

Photo-catalytic treatment of Azo dye: Optimization of Process Parameters Using Response Surface Methodology

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ABSTRACT

Water pollution poses serious threats to both the environment and the organisms that depend on their environment for survival. Due to the toxicity from dyes in textile wastewater, there is a dire need for the development of innovative and efficient treatment technologies. In this study efforts have been made to treat the wastewaters contaminated with reactive azo dye using photocatalytic process. Photocatalytic process uses TiO_2 as catalyst to generate OH^* radicals from air. In this study, optimized conditions were derived, using response surface methodology, for the degradation of reactive azo dye and to obtain efficient treatment. At $\text{TiO}_2 = 169.2 \text{ mg L}^{-1}$ and $\text{pH}=5.48$, 73.70% degradation was reported in the duration of 2 h. Therefore, in mid latitude regions such as India, where intensity of sunlight is prominent, photocatalytic processes can play a vital role in the treatment of textile industry wastewaters.

Keywords: Photocatalysis, Reactive azo dye, sunlight, water pollution, response surface methodology

1.0.INTRODUCTION

Textile industries have been growing at a higher rate and the discharge of dyes from these industries highly alters the chemical composition of the water and water becomes unsuitable for drinking purposes. Therefore, removal of toxicants from the wastewaters of the textile industries has become a crucial issue in various nations. Among the various types of industries, dye and textile industries have a huge impact. Among the numerous organic dyes, azo dyes and its pigments are most famous among users as they are easily bound to synthetic as well as natural textile fibers. The major problem with these azo dyes is their complex chemical structure due to which they are not easily degraded by microorganisms and they get accumulated in different food chains. Therefore, they finally enter into bodies of living beings and affect their body. These complex compounds if enter in human body could cause carcinogenic effects. Chemical structure of an azo dye is shown in figure 1.1.:

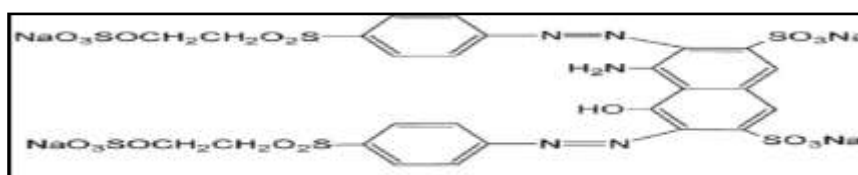


Figure 1. Chemical structure of an Azo dye



In earlier years, primitive technologies were used for the treatment of wastewater coming from textile industries. Biological treatment of dyes poses serious problems because of the presence of non-biodegradable compounds. Therefore, pre-treatment methods, such as adsorption on activated carbon, coagulation, precipitation and chemical oxidation, have been applied to treat the effluent from textile industries. Among the chemical oxidation processes, advanced oxidation processes (AOPs) offer great potential for dyes treatment (Glaze, et al. 1997; Deng et al., 2006). From different types of AOPs, heterogeneous photocatalysis, has emerged as an efficient water treatment technology because of its ambient operation conditions, non-toxicity and inexpensiveness (Pekakis, et al., 2006).

In TiO_2 photocatalysis, catalyst is radiated by UV light (300-400 nm; black light) which excites its electrons from valence band to conduction band, leading to generation of hole in valence band. These excited electrons and valence band holes react with oxygen and water molecules to produce various oxidizing species such as OH^\cdot ; e^- and H^\cdot . These oxidizing species causes degradation of organic compounds such as reactive azo dye (Hoffmann, et al., 1995; Mills and Hunte, 1997).

Various studies have investigated the photocatalysis for the treatment of dyes however much work has not been done on treatment of a reactive azo dye using chemical processes. Therefore in present study this effort has been made and investigations have also been made in using the multivariate statistical approach for optimizing the process parameters to achieve maximum degradation of reactive azo dye.

2.0. MATERIALS AND METHODS

2.1. Chemicals and reagents

pH of the reaction mixture was maintained using Sulphuric acid and Sodium hydroxide. These chemicals were supplied by Sigma Aldrich and were of analytical grade as well. TiO_2 (anatase, purity > 99%), also known as Titania, used in photocatalytic and adsorption studies was purchased from Sigma Aldrich. Chlorpyrifos with technical grade (99.5% purity) were purchased from Sigma Aldrich.

