2.3. **Methodology**

Brief outline of the methodology followed in this study is shown in figure (3):

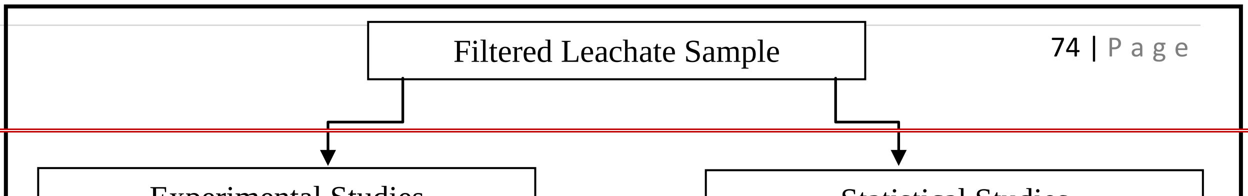


Figure3. Methodology followed in the study

2.4. Experimental design and statistical analysis

Instead of using a time consuming and labor demanding one variable at a time (OVAT) approach a multivariate statistical approach was used to generate a relation between operating parameters and response (i.e., % COD degradation). A three level (i.e., -1, 0, +1) BBD in combination with RSM was used to design experiments and generate models based on quadratic relations between the operating and response parameters. The relation developed between the operating and process parameters using this approach can be described using equation (5):

$$X = c_o + c_1 Y_1 + c_2 Y_2 + c_3 Y_3 + c_{12} Y_1 Y_2 + c_{13} Y_1 Y_3 + c_{23} Y_2 Y_3 + c_{11} Y_1^2 + c_{22} Y_2^2 + c_{33} Y_3^2 \quad (5)$$

Where, c_i = response function coefficients which were determined using Stat–Ease Design Expert (version 8.0.7.1) regression software.

The software was also used to assess the adequacy of the generated models using analysis of variance (ANOVA). The various parameters calculated for the adequacy check were correlation regression coefficients, adjusted regression coefficients and goodness of fit. After all the statistical analysis, 3D plots of the results were also generated using RSM. Using these plots the optimum operating parameters for maximum COD degradation were evaluated.

2.4.1. Levels of operating parameters

The optimization of Reactive azo dye treatment was initialized by deciding the three levels (i.e., -1; 0; +1) of the operating parameters. Firstly the dosage of H_2O_2 was decided on the basis of the theoretical mass ratio of removable COD to H_2O_2 as worked out using equation (6):

$$\mathrm{K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2} \quad (6)$$

This ratio was found to be 0.470 mg/L and accordingly, for the treatment of 3500 mg/L COD, an initial dosage of 2 to 4 g/L of H_2O_2 was chosen for optimization experiments.

To cut down the operational cost of Fenton based treatment processes, it is very important to optimize the dosage of Fe^{2+}. Also, excess of Fe^{2+} dosage increases the quantity of iron sludge that not only increases the post-treatment costs but also blocks the sun rays from reaching H_2O_2(Gogate and Pandit, 2004; Kim and Huh, 1997). Therefore, after finding the three levels of H_2O_2, for both the treatment processes, levels of Fe^{2+} concentration were also found out using test runs at 3.5 g/L of H_2O_2 and pH – 3.

The pH at which best results were reported in the literature was used for the initial test runs in the study (i.e., pH = 3) (Benatti et al., 2006; Kiril et al., 2010; Wang et al., 2000). Production of reagents, i.e. Fe^{2+} and OH radical, depends on the pH of the reaction mixture. Therefore, based on the literature, three levels of pH were chosen below neutral pH.

The three levels of operating parameters which were used for the optimization study are shown in Table 1:

Table 1: Coded representation of operating parameters for Statistical analysis

S.No.	Operating Parameters	Symbolic representation	Units	Coded Values -1 (Low)	 0 (Center)	 +1 (High)
1	$FeSO_4.7H_2O$	Y_1	mg/L	200	400	600
2	H_2O_2	Y_2	g/L	2	3	4
3	pH	Y_3	-	2	4	6

3.0. RESULT AND DISCUSSION

3.1. RSM and statistical results

The quadratic equations developed using BBD are mentioned in Eq. (1) through Eq. (4):

For Fenton treatment

$$X_1 = 68 + 0.88\,Y_1 + 0.13Y_2 - 5Y_3 - 0.25Y_1Y_2 - 0.50Y_1Y_3 + 1.50Y_2Y_3 - 7.38\,Y_1^2 - 4.38Y_2^2 - 6.13Y_3^2 \qquad (1)$$

$$X_2 = 80 - 2.19Y_1 - 0.31Y_2 + 12.50Y_3 + 0.62\,Y_1Y_2 + 1.25Y_1Y_3 - 3.75Y_2Y_3 + 18.44Y_1^2 + 10.94Y_2^2 + 15.31Y_3^2 \qquad (2)$$

For Photofenton treatment

$$X_3 = 76 + 1.25\,Y_1 + 0.50Y_2 - 4.75Y_3 - 1.5Y_1Y_2 + 0.00Y_1Y_3 + 1.50Y_2Y_3 - 6\,Y_1^2 - 3.5Y_2^2 - 5Y_3^2 \qquad (3)$$

$$X_4 = 60 - 2.81Y_1 - 0.94Y_2 + 12.50Y_3 + 1.87\,Y_1Y_2 + 1.25Y_1Y_3 - 3.75Y_2Y_3 + 16.56Y_1^2 + 9.06Y_2^2 + 12.19Y_3^2 \qquad (4)$$

