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Decolorization and mineralization efficiency of the hetero-functional reactive dyes using advanced oxidation processes

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ABSTRACT

The current study was aimed at the decolorization and mineralization of six newly synthesized hetero-functional (vinyl sulfone and cyanuric chloride) azo reactive dyes (D-1 to D-6) using two advanced oxidation processes (Fenton and photo-Fenton). Results showed that both oxidation mechanisms effectively mineralized the synthesized hetero-functional azo reactive dyes. However, decolorization and mineralization of dyes through photo-Fenton oxidation were more effective than Fenton oxidation. The data revealed that process parameters (pH, Fe^{2+} dosage, concentration of H_2O_2, and reaction time) greatly affect the mineralization of the selected dyes. Decolorization efficiency (98%) and chemical oxygen demand (COD) removal (78%) was obtained for the six degraded azo reactive dyes under optimum conditions; pH (3), Fe^{2+} concentration (20 mg/L), H_2O_2 (500 mg/L), and contact time (80 min) using Fenton oxidation. On the other hand, 99% decolorization and 82% COD removal was achieved for the photo-Fenton oxidation process under optimum conditions of pH (3), Fe^{2+} (15 mg/L), H_2O_2 (300 mg/L), and irradiation time (60 min) for the six hetero-functional azo reactive dyes. From the above results, it was concluded, that both oxidation processes can be effectively employed for the degradation of the six hetero-functional azo reactive dyes.

Keywords: Decolorization; Mineralization; Reactive dyes; Fenton; Photo-Fenton

1. Introduction

Under the current scenario of progress in the industrial sectors, a great discharge of textile effluents related to the partial dye exhaustion onto textile throughout dyeing processes has been noticed [1–4]. A large amount of wastewater is produced by the textile industries in which heavy metals and dyes are present which causes different types of pollution. During fabric processing, the wastewater discharging from these industries containing minute amounts of metals such as chromium, copper, and zinc which are dangerous for the health as well as for the environment. Different diseases caused by the textile wastewater include nausea, ulceration, dermatitis, and hemorrhage. The chemicals which are present in wastewater inhibit the process of photosynthesis and re-oxygenation by blocking the sunlight and enhanced biochemical oxygen demand (BOD). It is predictable that about 100,000 units of fiber reactive dyes are in process and their production per annum in the whole world are more than 7×10^{-5} metric tons [5–9]. Additionally, reactive dyes are being used in plastic, printing, food, and leather industries. Many of them exist in the textile effluents which cause the contamination of water and disturbing the ecosystem [10–12].

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The limit of detection of reactive dye in wastewater by the human eye is approximately 0.005 mg/L and consequently, the existence of dyes beyond this limit would not be acceptable on the aesthetic ground [13]. The serious attention of civic and local legislation is required to eliminate the coloring materials from fabric effluents before releasing into the environment [14,15]. In the reactive dyes, the chromophore is present having a high capability of direct reaction with a substrate of the fiber and makes them more everlasting. The colors of reactive dyes are not simple to eliminate by wastewater treatment processes and in most of the cases it is not easily degradable [16–18].

Different methods for water treatment include adsorption, biological discoloration, and complex oxidation mechanism, for example, the photo-Fenton reaction [19], photocatalytic deprivation by ultraviolet irradiation, visible light, and microwave exonerate lamps. Incomplete mineralization of the textile effluents are carried out by the above methods converting them into small toxic molecules [20].

One of the largely promising unusual technologies is the utilization of complex oxidation processes. Advanced oxidation processes (AOPs) non-selectively and rapidly oxidize a wide variety of structurally miscellaneous organic pollutants, by producing highly reactive OH radicals which completely degrade the organic substances [21]. The standard Fenton reaction (Fe^{2+}/H_2O_2) has gained great attraction as a way for devastation of a broad variety of intractable compounds [22,23] owing to its simplicity of operation, the simple scheme and the opportunity to work in a broad range of temperature [24,25]. The general method via Fenton reagents, by which the OH radicals are produced is a cyclic reaction, which uses the ferrous and ferric ions as a catalyst to putrefy the hydrogen peroxide. At the end of the reactions, these ions are obtained in their original condition [26]. The velocity of degradation of organic compounds through the Fenton procedure is highly speed-up by irradiation with ultraviolet-visible light called as photo-Fenton procedure [27]. The reactivity of the photo-Fenton oxidation procedure highly depends upon the generation of OH radicals, by breaking the H_2O_2 in the presence of light and reduction of Fe ion in the presence of light. Highly reactive species OH^- and $^{\bullet}OH$ are produced by the decomposition of hydrogen peroxide through ultraviolet light [28–32]. Decomposition of H_2O_2 creates highly reactive oxygen species OH^-, $^{\bullet}OH$ in the photo-Fenton reaction which plays the principal role for the organic pollutant mineralization in the water [33,34]. Degradation of the organic pollutants increased as the generation of reactive species increased in the reaction medium [35]. The H_2O_2 photolysis rate directly depends on the intensity of the incident light. Low intensity of the UV light produced less hydroxyl radical due to the less dissociation of H_2O_2 while at a high light intensity, the rate of photolysis of H_2O_2 was higher, therefore, increasing the removal rate [36–38]. Number of experiments were conducted for the optimization of process parameters of Fenton and photo-Fenton to achieve the complete mineralization of the selected hetero-functional dyes. The Fenton oxidation mechanism generates hydroxyl radicals ($^{\bullet}OH$) from the catalyzing reaction between ferrous or ferric ion (Fe^{2+}/Fe^{3+}) and hydrogen peroxide (H_2O_2) under acidic conditions (pH 2–6). This mechanism is helpful in reducing the organic load and toxicity of different wastewater from chemical industries which reduces the chemical oxygen demand (COD) values. The effectiveness of the process depends on the initial pH, the ratio of [H_2O_2] to [COD], and the ratio of [H_2O_2] to [Fe^{3+}].