Analysis of COD was done using potassium dichromate, mercuric sulphate, silver sulphate, sulphuric acid, ferrous ammonium sulphate and ferroin indicator. All these reagents were supplied by Merck. All the chemicals were stored at 4°C away from light.

2.1.1. Photo-chemical reactor

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

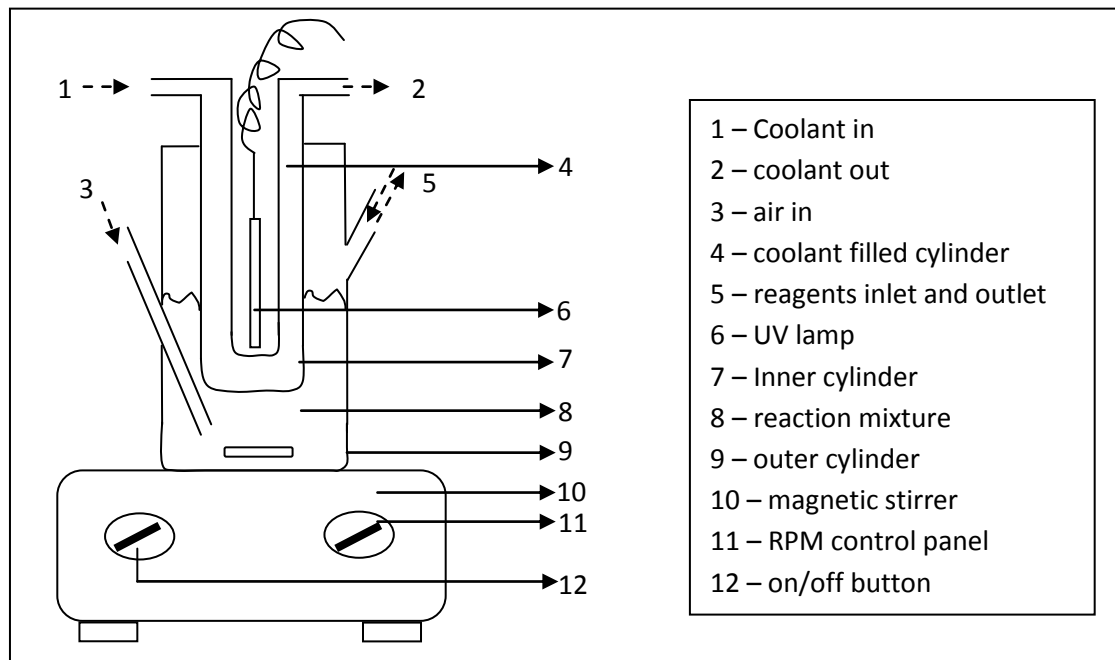


Figure 2. Experimental setup for Photocatalytic treatment

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 oxidants, 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. Biochemical Oxygen Demand (BOD₅) was analyzed using *Standard Methods* (Wu, 2010).

2.1.2. Preparation of reaction mixture

Reactive azo dye contaminated water sample (500 mg/L) was prepared fresh every time before initiating the reaction. Firstly, 100 ml of the reactive azo dye contaminated solution was added in the outer cylinder of a photo reactor having a capacity of 250 ml. Now, required amount of TiO₂ was added to the solution

under steady stirring using magnetic stirrer at 300 rpm. Afterwards pH was set, according to the requirements of the experiment, using sulphuric acid and sodium hydroxide. Finally the volume of the reaction mixture was made up to 200 ml using reactive azo dye contaminated solution.

2.2. Experimental procedure

2.2.1. 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 2 level central composite design (CCD) approach in combination with Response Surface Methodology (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 Eq. (1):

$$X = c_0 + c_1Y_1 + c_2Y_2 + c_3Y_3 + c_{12}Y_1Y_2 + c_{13}Y_1Y_3 + c_{23}Y_2Y_3 + c_{11}Y_1^2 + c_{22}Y_2^2 + c_{33}Y_3^2 \quad (1)$$

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.