Where, $X_{1,3}$ = % degradation; $X_{2,4}$ = COD

Y_1 = $FeSO_4.7H_2O$ concentration; Y_2 = H_2O_2 concentration; Y_3 = pH

All the response function coefficients are mentioned without considering their statistical significance. The values for response parameters generated using these equations are compared with the experimental results, in Table 2:

Table 2: Experimental and predicted responses from the Box-Behnken designed experiments for Fenton treatment

	Variables						Experimental Responses		Predicted Responses	
	pH		H_2O_2		$FeSO_4,7H_2O$					
S.No.	Coded values	Actual values	Coded values	Actual values	Coded values	Actual values				
				mg/L		mg/L	X_1	X_2	X_1	X_2
1	0	4	-1	500	+1	600	55	112.5	61.12	82.75
2	0	4	0	1000	0	400	68	80	53.62	70.75
3	-1	2	0	1000	+1	600	60	100	52.38	67.25
4	0	4	0	1000	0	400	68	80	41.88	54.25
5	+1	6	0	1000	+1	600	53	117.5	55.87	73.5
6	+1	6	+1	1500	0	400	48	130	49.37	60.5
7	0	4	0	1000	0	400	68	80	51.63	64.5
8	-1	2	0	1000	-1	200	65	87.5	40.13	52.5
9	0	4	-1	500	-1	200	52	120	55.99	71.76
10	0	4	+1	1500	-1	200	58	105	43.75	56.26
11	+1	6	-1	500	0	400	51	122.5	47.25	63.76
12	0	4	+1	1500	+1	600	60	100	39.01	47.26
13	-1	2	+1	1500	0	400	59	102.5	61	83
14	0	4	0	1000	0	400	68	80	61	83
15	+1	6	0	1000	-1	200	52	120	61	83
16	0	4	0	1000	0	400	68	80	61	83
17	-1	2	-1	500	0	400	60	100	61	83

Table 3: Experimental and predicted responses from the Box-Behnken designed experiments for photoFenton treatment

	Variables						Experimental Responses		Predicted Responses	
	pH		H_2O_2		$FeSO_4,7H_2O$					
S.No.	Coded values	Actual values	Coded values	Actual values	Coded values	Actual values				
				mg/L		mg/L	X_3	X_4	X_3	X_4
1	0	4	0	500	0	600	76	60	61.12	82.75
2	0	4	-1	1000	+1	400	67	87.5	53.62	70.75
3	+1	2	+1	1000	0	600	60	105	52.38	67.25

4	0	4	0	1000	0	400	76	60	41.88	54.25
5	0	6	0	1000	0	600	76	60	55.87	73.5
6	-1	6	0	1500	+1	400	70	75	49.37	60.5
7	0	4	+1	1000	-1	400	69	80	51.63	64.5
8	0	2	+1	1000	+1	200	70	75	40.13	52.5
9	-1	4	-1	500	0	200	70	75	55.99	71.76
10	+1	4	0	1500	+1	200	63	92.5	43.75	56.26
11	+1	6	0	500	-1	400	62	95	47.25	63.76
12	0	4	0	1500	0	600	76	60	39.01	47.26
13	-1	2	0	1500	-1	400	75	62.5	61	83
14	0	4	-1	1000	-1	400	60	100	61	83
15	+1	6	-1	1000	0	200	61	97.5	61	83
16	0	4	0	1000	0	400	76	60	61	83
17	-1	2	+1	500	0	400	69	77.5	61	83

A significant similarity was observed between the experimental and predicted results. At 95 % confidence level predicated results were plotted against actual experimental results in figure (4) through and figure (7) which showed that a significant relationship exists between both of them.

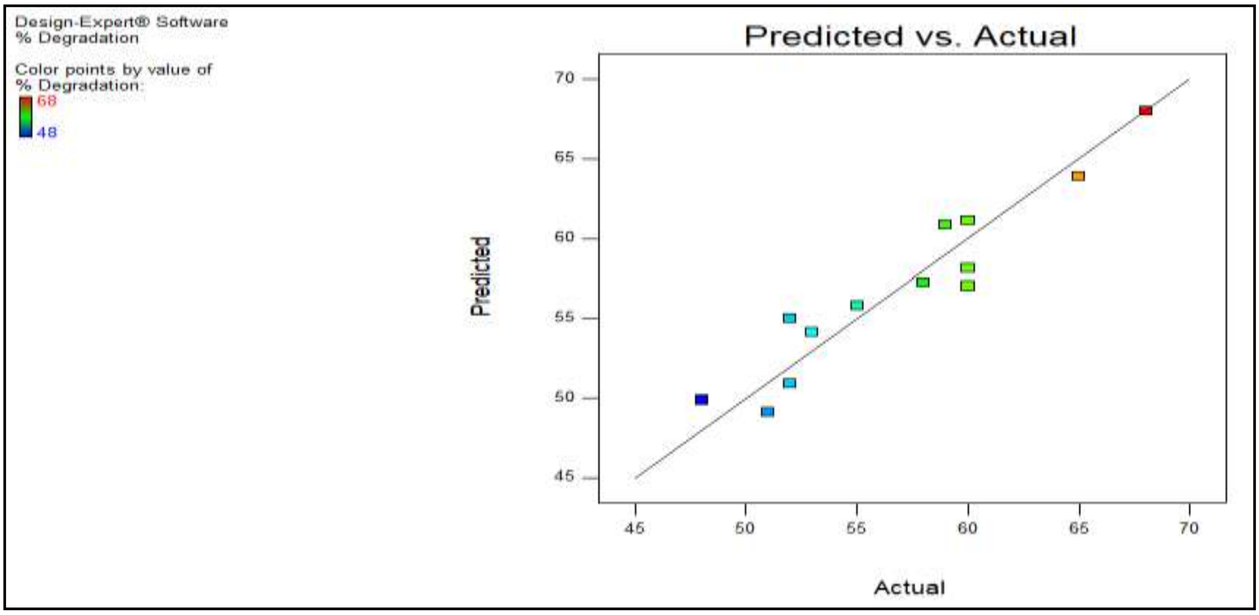


Figure 4. Plot of actual vs predicted responses for % degradation in Fenton treatment process