The current study was carried for the mineralization of the six hetero-functional azo reactive dyes (D-1 to D-6) that were previously [39,40] synthesized and applied on cellulosic fabric through exhaust and pad dyeing method. Mineralization of these hetero-functional azo reactive dyes was carried out through Fenton and photo-Fenton processes and has not been reported yet. The mineralization process of these dyes was improved by optimizing the important process parameters.

2. Materials and methods

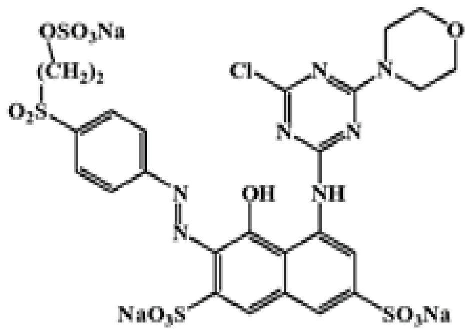
Six hetero-functional azo reactive dyes were synthesized and their characterization study was carried out through spectroscopic methods. Synthesized dyes structures are shown in Fig. 1. All chemicals used during the study were of analytical grade and purchased from Sigma Aldrich. All solutions were prepared in distilled water throughout the experimental process. The pH of the medium was adjusted using 0.1 M NaOH or 0.1 M H_2SO_4 as per requirement. Experiment was conducted with 100 mL dye solution to check the influence of different parameters on the decolorization efficiency. At the start of the reaction, the required amount of H_2O_2 and $FeSO_4$ was added to the Erlenmeyer flasks (500 mL) covered with aluminum foil at room temperature and placed on a water bath shaker at 100 rpm. Different experimental parameters including pH (2, 3, 5, 7, and 9), H_2O_2 dose (100, 300, 500, 700, and 900 mg/L), contact time (20, 40, 60, 80, and 100 min) and $FeSO_4$ concentration (5, 10, 15, 20, and 25 mg/L) were employed to check the decolorization of reactive dyes by Fenton's reagent [28,41].

2.1. Photo-Fenton oxidation

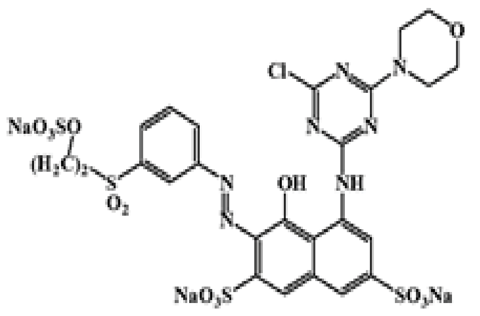
Degradation rate of the new hetero-functional reactive dyes was investigated by irradiating the sample under UV lamp using 54 W light intensity in case of photo-Fenton process. For this purpose, 500 ppm dye solution was prepared by adjusting its pH through the digital pH meter. 100 mL dye solution was taken in the flask at start of reaction and 30% H_2O_2 was added in it, covered it with aluminum foil and placed on magnetic stirrer under UV lamp. The constant shaking speed was about 100 rpm. In order to check the possible maximum removal of dye, the effect of different experimental parameters was checked on the decolorization of reactive dyes by photo-Fenton's reagent [42]. The effect of time was evaluated by periodically withdrawing the sample from the flask and percent decolorization of the samples was checked.

2.2. Decolorization efficiency

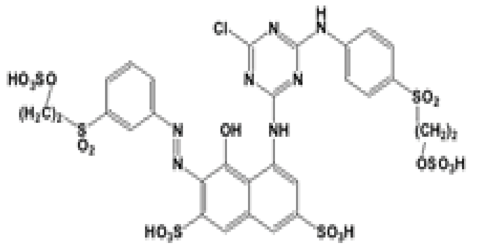
The percent removal or decolorization efficiency of the six hetero-functional reactive dyes was calculated using Eq. (1). Dye concentrations were measured using UV-visible spectrophotometer:



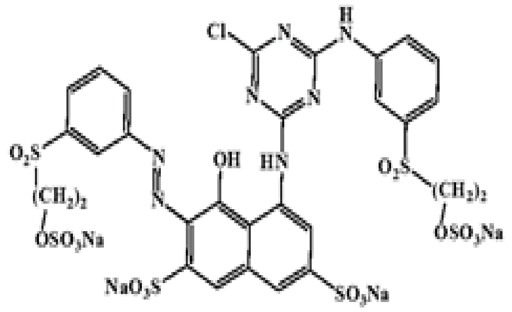
D-1 Vinylsulphone para ester



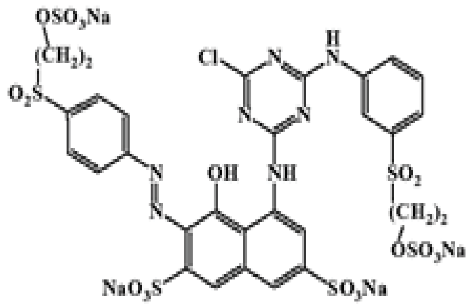
D-2 Vinylsulphone meta ester



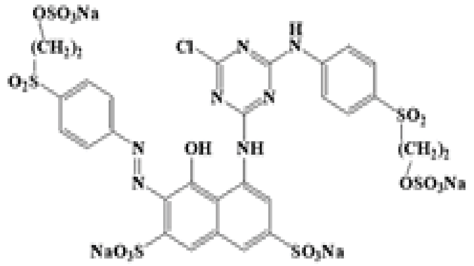
D-3 Meta and Para ester Vinylsulphone



D-4 Meta and Meta ester Vinylsulphone



D-5 Para and Meta ester Vinylsulphone



D-6 Para and para ester vinylsulphone

Fig. 1. Structures of dyes used for degradation studies.

$$\text{Removal}(\%) = \frac{\left(C_i - C_t\right)}{C_i} \times 100 \tag{1}$$

where C_i and C_t represent the initial and final concentrations of dye before and after treatment, respectively.

2.3. Analytical methods

At wavelength of maximum absorption UV/vis absorption spectra was studied using Perkin Elmer Lambda (CE-7200) double beam UV/vis spectrophotometer for dye solutions before and after degradation. Digital pH meter was used for the determination of pH of the dye solutions. For the evaluation of dye degradation, Fourier transform infrared (FT-IR) analysis was carried out [21].

3. Results and discussion

The experiments were repeated three times, and data was analyzed by analysis of variance (ANOVA), the main purpose of ANOVA (Table 1) was to determine the effect of each parameter of the results, regarding the total variance of all parameters. The *F*-test showed that under the studied levels of each factor, the Fe^{2+} and H_2O_2 dosages, pH as well as contact time has significant effect on mineralization and degradation efficiency of dyes. Also, the *F*-test was performed for all the parameters at 95% confidence level.

Table 1
ANOVA results for Fenton and photo-Fenton process

Source	Sum of square	df	Mean square	*F*-value	*p*-value
			Fenton process		
Design	7.87	9	0.87	6.18	0.0002
pH	0.81	1	0.81	5.72	0.0001
Fe^{2+} dosage	6.40	1	6.40	4.32	<0.0002
H_2O_2 dose	2.77	1	2.77	19.59	<0.0002
Time	2.45	1	2.45	0.17	0.0001
Residual	1.42	10	1.42		
Pure error	0.37	5	0.27		
			Photo-Fenton process		
Design	15.8	9	1.76	12.93	0.0002
pH	2.26	1	2.26	16.59	0.0002
Fe^{2+} dosage	1.77	1	1.77	13.03	<0.0001
H_2O_2 dose	0.77	1	0.77	5.64	<0.0001
Contact time	0.27	1	0.27	1.96	0.0005
Residual	1.36	10	0.14		
Pure error	0.58	5	0.59		

3.1. Effect of pH on Fenton process

Acidic conditions can affect the hydrogen peroxide and generate oxonium with high stability. On the other hand, the presence of high excess proton can scavenge hydroxyl radicals. In addition, hydrogen peroxide is decomposed in acidic condition to water [43,44]. Oxidation of the organic substances has been affected by the pH directly and indirectly. Textile wastewater pH is a very important factor in the AOPs. The pH of the solution is a key parameter during the treatment efficiency for Fenton's reagent. Hydroxyl radical's generation and Fe^{2+} concentration during the reaction are controlled by the pH of the solution [45]. The pH effect was studied with the experimental conditions by taking 100 ppm dye solution, 25 mg/L Fe^{2+} with 250 mg/L H_2O_2 at 30°C temperature for 1 h at shaking speed of 100 rpm.

It is illustrated in Fig. 2 that the maximum dye decolorization was achieved at pH 3 in case of all reactive dyes and then up to pH 9 the percentage removal efficiency decreased continuously up to 50%. The removal efficiency strongly decreased because precipitation of the iron starts as hydroxide ion at a pH above 4. Oxidation of hydroxyl radical decreased by decreasing the pH and at a pH lower than 2, stability of the hydrogen peroxide increased due to the formation of H_3O^+ ion possibly by solvating a proton. A H_3O^+ ion significantly reduces the reactivity of the hydroxide ion with the ferrous ion making it more electrophilic and enhancing its stability. Consequently, hydroxyl radical's amount will decreased thus reducing the removal efficiency [46].