3.0. RESULTS AND DISCUSSION

3.1. RSM and statistical results

The quadratic equations, developed using CCD for photocatalytic treatment, are mentioned in Eq. (2) through Eq. (3):

$$X_1 = 77 + 5.61 Z_1 + 2.06Z_2 - 1.0Z_1Z_2 - 11.81 Z_1^2 - 6.56Z_2^2 \quad (2)$$

$$X_2 = 57.5 - 14.02 Z_1 - 5.15Z_2 + 2.5Z_1Z_2 + 29.53Z_1^2 - 16.41Z_2^2 \quad (3)$$

Where, X_1 = % degradation; X_2 = COD

Z_1 = TiO₂ concentration; Z_2 = pH

All the response function coefficients in these equations are mentioned without considering their statistical significance. The values for response parameters generated using these equations are compared with the experimental results, in Table 1:

Table 1: Experimental and predicted responses from the CCD experiments for Photocatalytic treatment

Variables								
S.No.	pH		TiO ₂		Experimental Responses		Predicted Responses	
	Coded values	Actual values	Coded values	Actual values	X ₁	X ₂	X ₁	X ₂
			mg/L	mg/L				
1	0	4	*Misc	18.93	45	137.5	61.12	82.75
2	-1	2	-1	50	50	125	53.62	70.75
3	0	4	0	125	77	57.5	52.38	67.25
4	+1	6	+1	200	63	92.5	41.88	54.25
5	0	4	0	125	77	57.5	55.87	73.5
6	0	4	0	125	77	57.5	49.37	60.5
7	+1	6	-1	50	56	110	51.63	64.5
8	0	4	0	125	77	57.5	40.13	52.5
9	-1	2	+1	200	61	97.5	55.99	71.76
10	*Misc	6.8	0	125	68	80	43.75	56.26
11	*Misc	1.17	0	125	62	95	47.25	63.76
12	0	4	*Misc	231.06	64	90	39.01	47.26
13	0	4	0	125	77	57.5	61	83

*Misc = values considered randomly by software

A significant similarity was observed between the experimental and predicted results. At 95 % confidence level predicted results were plotted against actual experimental results in figure 3 and figure 4. which showed that a significant relationship exists between both of them.

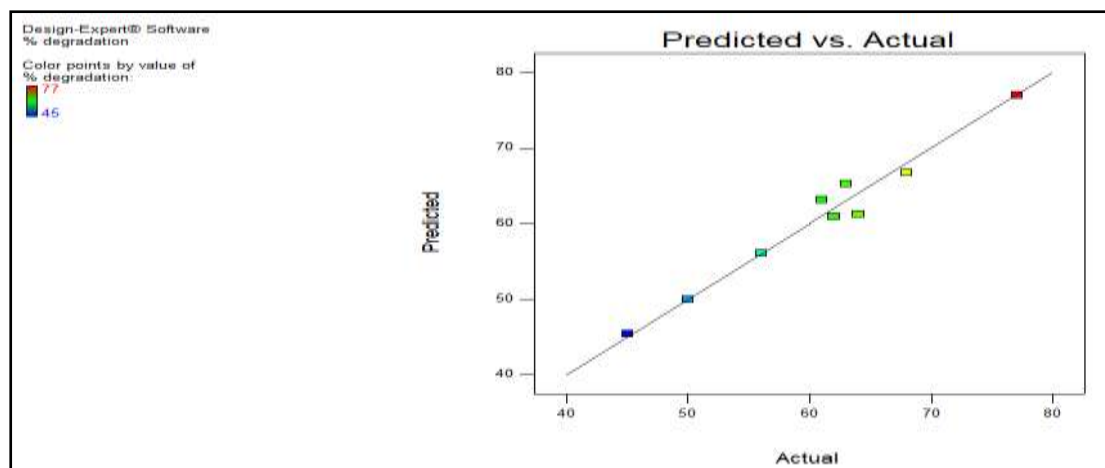


Figure 3: Plot of actual vs predicted responses for % degradation in Photo-catalytic treatment