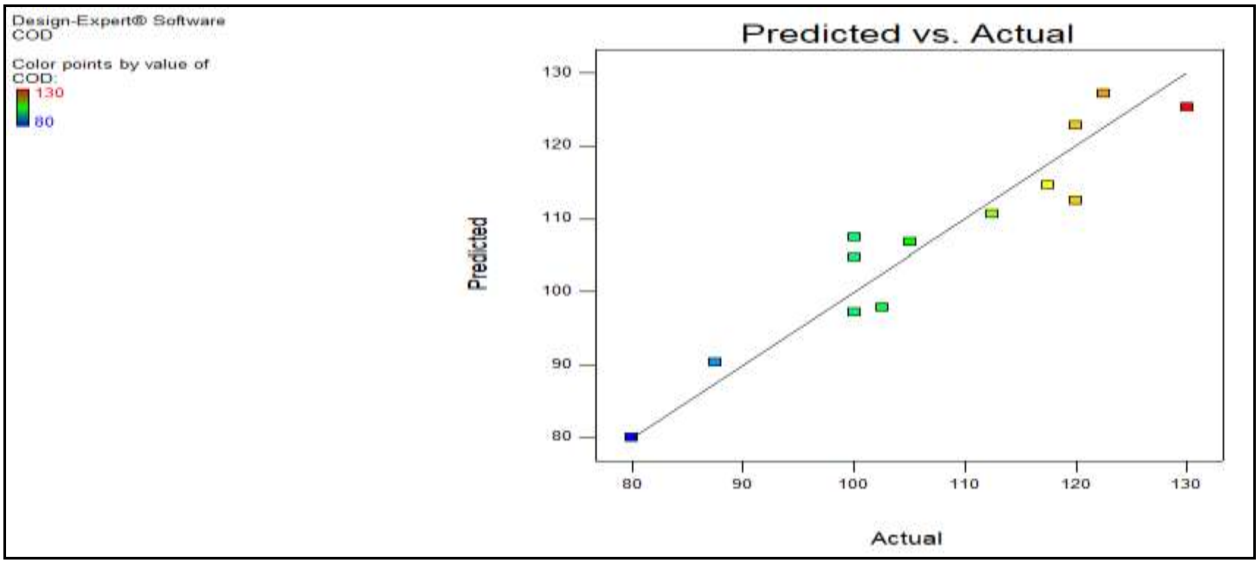


Figure 5. Plot of actual vs predicted responses for COD in Fenton treatment process

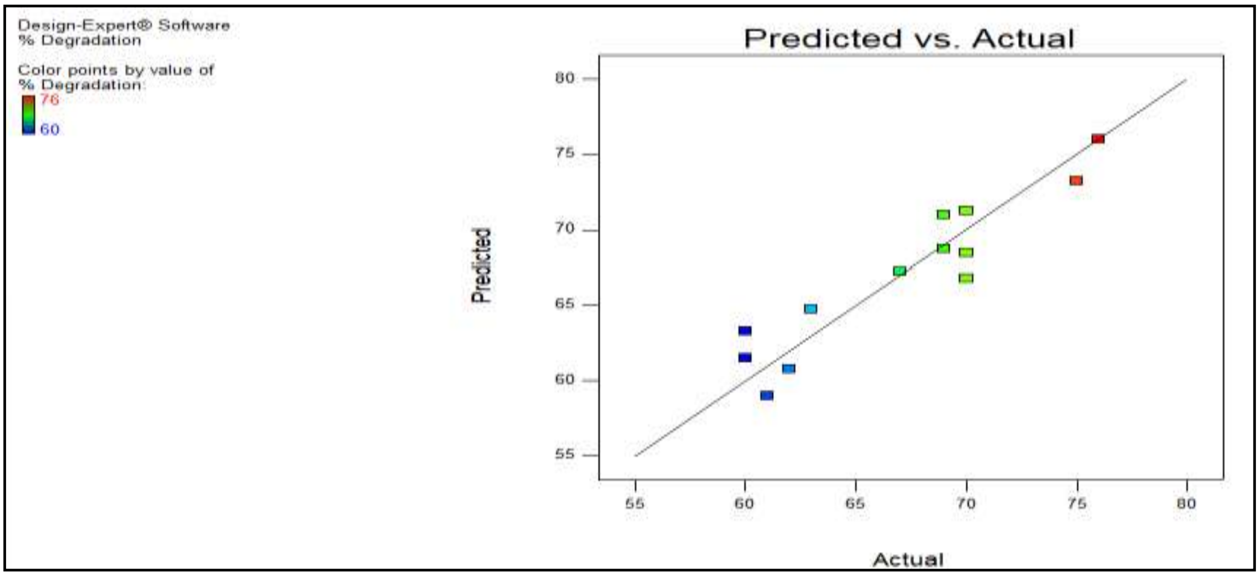


Figure 6. Plot of actual vs predicted responses for % degradation in Photo-Fenton treatment

