UV Radiations Assisted Advanced Oxidation Approach for the Degradation of Reactive Azo Dye, Using TiO$_2$ Photocatalyst

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Summary: About 10,000 tons of different reactive dyes are produced every year all over the world. A huge amount of these dyes is discharged out into water bodies as textile effluents causing environmental hazards. It is necessary to eliminate such persistent contaminants from environment. In present project, solution of reactive azo dye was irradiated which resulted in the free radical degradation known as radiolysis. For the treatment of dye solution, variable parameters such as pH, concentration of H$_2$O$_2$, concentration of TiO$_2$, time of UV irradiation was optimized for the achievement of higher degradation rate of dyes. The response surface methodology (RSM)) was applied for theoretical optimization and collected data interpretation. UV/Visible and FT-IR (Fourier Transform Infrared) spectroscopic techniques were employed for the analysis of extent of dye degradation. The optimized conditions can be employed for the treatment of textile industry wastewater on pilot scale. This heterogeneous photo catalytic method has been found an economical and efficient way for the advanced oxidation treatment of textile industry waste water. The treated water can be reused for industrial and agricultural purposes.

Keywords: Reactive dyes; Contaminant; Response Surface Methodology; Photocatalysis; FTIR.

Introduction

From the last few decades, there is a growing concern of pollution due to its harmful effects on living organisms. Reactive dyes are used almost in all divisions of the textile industry. Certainly, there are dye losses during industrial and processing operations which lead to water pollution on alarming level [1-3]. A huge number of fabric pollutants in the group of azo dyes are categorized by an azo group containing two nitrogen atoms. Azo dyes in textile wastewater are the maximum persistent pollutants as their degradation products are very reactive [4-6].

Removal of dyes from wastewater is required since the color will be observable even at low level of application [7].

Chemical oxidation processes involve reaction mechanisms which generally alter the chemical properties and structures of the toxic organic substances. During the oxidation process molecules decompose in smaller fragments with less toxic nature. Oxidation of organic compounds with oxidants like ozone or HO$^{\bullet}$ radicals lead to the formation of oxidized species which may be more easily degraded as compared to the parent ones. Hydroxyl radicals are responsible for advanced oxidation processes. These radicals oxidize biological contaminants; efficiently eliminate dyes and biological type dyestuffs.

The hydroxyl radical generated in the process convert the whole contaminant to CO$_2$, mineral acids and water. There are a number of merits of Photo-Fenton process, such as an increased reaction rate in the presence of solar radiations, inexpensive chemicals required and non-toxic end products (Esplugas *et al*., 2002). For the textile waste water AOPs are observed as effective treating systems. The mineralization of contaminants can be influenced by various parameters, such as type of radiations, absorbed dose and synergistic effects of radiations, pollutant concentration and dose rate [8, 9].

There are various AOPs involving the use of UV radiations and H$_2$O$_2$. Hydroxyl radicals being produced in this method are short lived and highly reactive chemical species. They react non-selectively in water with biological compounds. Effectiveness of this method owe to the formation of non toxic end products like CO$_2$, H$_2$O and oxygen with no sludge remaining. It may also be accompanied by the production of low molecular weight aliphatic carboxylic acids which may alter the pH of water upto a very little extent [10-12]. Coagulation and flocculation, reverse osmosis, adsorption on activated carbon are various chemical and physical procedures. These procedures are inadequate to decay the colored compounds in textile waste water. A lot of sludge formation is a major issue associated with these procedures [13].

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Table-1: Experimental runs optimizing various parameters.

Run	Factor 1 A: pH	Factor 2 B: TiO2 (g/L)	Factor 3 C: H2O2 (%)	Factor 3 D: Irradiation Time (minutes)	Response: Degradation (%)
1	4	0.75	6.5	90	45
2	6	0.5	2	60	40
3	8	0.75	3.5	90	30
4	2	0.5	5	60	50
5	6	0.5	5	120	67
6	4	0.25	3.5	90	50
7	4	0.75	3.5	90	90
8	2	1	5	120	65
9	4	0.75	3.5	90	90
10	4	0.75	3.5	90	70
11	4	1.25	3.5	90	95
12	2	1	5	60	77
13	6	0.5	5	60	53
14	4	0.75	3.5	150	85
15	6	1	2	120	60
16	2	0.5	2	120	85
17	2	0.5	5	120	90
18	4	0.75	3.5	90	90
19	2	0.5	2	60	72
20	4	0.75	0.5	90	60
21	6	1	2	60	50
22	2	1	2	60	65
23	4	0.75	3.5	90	90
24	6	1	5	120	50
25	6	1	5	60	30
26	2	1	2	120	90
27	2	0.75	3.5	90	89
28	4	0.75	3.5	90	90
29	6	0.5	2	120	60
30	4	0.75	3.5	30	40