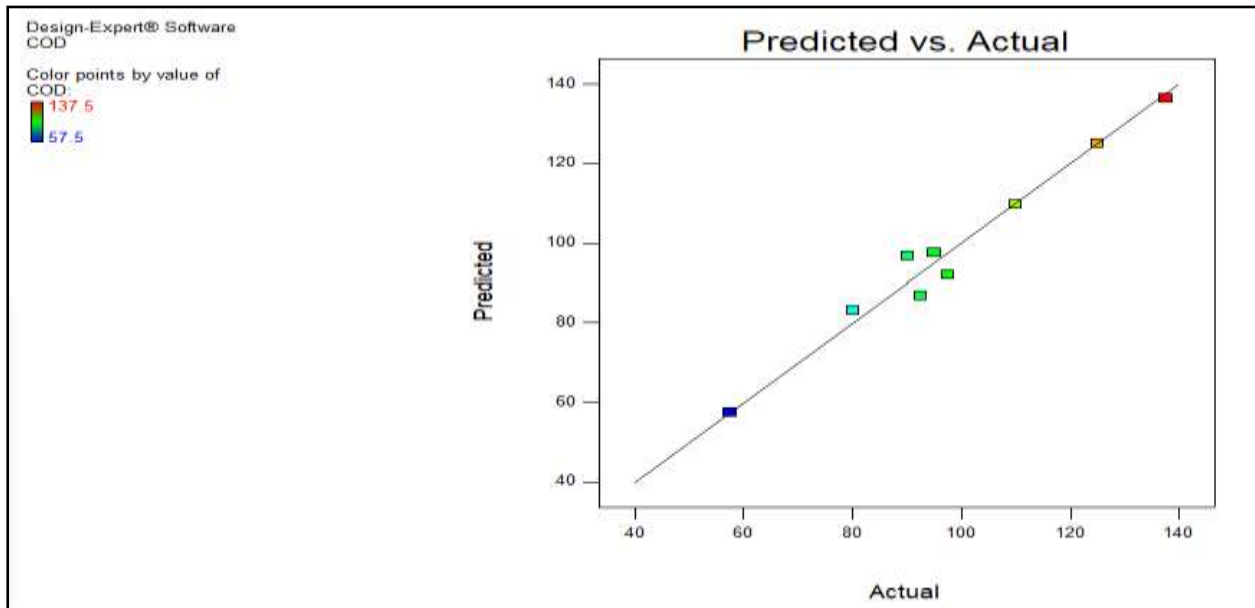


Figure 4: Plot of actual vs predicted responses for COD in Photo-catalytic treatment

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 2:

Table 2: ANOVA test for response parameters X_1 and X_2 for photocatalytic treatment

Source	Sum of Squares		df	Mean Square		F-ratio		P-Value	
	X_1	X_2		$X_1 \& X_2$	X_1	X_2	X_1	X_2	X_1
Model	1438.8	8992.4	5	287.8	1798	100.8	100.8	<0.0001	<0.0001
Z_1	251.67	1572.9	1	251.7	1573	88.13	88.13	0.0001	<0.0001
Z_2	33.97	212.32	1	33.97	212.3	11.90	11.90	<0.0107	0.0107
$Z_1 Z_2$	4	25	1	4	25	1.4	1.4	<0.2752	0.2752
Z_1^2	970.68	6066.8	1	970.7	6066	339.9	339.9	0.0001	<0.0001
Z_2^2	299.59	1872.5	1	299.6	1872	104.9	104.9	0.0001	<0.0001
Residual	19.99	124.9	7	2.86	17.85				
Lack of fit	19.99	124.9	3	6.66	41.64				
Pure Error	0.00	0	4	0.000	0				
Total (Corr)	1458.7	9117.3	12						