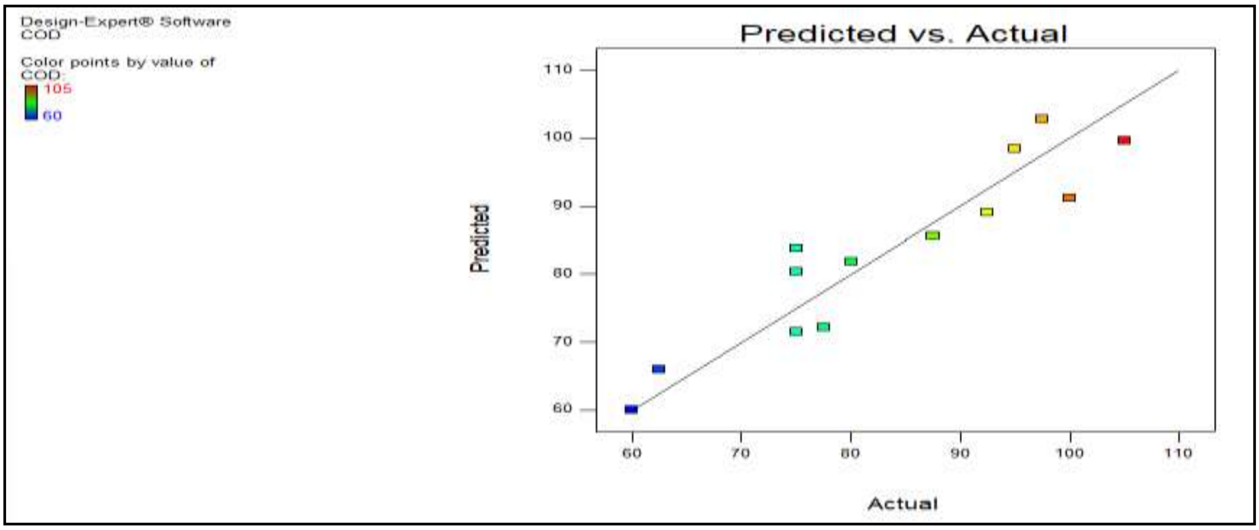


Figure 7. Plot of actual vs predicted responses for COD in Photo-Fenton treatment

3.2. Analysis of variance

ANOVA was performed to assess the adequacy of the generated models at 95 % confidence level. The results obtained from this process are shown in Table 4 through Table 5:

Table 4. ANOVA test for response parameters X_1 and X_2 for Fenton treatment

Source	Sum of Squares		df	Mean Square		F Value	P-Value
	X_1	X_2	X_1& X_2	X_1	X_2	X_1& X_2	X_1& X_2
Model	735.87	4599.2	9	81.76	511.02	14.96	<0.0009
Y_1	6.13	38.28	1	6.13	38.28	1.12	0.3249
Y_2	0.13	0.78	1	0.13	0.78	0.023	<0.884
Y_3	200	1250	1	200	1250	36.60	<0.0005
Y_1Y_2	0.25	1.56	1	0.25	1.56	0.046	0. 8367
Y_1Y_3	1	6.25	1	1	6.25	0.18	0.6817
Y_2Y_3	9	56.25	1	9	56.25	1.65	0.2402
Y_1^2	229.01	1431.3	1	229.01	1431.3	41.91	<0.0003
Y_2^2	80.59	503.7	1	80.59	503.7	14.75	<0.0064
Y_3^3	157.96	987.25	1	157.96	987.25	28.91	0.0010
Residual	38.25	239.06	7	5.46	34.15		
Lack of fit	38.25	239.06	3	12.75	79.69		
Pure Error	0.00	0.00	4	0.000	0.00		
Total (Corr)	774.12	4838.2	16				

R^2 for X_1& X_2 = 0.9506; R^2_{adj} for X_1& X_2 = 0.8871

Table 5. ANOVA test for response parameters X_3 and X_4 for photo Fenton treatment

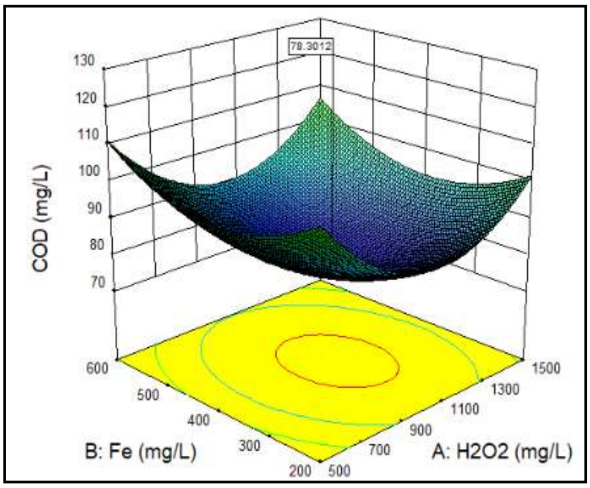
Source	Sum of Squares		df	Mean Square		F-ratio		P-Value	
	X_3	X_4	X_3&X_4	X_3	X_4	X_3	X_4	X_3	X_4
Model	555.47	3753	9	61.72	417	10.05	9.11	<0.0030	<0.0041
X_1	12.50	63.28	1	12.50	63.28	2.03	1.38	0.1968	<0.2780
X_2	2.00	7.03	1	2	7.03	0.33	0.15	<0.5861	0.70.67
X_3	180.5	1250	1	180.5	1250	29.38	27.32	<0.0010	0.0012
X_1X_2	9	14.06	1	9	14.06	1.47	0.31	0. 2654	0.5966
X_1X_3	0	6.25	1	0	6.25	0.00	0.14	1.0000	0.7226
X_2X_3	9	56.25	1	9	56.25	1.47	1.23	0.2654	0.3042
X_1^2	151.58	1155	1	151.5	1155	24.68	25.24	<0.0016	<0.0015
X_2^2	51.58	345.8	1	51.58	345.8	8.4	7.56	<0.0231	<0.0285
X_3^3	105.26	625.41	1	105.2	625.4	17.14	13.67	0.0044	0.0077
Residual	43	320.31	7	6.14	45.76				
Lack of fit	43	320.31	3	14.33	106.8				
Pure Error	0.00	0	4	0.000	0.000				
Total (Corr)	598.47	4073.5	16						