Ultraviolet assisted photolysis in the presence of hydrogen peroxide (UV/H_2O_2) is one of the maximal suitable modern oxidation processes for the elimination of poisonous organics from water. This procedure includes the manufacturing of non-selective hydroxyl radicals (HO$^\bullet$) which deteriorate the dye structure by the following reactions:

$$H_2O_2 + hv \rightarrow 2\ HO^\bullet \qquad (1.1)$$
$$HO^\bullet + dye \rightarrow oxidation\ product \qquad (1.2)$$
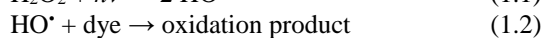
The treatment is beneficial as most of the recalcitrant agents are degraded with no poisonous chemicals remaining[14] [15].
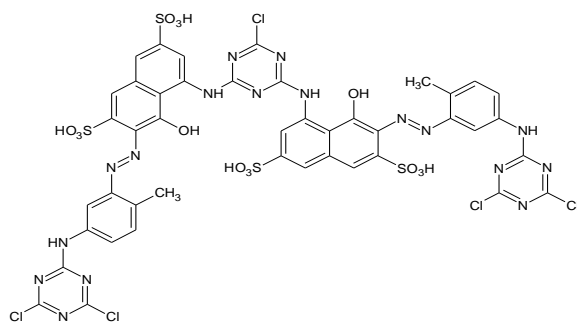

Fig. 1:   Molecular Structure of azo dye.

Keeping in view the above mentioned effectiveness of the AOP and need of the hour, to overcome the environmental hazards of industrial effluents, a project was planned to evaluate the photo catalytic effectiveness of advanced oxidation processes for the degradation of azo dye (Fig. 1). This is a major pollutant of the textile effluent in the dyeing process and need to be degraded. A suitable way to meet the degradation aims can minimize the toxicity and water pollution issue.

Experimental

Materials Required

All of the chemicals used were of analytical grade. Reactive dye having anionic structure was used as model compound. Oxidant used was H_2O_2 35% (Merck), HCl (Merck) and NaOH (Sigma Aldrich) were used for pH adjustment.. Deionized H_2O from Hi-Tech Lab (UAF) conductivity <1 simens m^{-1} was used throughout for solution preparation and dilution. Commercial TiO_2 Degussa p25 was used as photo catalyst. Dye sample which was synthesized in Radiation Chemistry Lab (Department of Chemistry, University of Agriculture Faisalabad), collected for degradation. Its solution having concentration 80 mg/L were prepared for further treatment with UV radiations and H_2O_2/TiO_2 for dye degradation.

Instrumentation

Weighing of chemicals was done by using analytical balance (Sartorius TE 214 S) and centrifugation was done on centrifuge machine 4000

rpm (China) and spectrophotometric measurements were performed on UV/Vis double beam spectrophotometer (CE Cecil 7200, Germany). The treated and untreated samples were analyzed by FT-IR spectroscopy (Bruker IFS 125HR Japan).

Statistical Analysis

The obtained data was analyzed statistically by the application of Response Surface Methodology (RSM). This techniques designate the relationship between explanatory and response variables [16]. Explanatory variable used were pH (2 to 6), concentration of TiO_2 (0.5g/L to 1g/L), dose of H_2O_2 (2 to 5%) and irradiation time (60mins to 120mins).

Response Surface Methodology

Optimization of dye degradation was carried out by response surface methodology (RSM). RSM based on four levels four variable central composite design was used to evaluate the effects of important parameters on the degradation of dyes.

Experimental Runs

The experimental runs detail has been given in Table-1. It included 30 runs in total for the optimization of four parameters that may influence percentage degradation such as pH, H_2O_2 concentration, TiO_2 concentration and irradiation time. Table-1 also indicated the response of each experimental run which was later interpreted as contour diagrams in results section [17].

Results and Discussion

The results were recorded and presented as below after experimentation.

Degradation of monoazo reactive Dye

Optimization experiments on direct photolysis of reactive dye were initially carried out by irradiating the aqueous solution to determine the effect of initial concentration of H_2O_2, pH, photo-catalyst loading and irradiation time. Optimization of independent variables for the effect of photo catalyst was studied and % degradation was theoretically calculated through response surface model (RSM) using polynomial equations.

Statistical Analysis of Degradation

Optimization of dye degradation was carried out by response surface methodology (RSM). RSM

based on four levels four variable central composite design was used to evaluate the effects of important parameters on the degradation of dye. The parameters studied were pH (2-6), TiO_2 photo catalyst loading (0.5-1g), H_2O_2 (2-5%) and UV irradiation time (1-2 h).