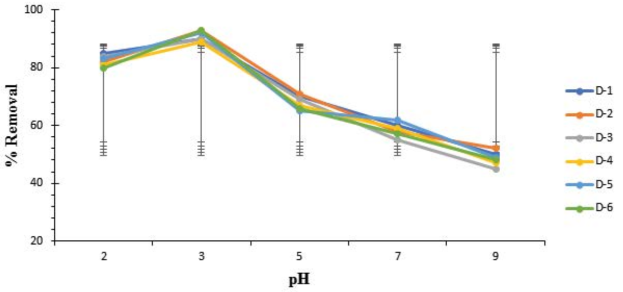


Fig. 2. Effect of pH on the % removal of six novel reactive dyes by Fenton oxidation.

3.2. Effect of Fe^{2+} dosage

Removal efficiency of novel reactive dyes was also varied by varying the concentration of Fe^{2+} with different ranges. In this study the concentration range of Fe^{2+} was 5, 10, 15, 20, and 25 mg/L while keeping the pH 3, contact time 1 h, 250 mg/L H_2O_2 at 30°C temperature and shaking speed 100 rpm. Fig. 3 illustrates that the maximum removal (up to 96%) of novel dyes was done with 20 mg/L of Fe^{2+}. In the start, the removal was 50% then it observed to be increased continuously and reached the maximum level then again decreased up to 74% at the 25 mg/L concentration of Fe^{2+}. There is no evidence for the generation of the hydroxyl radical by the

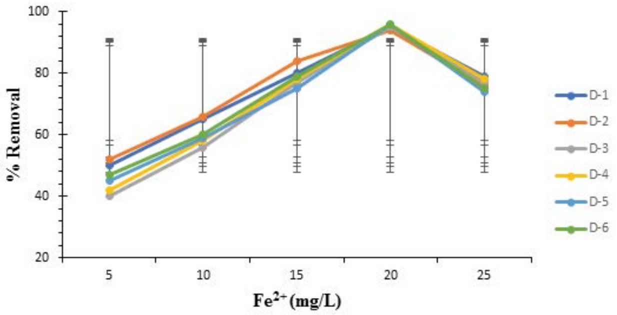


Fig. 3. Effect of Fe^{2+} dosage (mg/L) on the removal of novel reactive dyes by Fenton.

addition of H_2O_2 to wastewater in the absence of the iron. As iron concentration is increased, the dye percent removal increases up to the point from where further addition of iron becomes ineffective. This is distinguishing feature (an optimal dose range for iron catalyst) of Fenton's reagent. Such negative effect of higher catalyst dose could be attributed to other competitive and undesirable reactions that reduced the quantity of the radicals accessible for the oxidation of the organic matter by reaction with excess Fe^{2+} ions. It was analyzed at high Fe^{2+} concentration the low percent removal was due to opposing hydroxyl radicals with dye molecules which can be expressed by the Eqs. (2) and (3):

$$\text{Dye}^{+}\text{ (or dye)} + OH^{\bullet} \rightarrow \text{degradation product} \quad (2)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \quad (3)$$

So, in order to obtain the proper desired percent removal during the reaction period, the Fe^{2+} concentration should be properly controlled [47].

3.3. Effect of H_2O_2 dose

Fenton's reagent generates the hydroxyl free radical which is a powerful, non-selective oxidant. The removal efficiency of novel reactive dyes was also varied by varying the concentration of H_2O_2 with different ranges. In higher H_2O_2 concentration, a chain reaction occurs in which hydroperoxyl radicals react with hydroxyl radicals and itself to produce hydrogen peroxide [44]. In the present study, concentration range of H_2O_2 was 100, 300, 500, 700, and 900 mg/L while keeping the pH 3, contact time 60 min, 20 mg/L of Fe^{2+}, 30°C temperature and shaking speed 100 rpm applied for removal of dyes. It is confirmed from the Fig. 4 that the maximum removal (98%) was done with 500 mg/L concentration. In the start, the percentage removal was 40%, then it is accelerated continuously and reached the maximum level (98%) at 6,500 mg/L of H_2O_2 then again decreased up to 72% at the 900 mg/L concentration of H_2O_2. Surplus H_2O_2 generated per-hydroxy radical which had lower oxidation potential than the former because hydrogen peroxide molecules (Eq. (4)) acted as scavenger of hydroxyl radical [48]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}OOH \quad (4)$$

3.4. Effect of contact time

For an economical treatment of the wastewater system, the equilibrium time is one of the most important parameters. The reactions were followed for all dyes at their optimum pH 3 by keeping other process parameters constant, for example, temperature (30°C), Fe^{2+} dosage (20 mg/L), H_2O_2 dose (250 mg/L), and shaking speed (100 rpm). 20–100 min range with an interval of 20 min was selected for the reactions. It was observed from Fig. 5 that the maximum decolorization (up to 98%) of novel dyes was taken place in 80 min. This can be explained by the fact that most of the hydrogen peroxide reacted with Fe(II) in the beginning of the reaction. The rate of the reaction was high at start of the reaction than it increased slowly and became constant. Hydroxyl ions were furnished in the aqueous dye solution due to the dissociation of the hydrogen peroxide. Hydrogen peroxide has become the limiting reactant with the passage of time and the dye degradation rate becomes slower because the required stochiometric amount of hydrogen peroxide is depleted with time.