R^2 for X_3 = 0.9282, R^2 for X_4 = 0.9214; R^2_{adj} for X_3 = 0.8358, R^2_{adj} for X_4 = 0.8203

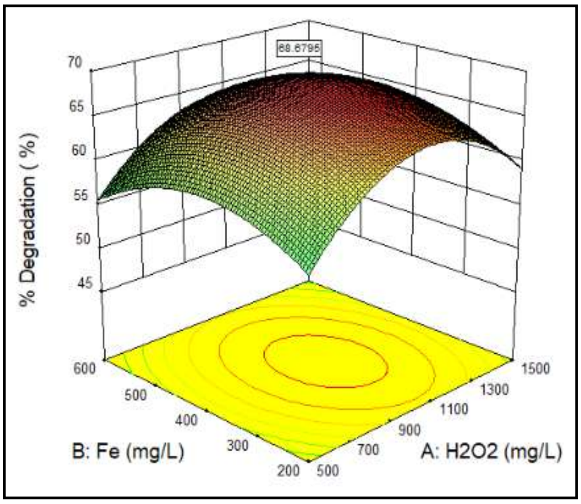
It was observed that the models generated are adequate for the prediction of optimal values of the operating and response parameters as P value were very low. The values of regression coefficients generated using ANOVA for Fenton, photo Fenton and photocatalytic processes were 0.9506 and 0.9282respectively for % degradation and 0.9506 and 0.9214, respectively for COD removal. These values being close to 1 show that variations observed among experimental and observed results are insignificant and models generated are adequate for the present study (Kiely, 1997; Ehrig, 1992). The generated models can also be used satisfactorily to analyze the responses from even more input variables as the values of correlation coefficients were very close to adjusted correlation coefficients (R^2_{adj}) (Ehrig, 1992).

3.3. Response surface plots and optimization

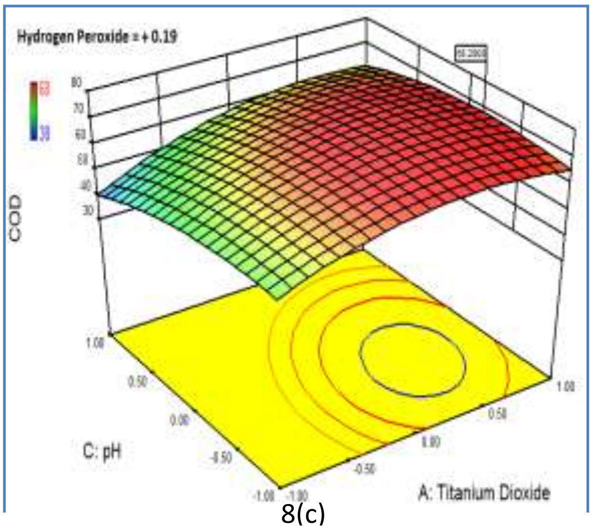
After the validation of models, Design Expert software was used to plot 3-Dimensional surface plots for all the operating parameters. RSM approach was used to draw these plots as shown in figure (8) through figure (9):



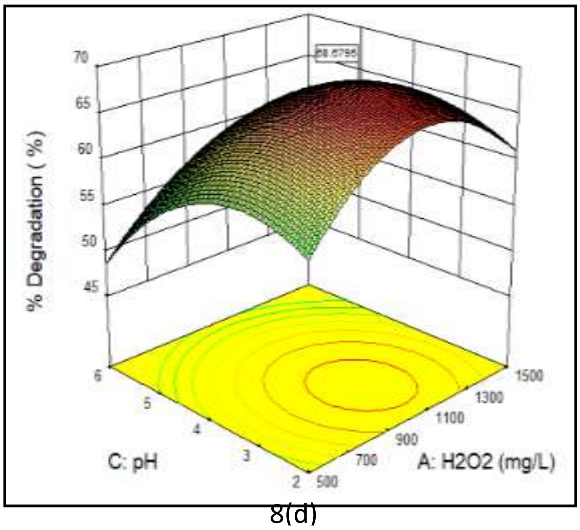
8(a)



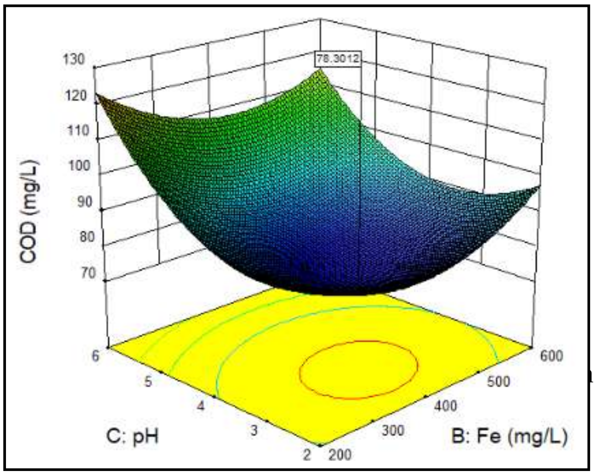
8(b)