Central composite design was utilized in order to optimize photo degradation process with total 21 experiments in experimental modeling. Regression model tests, individual model coefficients and lack of fit tests were performed in order to ensure it as good model for present study while adequacy of the model was further analyzed through ANOVA. From ANOVA lower value of probability factor F> 0.005 indicated that variables have significant effect on response [18].

From the obtained data analysis a second order polynomial equation is obtained as follows (**Eq 1**):

$$y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_1x_1^2+\beta_2x_2^2....(1)$$

where degradation (Y) represents the optimal response of influencing variables and A, B, C, D are the coded representations of photo-catalyst dose, percentage H_2O_2, pH and UV irradiation respectively. Three dimensional graphical representation and contours represent the regression equation for optimization of reaction conditions with interactive response. Results of interactive effect of different operational independent variables and dependent variables are shown in (Fig. 2)

Role of interacting parameters on degradation of mono azo reactive dyes

The individual and interactive effect of irradiation time and concentration of H_2O_2 was investigated and represented in Fig 2 (a, a1), (b, b1), (c, c1), (d, d1), (e, e1), (f, f1).

Interactive effect of photo catalyst and pH

Fig 2 (a and a1) demonstrates the interactive effect of photo catalyst and pH. It was observed that when the amount of photo-catalyst was 0.5g/L the maximum degradation was noted 85% at pH 2. The pH of the solution strongly influences on the surface properties of TiO_2. Therefore, the effect of pH on the removal of dye over photo-catalysis, it is observed that the percent removal increased in acidic pH and decreased in basic pH. Point of zero charge (pzc) of photo-catalyst determines its operative range. It was examined that the degradation rate was higher at pH

less than pzc, as positive charge is attained at the surface of photo-catalyst which can attract oppositely charged pollutant molecules. The anions of Pollutant strongly adsorbed on the surface of photo-catalyst. More the adsorption, higher was the mineralization rate [19]. As dye has two sulfonic groups (negatively charged), it was most probable that at acidic pH, attractive forces are developed between dye and TiO_2 surface, resulting in high adsorption of dye. As the pH increased, TiO_2 surface developed negative charge, resulting in repulsive forces between the dye and TiO_2 surface thus reducing degradation.

Interactive effect of H_2O_2 and pH

An elevated trend of degradation influenced by acidic pH and moderate concentration of H_2O_2 was observed (Fig 2 (b and b1)). At pH below 3.5,

enough HO• were generated leading to the dye degradation. As the degradation rate is directly proportional to the HO• generated. Therefore dye degradation got accelerated at acidic pH.