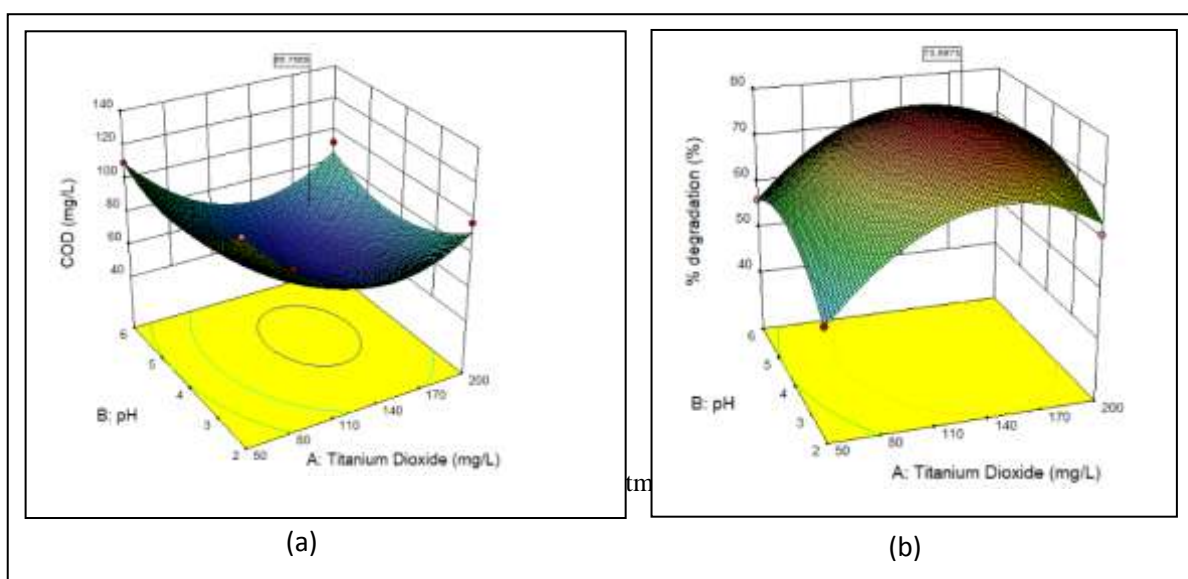
R^2 for $X_1 = 0.9681$, R^2 for $X_2 = 0.9414$; R^2_{adj} for $X_1 = 0.9538$, R^2_{adj} for $X_2 = 0.9103$

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 was 0.9681 for %degradation and 0.9414 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 of responses

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 5:



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 3 and shown in figure 6:

Table 3: Maximum values of responses at optimum condition in photocatalytic treatment

S.No.	Control Parameters	Symbolic representation	Maximum values for Responses
			% degradation ($X_1 = 73.70$)
1	TiO ₂	Y ₁	169.2
2	pH	Y ₂	5.48