8(c)



8(d)



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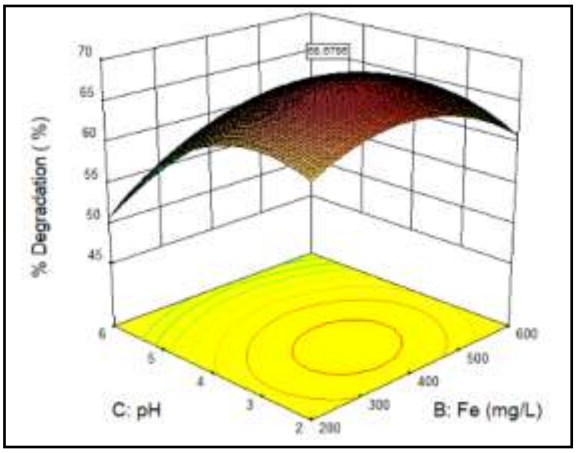
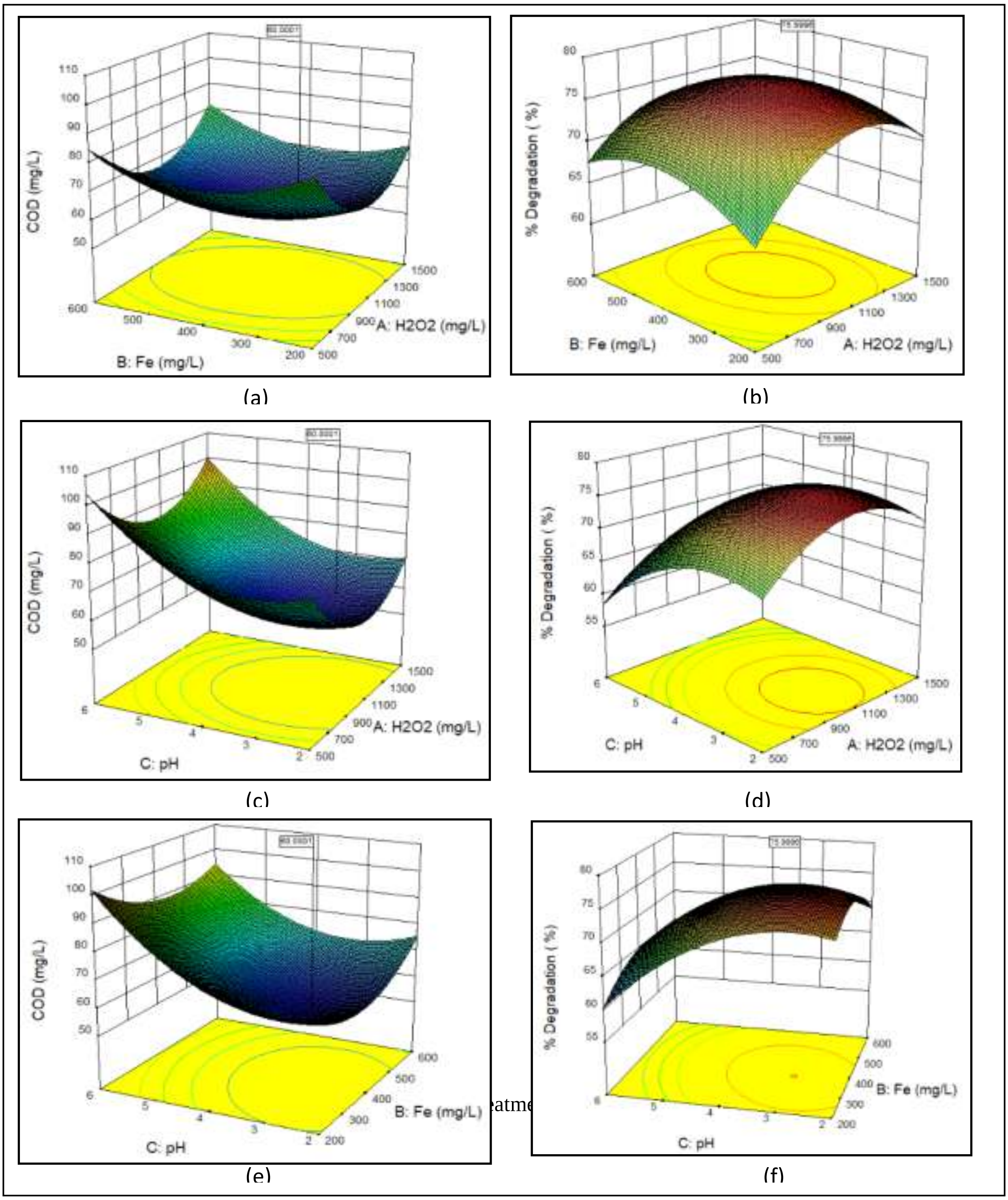


8(e)

8(f)



(a)

(b)

(c)

(d)

(e)

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Optimal values of the operating parameters causing maximum COD degradation are shown with a marker at surface plot of each figure. Maximum COD degradation at different optimum operating conditions is described in Table 6 through Table 7 and shown in figure (10) through figure (11):

Table 6: Maximum values of responses at optimum condition in Fenton treatment

S.No.	Control Parameters	Symbolic representation	Maximum values for Responses % degradation ($X_1 = 68.68$)
1	$FeSO_4.7H_2O$	Y_1	358.66
2	H_2O_2	Y_2	952.32
3	pH	Y_3	2.9

Table 7: Maximum values of responses at optimum condition in photo Fenton treatment