Interactive effect of Irradiation time and pH

pH is an optimizing factor that influences the degradation of dye in the presence of photocatalyst (TiO_2) or H_2O_2. Degradation got accelerated at acidic pH. On the other hand an increase in irradiation time resulted in greater degradation extent. Therefore Irradiation and pH has a little interactive effect for the degradation of dye (Fig 2 (c and c1)). A moderate range may be suggested when they are to be considered in combination.
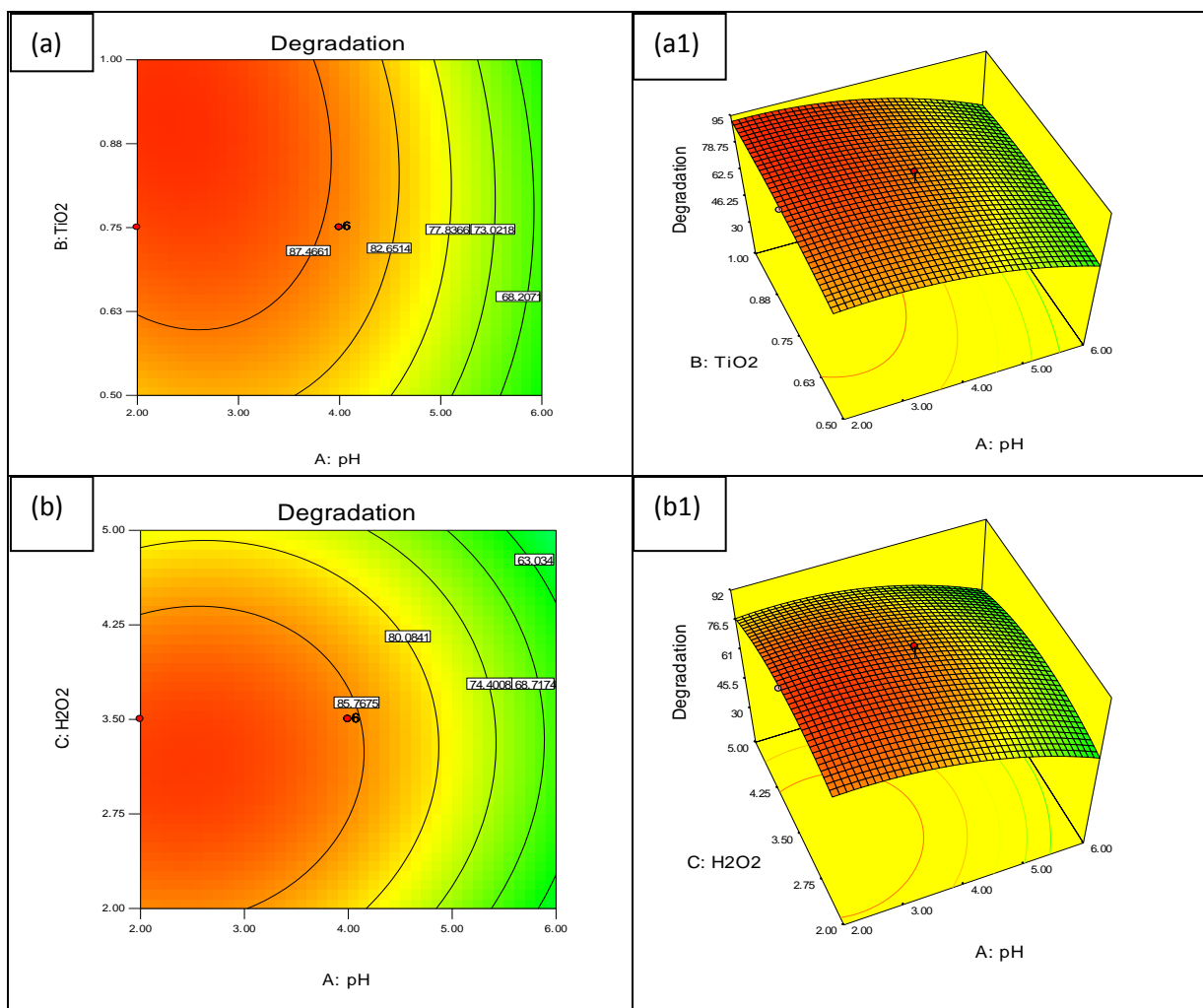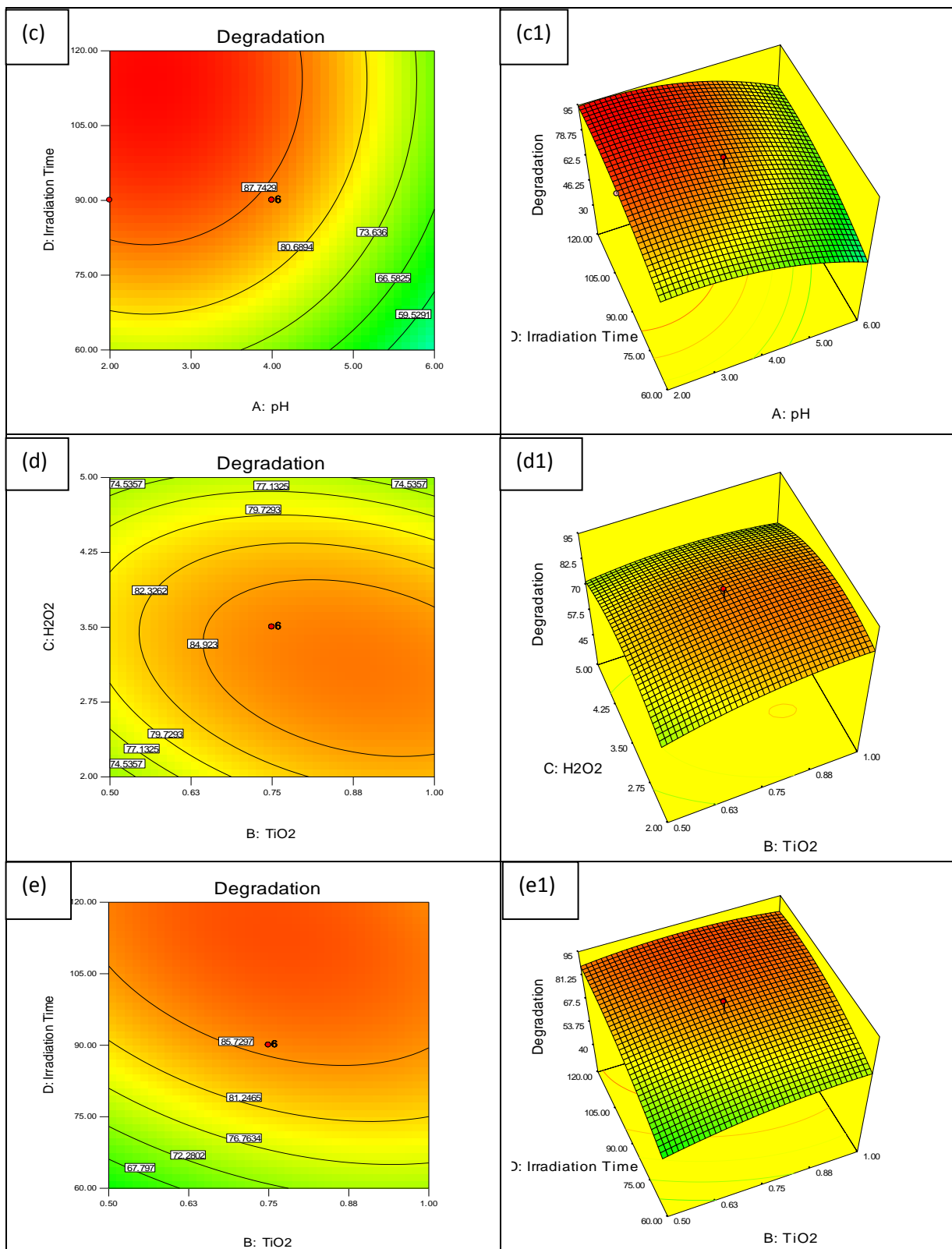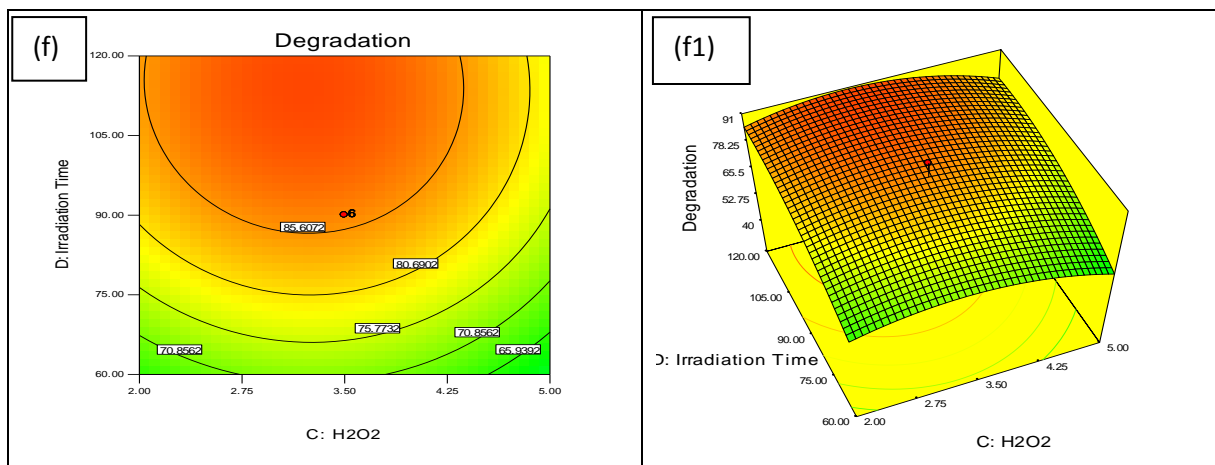
Fig. 2:   Contour and 3D response surface graphs showing extent of degradation by the effect of TiO_2 and pH (a and a1), H_2O_2 and pH (b and b1), irradiation time and pH (c and c1), H_2O_2 and catalyst (d and d1), irradiation time and catalyst (e and e1), irradiation time and H_2O_2 (f and f1).