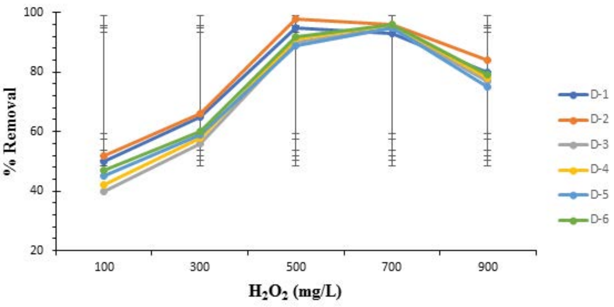


Fig. 4. Effect of concentration H_2O_2 (mg/L) on the removal of novel reactive dyes by Fenton oxidation.

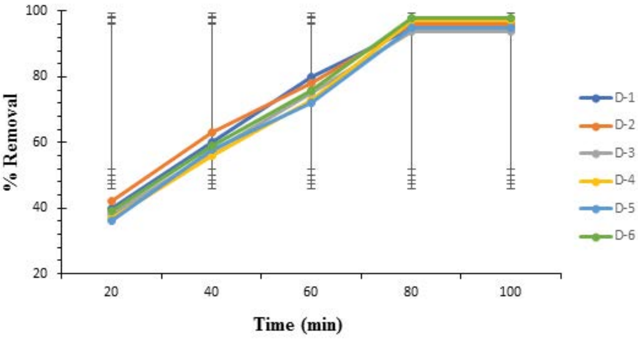


Fig. 5. Effect of time on the removal of novel reactive dyes by Fenton oxidation.

3.5. Effect of UV radiations (photo-Fenton)

It was observed that radiation energy increases the rate of degradation of organic compounds. In present research work, the decolorization study of novel reactive dyes was carried out by sample irradiation under UV lamp using 54 W light intensity. In order to check the possible maximum removal of dye, the effect of different experimental parameters such as pH (2, 3, 5, 7, and 9), contact time (20, 40, 60, 80, and 100 min), H_2O_2 dose (100, 300, 500, 700, and 900 mg/L), $FeSO_4$ concentration (5, 10, 15, 20, and 25 mg/L), were checked on the decolorization of reactive dyes by photo-Fenton's reagent and results are presented in Figs. 6 and 7. The effect of UV radiation on the degradation of the novel dyes was studied at different time intervals 20, 40, 60, 80, and 100 min by keeping all other parameter constant. It was analyzed from the Fig. 7b that the percent removal of all dyes increased with the passage of time and was maximum at 60 min. This was due to the fact that maximum $OH^{\bullet}$ radicals were produced at highest intensity so the decolorization efficiency was also enhanced. Dye decolorization was mainly due to the generation of the hydroxyl

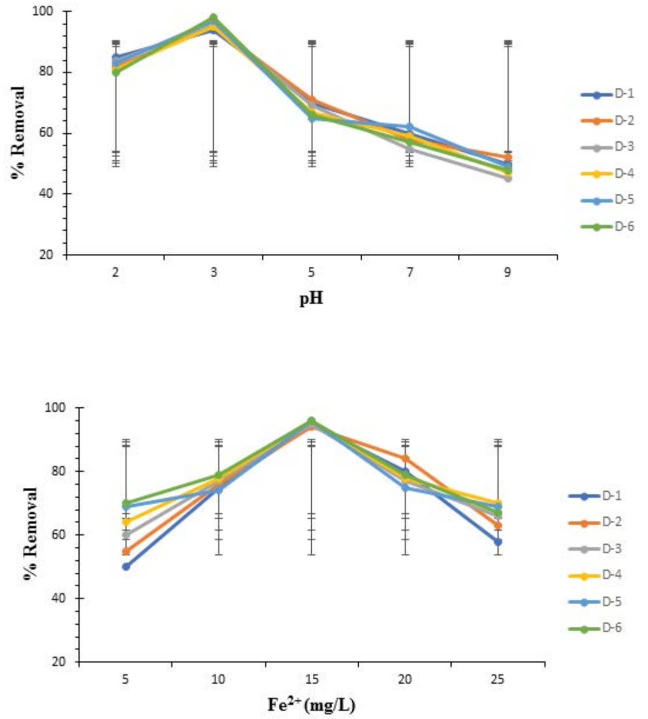


Fig. 6. Effect of (a) pH and (b) Fe^{2+} on the removal of novel reactive dyes by photo-Fenton oxidation.