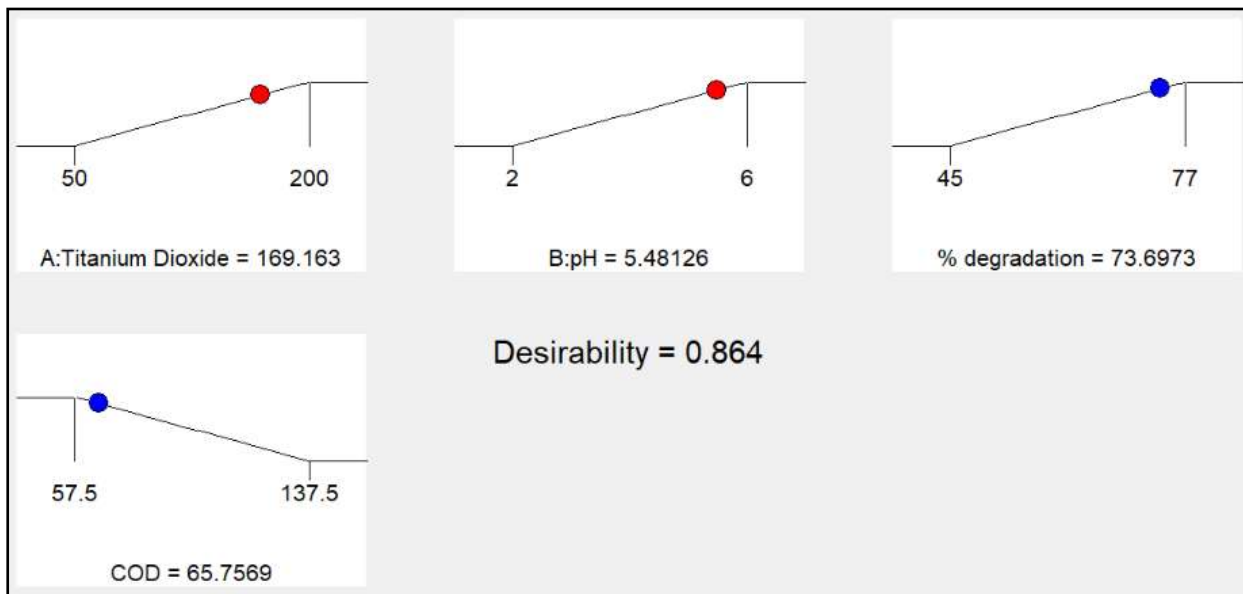


Fig 6: Results of optimization for Photocatalytic treatment

3.4. Effects of pH

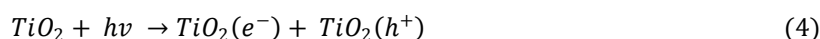
pH of the reaction mixture in advanced oxidation processes plays a very crucial role. Most of the AOPs show best efficiency in acidic conditions i.e pH of about 2 to 6 i.e. acidic pH (Benatti, 2006; Kiril, 2010, Wang, 2000). In this study the surface plots of pH/TiO₂ show increase in degradation with increase in pH up to 5.48 after which the rate of degradation started decreasing slowly.

Such a pattern was reported because at pH lower than optimal conditions, the production of OH radicals is comparatively less that leads to lesser oxidation of organic contaminants (Deng and Englehardt, 2006).

Whereas increasing the pH of the reaction mixture above optimum conditions decrease in production of H⁺ ions occurs that further leads in lesser generation of OH radicals (Walling, 1975)

3.5. Effects of TiO₂

TiO₂ particles help in removal of reactive azo dye from contaminated water by not only adsorption but also by oxidation. Photons generated from UV lamp leads to charge separation on TiO₂ particles as described in Eq. (4):



The free electrons and holes generated in this reaction help in enhancing the degradation of reactive azo dye. The free electrons react with oxygen molecule and generate oxidizing radicals and holes causes

oxidation of reactive azo dye molecules by producing hydroxyl radicals from water molecules as shown in Eq. (5) and Eq. (6):



Therefore, with the increase in its concentration the degradation of reactive azo dye is reported in all the surface plots. In this study at optimum conditions of pH and H₂O₂ maximum reactive azo dye degradation was reported at the 169.2 mg/L of TiO₂ concentrations. Degradation of reactive azo dye also showed decrease with TiO₂ after certain concentration of TiO₂. This could be explained due to increase in opacity and hindrance of passage of UV light due to excess of TiO₂ catalysts (Toor, 2005). Studies also reported that increase in opacity leads to collision of ground state and activated molecules that further causes latter's deactivation (Fu, 2007). This collision reduces the effective surface area of the catalyst particles for adsorption of the contaminants (Davis, 1995).

Similar behavior was reported in studies conducted on other organic chemicals such as bisphenol (Kaneco, 2004), hymatoxylin (Sioi, 2006), chloramphenicol (Chatzitakis, 2008) and paracetamol (Yang, 2008).

4.0. CONCLUSIONS

From the above mentioned outcomes of this study, it could be concluded that photocatalytic treatment of wastewater contaminated with reactive azo dye has proven to be a promising method. At 169 mg/L concentration of TiO₂ and pH of 5.48 an efficient treatment of 73.3% of the dye was achieved. Moreover, response surface methodology has also proven to be an prominent technique in reducing the number of steps for optimization of the process parameters and vis-à-vis lower down the cost of the treatment process. Along with this, in countries like India where a sunlight is available almost all around the year and where textile industry is also advancing, such a treatment technology can prove to be beneficial.

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