S.No.	Control Parameters	Symbolic representation	Maximum values for Responses % degradation ($X_3 = 75.99$)
1	$FeSO_4.7H_2O$	Y_1	371.82
2	H_2O_2	Y_2	1282.22
3	pH	Y_3	2.95

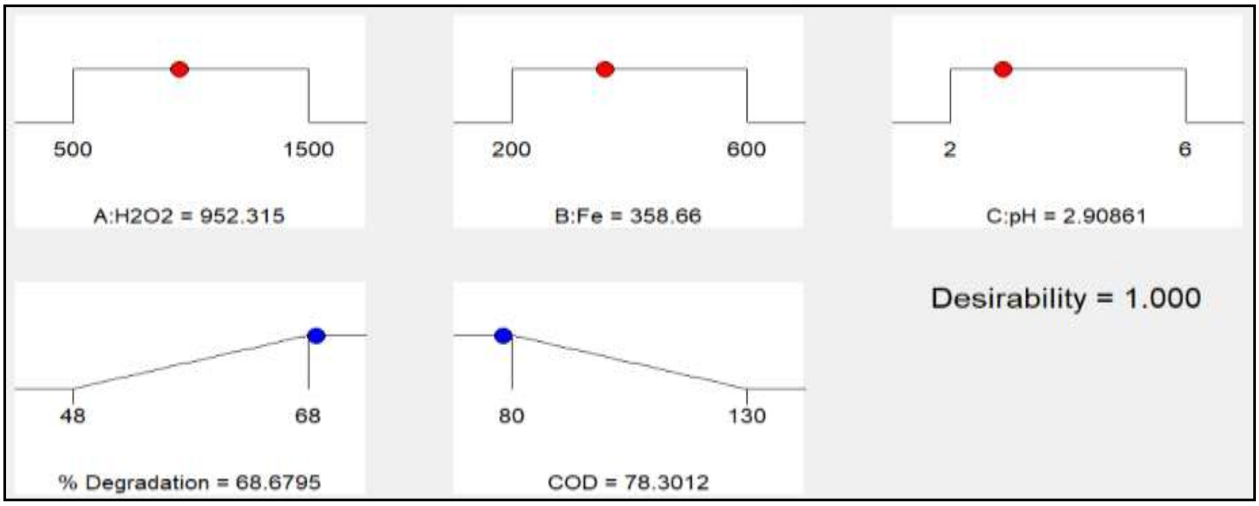

Figure 10: Results of optimization for Fenton treatment

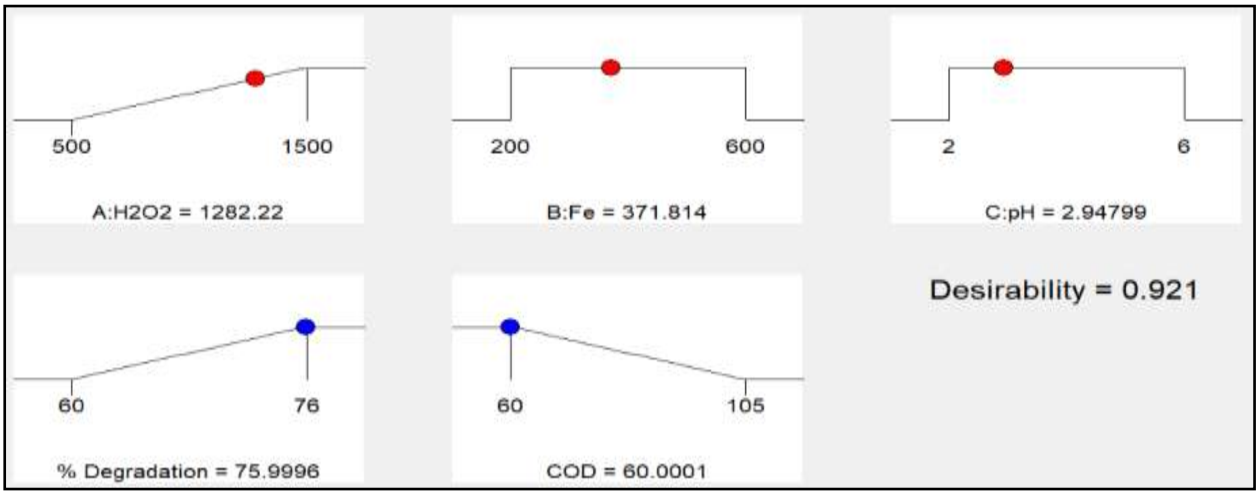

Fig 11: Results of optimization for Photofenton treatment

3.4. Effects of H_2O_2 concentration in Fenton and Photofenton treatment

Figure 8 (a, b, c, d) and 9 (a, b, c, d)shows the % degradation and COD removal of reactive azo dye solution with increasing concentrations of H_2O_2.

From the results, it can be interpreted that up to certain concentration of H_2O_2, the COD removal and % degradation increased with increase in concentration of H_2O_2. Beyond this concentration of H_2O_2 increase in COD degradation is only marginal, in case of Fenton process. In case of photo Fenton process, the COD degradation increases with the increase in H_2O_2 concentration. Therefore, 952 mg/L of H_2O_2 concentration was chosen as the optimal concentration for Fenton process whereas the optimum concentration in case of photo Fenton processes was 1282 mg/L. At these optimal concentrations of H_2O_2, about 68.68% and 75.99% of % degradation was reported in case of Fenton and photo Fenton process respectively.