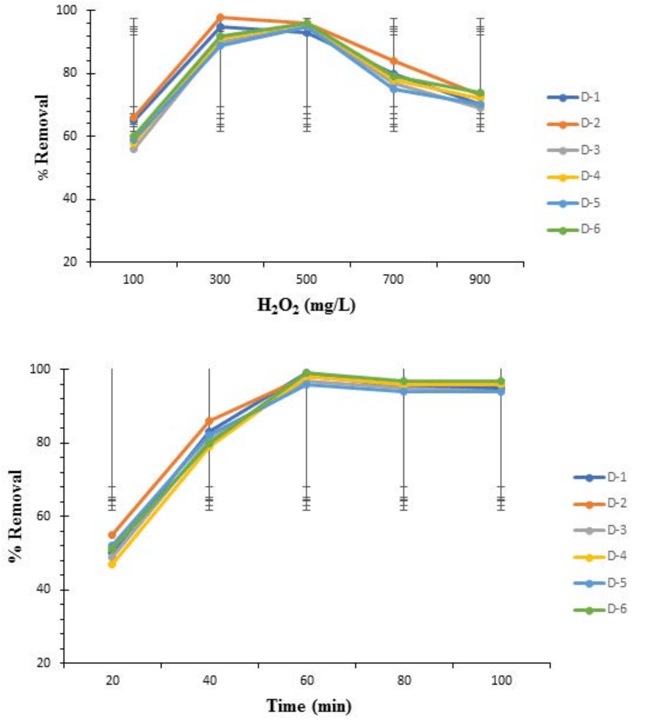


Fig. 7. Effect of (a) H_2O_2 and (b) time on the removal of novel reactive dyes by photo-Fenton oxidation.

Table 2
Optimized process parameter conditions for mineralization of new azo reactive dyes (D-1 to D-6) through Fenton and photo-Fenton oxidation

Selected parameters	Fenton oxidation	Photo-Fenton
pH	3	3
Fe^{2+}	20 mg/L	15 mg/L
H_2O_2	500 mg/L	300 mg/L
Reaction time	80 min	60 min
Decolorization (%)	98	99
COD removal (%)	78	82

radicals through the chemical and photochemical reactions. The increase efficiency of photo-Fenton process was attributed to the generation of additional hydroxyl radicals than produced in the Fenton process. Intensity of the UV light was principally used for H_2O_2 photolysis and for the photo-reduction of ferric ion to ferrous ion. The increase in the percent removal was due to the generation of the hydroxyl radicals. Table 2 shows optimized conditions for both Fenton and photo-Fenton oxidation methods for reactive dyes.

3.6. λ_{max} *of the aqueous solutions of degraded novel reactive dyes*

UV/vis absorption peaks of the reactive dye solutions (D-1, D-2, D-3, D-4, D-5, and D-6) before and after degradation were obtained (Fig. 8). The absorption bands in the visible region as presented in Table 3 were accredited to the conjugated structures constructed through azo bond. It decreased during the degradation process, representing the decomposition of the aqueous dye solutions and decolorization of the solution. A new band in the UV region appeared, suggesting the formation of intermediate product after degradation.

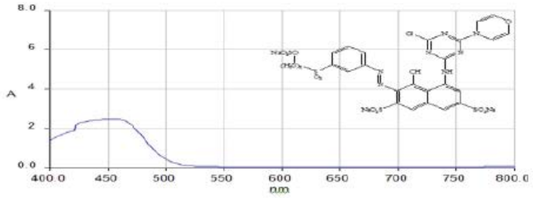
The decreasing trend in the absorption peak and their shift in the UV region are predicted due to the degradation of the characteristic chromophoric functional groups which are translated into smaller fragmentation, that is, carboxylic acids from the complex dye molecule structure [49].

3.7. *FT-IR spectrometric studies for degraded dye solutions*

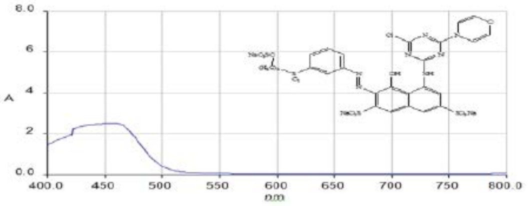
Fenton and photo-Fenton oxidation processes were used for the degradation studies of the novel reactive

Table 3
λ_{max} of aqueous solutions of novel reactive dye before and after degradation

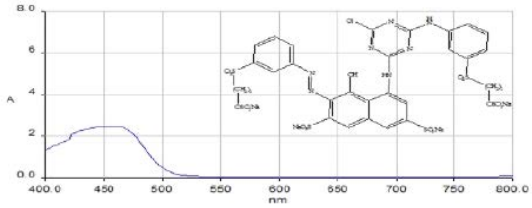
Dye	λ_{max} before degradation	λ_{max} after degradation
D-1	459 nm	340 nm
D-2	462 nm	337 nm
D-3	475 nm	335 nm
D-4	477 nm	330 nm
D-5	475 nm	376 nm
D-6	480 nm	329 nm