Interactive effect of concentration of H_2O_2 and $Ti O_2$

The individual and interactive effect of concentration of H_2O_2 and photo-catalyst has been investigated and represented in Fig 2 (d and d1). In the presence of UV/H_2O_2, the dye degradation increased as compared to direct photolysis even at low initial H_2O_2 concentrations. However, increasing the initial hydrogen peroxide concentration increased the oxidation up to a certain level. On further increase of concentration, hydrogen peroxide inhibition was observed. From the experiments it was concluded that the optimum concentration of TiO_2 is 0.5 g/L and optimum H_2O_2 concentration was 3 % at which maximum percentage removal rate i.e. 77 % of the dye was achieved. While by increasing concentration of TiO_2 and H_2O_2 at different values ranging from (0.6 g/L-1 g/L and 3.5-5 %) respectively degradation rate was low i.e. 67 to 60%. Hence it might be reported that loading an in-appropriate amount of photo-catalyst could result in declining rate of degradation of pollutants.

Interactive effect of Irradiation time and TiO_2

The experiments were carried out by varying the TiO_2 concentration from 0.5 g/L to 1g/L with variable reaction time i.e. 60-120 min. These experimental results shown in Fig 2 (e and e1) revealed that at 0.5 g/L of TiO_2 concentration the maximum of 82% removal was achieved in UV/H_2O_2/TiO_2. It has been reported that loading an in-appropriate amount of photo-catalyst resulted in declining rate of degradation of pollutants. This happened probably due to two opposing factors. Insufficient photo-catalyst caused a limited generation of HO˙ due to the insufficient light energy being converted into chemical energy. However, excessive amount was converted into slurries which adversely affected the reaction rate and high concentration of photo-catalyst exceeding the optimum value caused turbidity, scattering and screening of radiations and ultimate decrease in penetration and absorption of photons.

Interactive effect of irradiation time and H_2O_2

The individual and interactive effect of Irradiation time and H_2O_2 concentration has been investigated and results have been shown by contour and response surface plots using 2%-5% concentration range of the commercial H_2O_2 (Fig 2 (f and f1)). During irradiation, H_2O_2 absorbed radiations of specific energy in UV range and O–O bond was cleaved leading to the production of activated HO˙ radicals and the atomic oxygen. By increasing nH_2O_2 concentration in the presence of radiation source, production of HO˙ radical was enhanced with the absorption of energy required for the cleavage of O–O bond [17]. The production of HO˙ radicals and the oxidative destruction of organic pollutants may be demonstrated as (Eq 3.1-3.2).

$$H_2O_2 + hv \rightarrow 2HO˙ \qquad (3.1)$$
$$RH + HO˙ \rightarrow H_2O + ˙R \rightarrow CO_2 + H_2O \qquad (3.2)$$
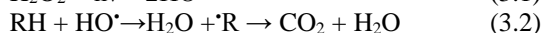
For higher concentrations of H_2O_2 caused recombination of HO˙ free radical and ultimate scavenging of oxidation chain reaction which resulted in low rate of mineralization [20].

Oxidation Potential of $HO_2^{\bullet}$ (hydroperoxyl free radical) is low so percentage degradation caused by such moieties was less (Prez *et al.*, 2002). Moreover, it may also be inferred that the H_2O_2 itself becomes an active competitor for $HO^{\bullet}$ [21]. Therefore, it was suggested to use minimum to moderate amount of H_2O_2 for photo-catalytic degradation of pollutants/dye.

As obvious from RSM 2D plots, increase in concentration of H_2O_2 from 2% to 4% has increased degradation by increasing irradiation time ranging between (30-120 mins) from 72% to 77% for 90 and 77% to 82% for 120 mins. Maximum degradation was achieved in case of 120 mins irradiation time at 3% H_2O_2 concentration. At higher concentration of H_2O_2 decrease in percentage degradation was noted i.e. 60.45% and 67.05% for 90 mins and 120 mins respectively using 5% of H_2O_2.

*FT-IR analysis of reactive dyes before and after treatment*

Bands appearing in FT-IR spectrum of treated and untreated reactive dye have been analyzed for the determination of extent of degradation. Fourier transform infrared (FT-IR) analysis of dyes was carried out before (Fig 3 (a)) and after irradiation (Fig 3 (b)). Un-irradiated dye sample showed many characteristic peaks of different functional groups.

Mono azo reactive dye was characterized by FT-IR before and after treatment to study the effect of UV radiations. Before radiation treatment, peaks were observed at 3741.90 cm^{-1}, 2927.94 cm^{-1}, 1745.58 cm^{-1}, 1556.55 cm^{-1}, 1479.40 cm^{-1}, 1388.75 cm^{-1}, 1138.00 cm^{-1}, 1014.56 cm^{-1}, 950.91 cm^{-1} and 754.17 cm^{-1} corresponding to hydroxyl (-OH), amino (-NH$_2$), azo (N=N), sulfo and substituted benzene ring peaks, respectively, as shown in Fig 3(a). It was observed that after radiation treatment main peaks of non-degraded dye sample were vanished. After exposing the dye solution to UV radiations, FT-IR spectrum exhibited bands at 3346.50 cm^{-1}, 1637.56 cm^{-1}, 665.44 cm^{-1}, 597.93 cm^{-1}, 577.43 cm^{-1} and 464.84 cm^{-1} which may be attributed to the presence of hydroxyl (OH), carbonyl (CO) and substituted benzene ring (in a little amount). Color imparting azo group was very sensitive to radiation and easily got ruptured when exposed to UV radiation.