Being an oxidizing agent, H_2O_2 reduces the COD of the wastewater by organic and inorganic compounds present in wastewater, into free radical molecules. These free radicals react with oxygen available in the reaction mixture and yield peroxyl radicals (Kang, 2000). When the concentration of H_2O_2 exceeds its optimal value, the oxidizing effects might have decreased due to the radical scavenging. In the process of radical scavenging, the excess H_2O_2 present reported to react with OH radicals to produce HO_2 radicals and in turn both HO_2 and OH radicals react to form H_2O molecules (Primo, 2008; Talini, 1992). Thus, an ultimate reduction in the concentration of OH radicals was reported, which resulted in lesser COD removal (Talini, 1992). The reactions involved are shown in Eq. (5) and Eq. (6):

$$H_2O_2 \; + \; {}^{*}OH \; \rightarrow \; HO_2^{*} \; + \; H_2O \qquad (5)$$

$$HO_2^{*} \; + \; {}^{*}OH \; \rightarrow \; H_2O \; + \; O_2 \qquad (6)$$

Studies performed at industrial scale observed floatation of iron sludge due to excess presence of H_2O_2. The higher COD degradation observed in case of photo Fenton process could be due to the photolysis and the production of additional OH radicals (Kim, 2001).

3.5. Effects of $FeSO_4.7H_2O$ concentration in Fenton and Photofenton treatment

Figure 8 (a, b, e, f) and Figure 9 (a, b, e, f) shows the % degradation and COD removal of reactive azo dye solution with increasing concentrations of Fe^{2+}.

In case of Fenton process, initially by increasing concentration of Fe^{2+} up to 358.66 mg/L, the COD degradation rate increased, beyond which decrease was reported. On the other hand, in case of photo Fenton process, COD degradation was highest (75.99%) at 371.82 mg/L of Fe^{2+} after which it showed a decreasing trend. Therefore, keeping in mind the economical factors of any operation/project, based on this study, the optimal concentrations of Fe^{2+} 358.66 and 371.82 mg/L for Fenton and photo Fenton process, respectively, could be proposed.

$FeSO_4.7H_2O$ when introduced in reaction mixture produces Fe^{2+} ions that act as oxidizing agents in Fenton and photo Fenton processes. But when introduced in excess, Fe^{2+} ions lead to formation of Fe^{3+}, on reacting with OH radicals. These Fe^{3+} molecules further react with OH^- ions to produce FeOH. Hence, excess Fe^{2+} ions reduce the concentration of OH radicals (Walling, 1970; Deng and Englehardt, 2006). This decrease in rate of COD reduction while increasing concentration of Fe^{2+} can be explained using Eq (8):

$$OH^* + Fe^{2+} \rightarrow OH^- + Fe^{3+} \rightarrow FeOH \qquad (8)$$

The FeOH molecules thus produced increases the sludge content in the reaction chambers. Hence, maintaining the dosage of Fe^{2+} in the oxidation processes not only helps in cost cutting but also decreases the iron sludge produced that would require further treatment (Gogate, 2004). At industrial scale, as well, photo Fenton processes may prove better because the energy photons from light enhance the reduction of Fe^{3+} to Fe^{2+}. Therefore, lesser sludge content is formed and more Fe^{2+} ions are available for OH free radical generation (Walling, 1970).

3.6. Effects of pH in Fenton and Photofenton treatment

Treatment of contaminated water using Fenton based processes is reported performing under acidic conditions. Therefore, in this study, the experiments for finding the optimal value of pH were studied in the acidic range of 2 to 6. Figure 8 (c, d, e, f) and figure 9 (c, d, e, f) show the effect of pH on the COD and % degradation of reactive azo dye, at optimal concentrations of H_2O_2 and Fe^{2+}.

It can be observed thatFenton and photo Fenton processes showed maximum COD reduction of 68.68%and 75.99% at pH 3 (approximately) for Fenton and Photofenton treatment process.

On decreasing the pH below the optimal value oxidation process is affected because the pace of reaction between $[Fe(H_2O)]^{2+}$ and H_2O_2 is reduced causing lesser production of OH radicals. Moreover, it has also been observed that at extremely low pH values the reaction between Fe^{3+} and H_2O_2 is also inhibited that also reduces generation of OH radicals (Tang and Huang, 1994). In case of photo Fenton processes, pH range of 2 to 4.5 was found to be optimum because in this range the generation of photo-reactive iron hydroxide complex i.e. $Fe(OH)^{2+}$, is more than Fe^{3+} (Faust and Hoigne, 1990).

When the pH of reaction mixture is increased above the optimal values, the availability of H^+ ions in the reaction mixture increases that hinders the generation of OH radical from H_2O_2 (Walling, 1970). Moreover, with the increase in pH of reaction mixture from acidic to neutral, the under-saturation of Ferric hydrite changes to over saturation because of which there is an increase in production of ferric oxyhydroxides that makes lesser availability of Fe^{2+} ions for breaking H_2O_2 (Bigda, 1996).

4.0. CONCLUSIONS

Fenton and photo Fenton processes have been proven promising treatment methods for wastewater contaminated with reactive azo dye. At optimal operating conditions Fenton (pH=2.9, H_2O_2 = 952mg/L, Fe^{2+} = 358.66 mg/L) and photo Fenton (pH =2.95, H_2O_2 = 1282 mg/L and Fe^{2+} = 371.82 mg/L) treatment process caused 68.68 % and 75.99 % degradation of the reactive azo dye. The Fenton based pre-treatment processes enhanced the biodegradability of contaminated water. The photo Fenton process was found more effective as compared to Fenton process. Also, it is proposed the photo Fenton process using solar radiation could offer an economical option for the pre-treatment of leachate, especially in the tropical countries.

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