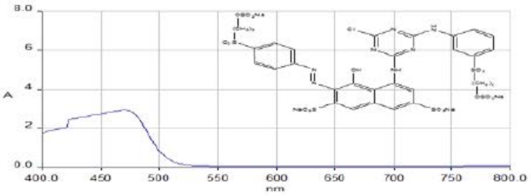
UV/Vis spectra of reactive azo dye D-1



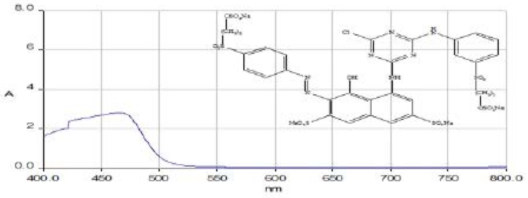
UV/Vis spectra of reactive azo dye D-2



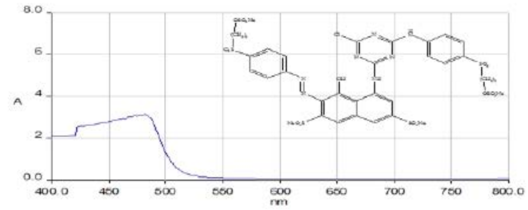
UV/Vis spectra of reactive azo dye D-3



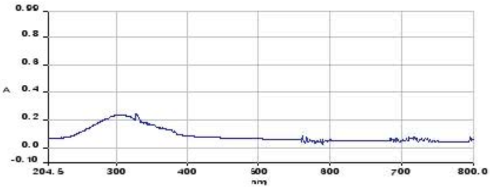
UV/Vis spectra of reactive azo dye D-4



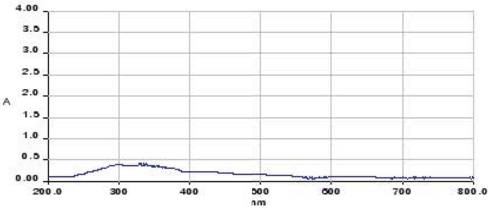
UV/Vis spectra of reactive azo dye D-5



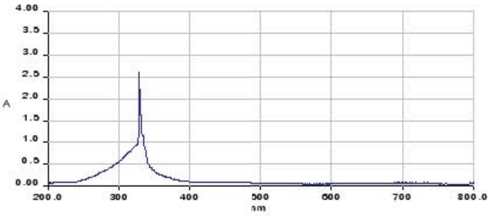
UV/Vis spectra of reactive azo dye D-6



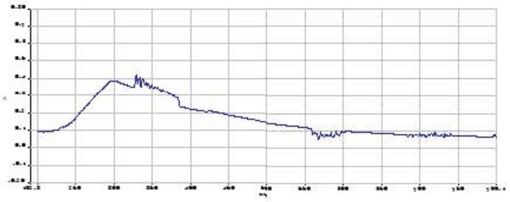
UV/Vis spectra of degraded dye D-1



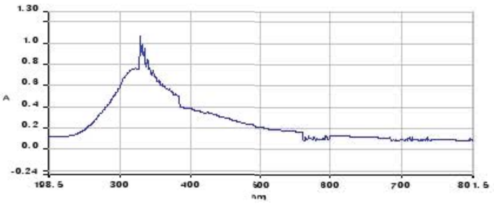
UV/Vis spectra of degraded dye D-2



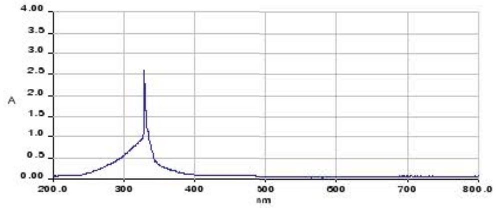
UV/Vis spectra of degraded dye D-3



UV/Vis spectra of degraded dye D-4



UV/Vis spectra of degraded dye D-5



UV/Vis spectra of degraded dye D-6

Fig. 8. UV-Vis spectra of dyes before and after degradation studies.

dyes. FT-IR spectra of dyes before and after degradation study were recorded. FT-IR profiles of the degraded dye samples (Fig. 9a and b) indicated that dye molecules have been degraded and decolorized into simpler and smaller intermediate molecules with advance oxidation processes.

Synthesized dye samples exhibited characteristic peaks of different functional groups, the most important were imino and azo group peaks at 3,400 and 1,550 cm^{-1}, respectively, because these groups were appeared during synthesis. Some minor peaks appeared 3,300–3,200 cm^{-1}