UV-Vis analysis

UV/Visible Spectroscopy was used for the study of discoloration after radiation treatment. It was clearly observed that absorption maxima (λ_{max}) have been shifted to ultraviolet region after irradiation. It means that interaction of radiation lead to the breakdown of coloring chromophoric azo group and new products were formed via degradation. The degraded product might be an intermediate or new product formed during UV radiation treatment. UV-Visible analysis of the dye was done before and after degradation treatment. Absorption peak was observed to be diminished in case of treated dye solution (Fig 4 (a)) which was previously noted near to 489 nm for un treated dye solution (Fig 4 (b)).
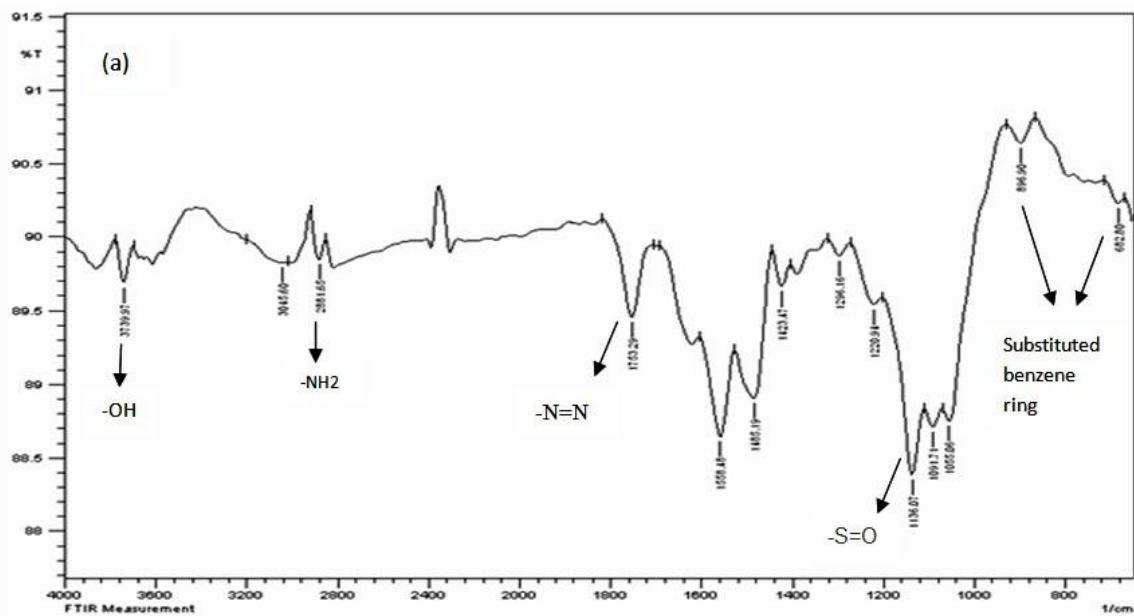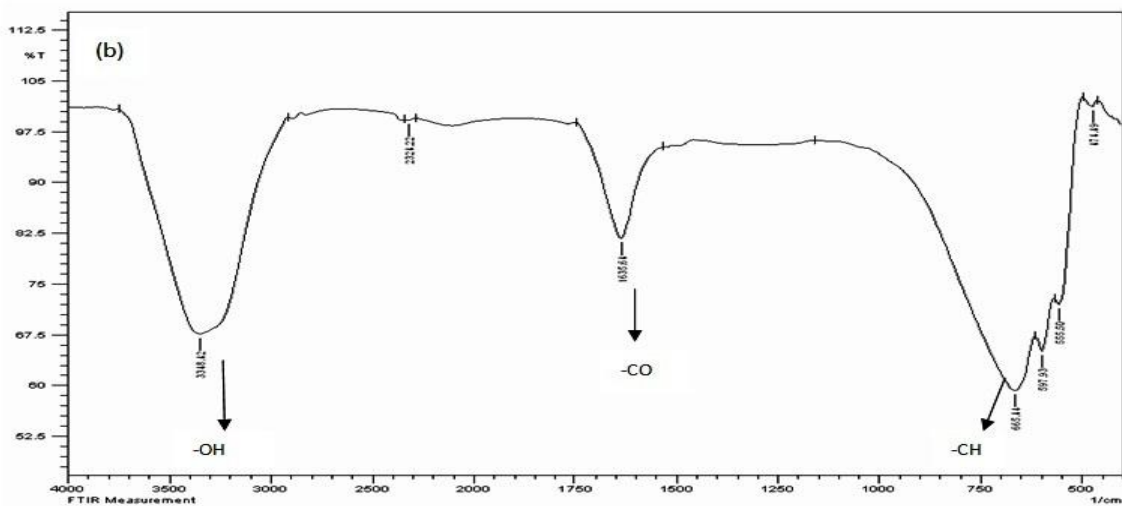
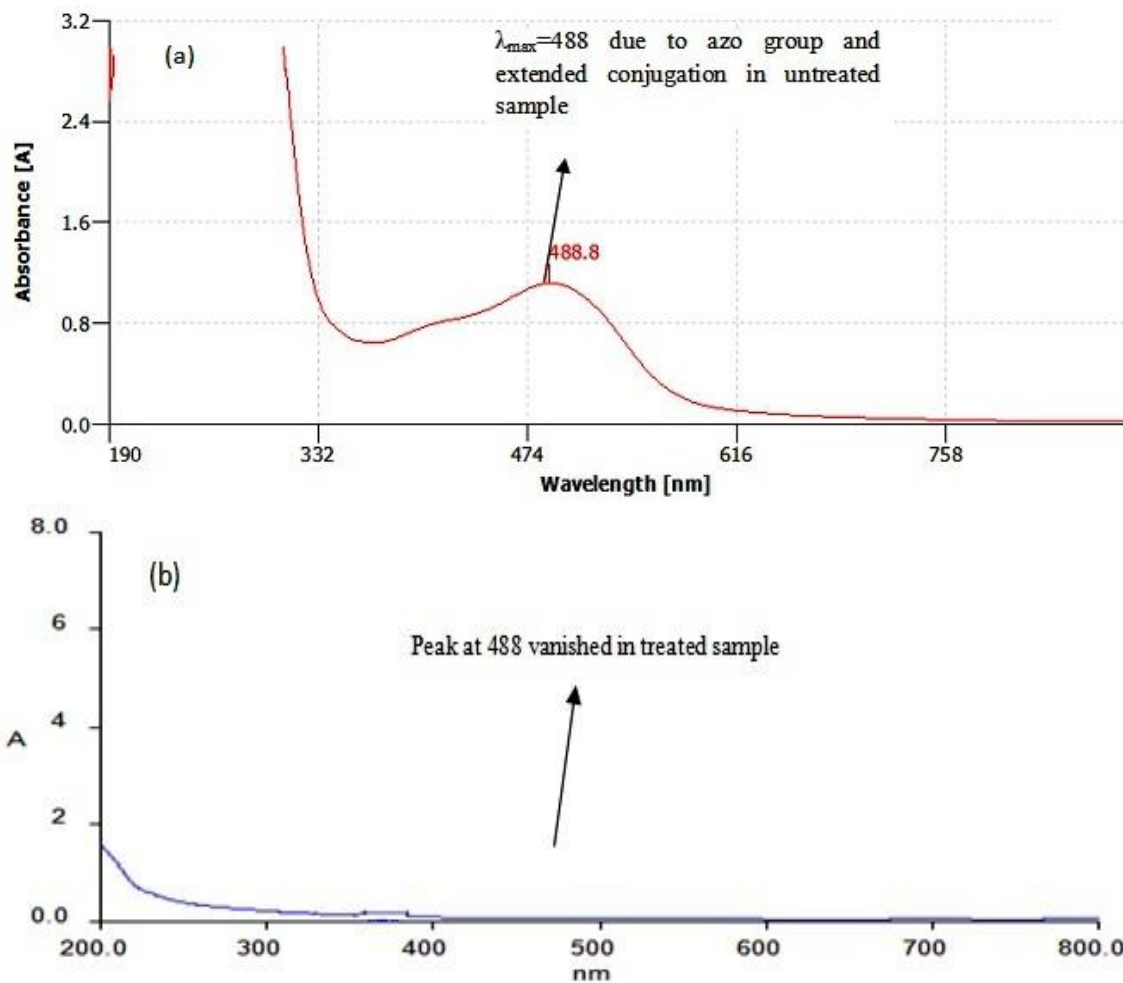Fig. 3:   FT-IR spectra of dye (a) before treatment (b) after treatment.

Fig. 4:   UV/Visible spectrum of model reactive azo dye (a) before irradiation and (b) after irradiation.

Conclusion

In this study, an investigation has been made for the degradation of azo dye by Advanced Oxidation Process (AOP) using TiO_2 as photocatalyst in the presence of UV radiations, pH, irradiation time, amount of photocatalyst, concentration of H_2O_2 which significantly affected the extent of degradation. It was observed from the results that appreciable degradation level may be achieved at acidic pH (below 3.5), moderate concentration of H_2O_2 and 2 hrs time of UV irradiation. Increasing trend of degradation was observed with concentration of photocatalyst. UV-Vis and FTIR spectroscopic analysis before and after dye degradation by AOP revealed maximum deterioration of most of the dye structure at optimized conditions, resulting in less to non toxic degradation products.

Acknowledgement

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