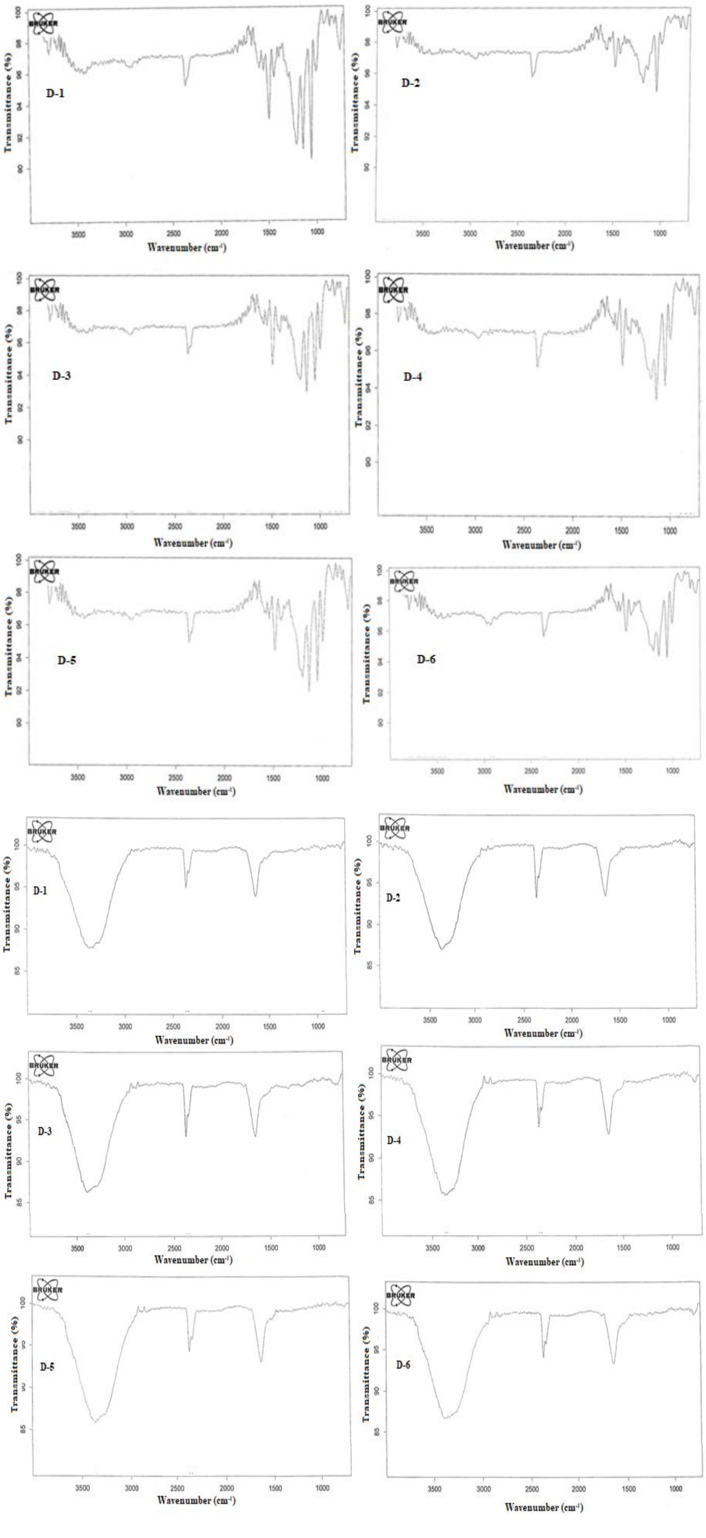


Fig. 9. FT-IR spectra of dyes before and after degradation studies.

for NH stretching signified that some of the –NH linkages has broken down or decreased due to the degradation processes. FT-IR profile of the treated dyes clearly indicated that dye molecules have been degraded as characteristic peaks between 1,700 and 1,500 cm^{-1} due to the N=N has been disappeared. Color imparting azo group is very sensitive to oxidation and easily ruptured. The results obtained in the degraded spectra of FT-IR are followed by the addition of –OH at the region of 3,300–3,400 cm^{-1} which indicates the oxidative degradation of azo reactive dyes through the breakdown of the bridging group in the dye moieties respectively. The degraded intermediates were scrutinized by means of FT-IR spectroscopy which confirmed the oxidative effectiveness. The FT-IR studies illustrated that the apparent functional group peaks (azo group and aromatic compounds) showed pronounced decrease in peak intensities after degradation studies.

3.8. Comparative study of Fenton and photo-Fenton degradation

Comparative study of degradation of six azo reactive dyes through Fenton and photo-Fenton oxidation process shows that decolorization and degradation of six azo reactive dyes was increased in the photo-Fenton process as compared to the Fenton oxidation process. This can be explained on the fact that production of reactive species $^{\bullet}$OH was catalyzed by ferrous ions from the H_2O_2 in the reaction medium of Fenton oxidation. As ferrous ions concentration increases up to the optimum level, the hydroxyl free radical concentration also increases in the reaction medium which in turn propagated the oxidation of the azo reactive dyes. The hydroxyl free radical generation was increased in the photo-Fenton oxidation due to the presence of UV light which ultimately increases the efficiency of photo-Fenton process. Table 1 shows that economically both Fenton and photo-Fenton oxidation methods were suitable for mineralization of selected hetero-functional reactive dyes. Dye decolorization was mainly due to the generation of the hydroxyl radicals through the chemical and photochemical reactions. The increase efficiency of photo-Fenton process was attributed to the generation of additional hydroxyl radicals than produced in the Fenton process. UV light was principally used for H_2O_2 photolysis and for the photo-reduction of ferric ion to ferrous ion. Only functional group position was changed in newly synthesized dyes and their effect on dyeing parameters was studied while no significant difference on the decolorization rate of dyes was observed.

4. Conclusion

In this study, AOP's (Fenton and photo-Fenton) were used for the decolorization and degradation study of six new hetero-functional reactive dyes synthesized for application on cellulosic fabric. It was cleared from results that both oxidation processes were effective for the degradation study of azo reactive dyes. Fenton oxidation showed decolorization efficiency up to 98% and COD removal up to 78% for the six degraded azo reactive dyes under optimum conditions. Whereas, the photo-Fenton oxidation process revealed 99% decolorization and 82% COD removal. The degraded intermediates were scrutinized by means of FT-IR spectroscopy which confirmed the oxidative effectiveness. The FT-IR studies illustrated that the apparent functional group peaks (azo group and aromatic compounds) showed pronounced decrease in peak intensities after degradation studies. From the above results, it was concluded, that both oxidation processes can be effectively employed for the degradation of the six hetero-functional azo reactive dyes.

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