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The Oxidative Response and Viable Reaction Mechanism of the Textile Dyes by Fenton Reagent

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Abstract
The mechanism of the degradation of the Reactive Red 239 and Reactive Blue 19 by Fenton reagent was studied by advanced oxidation process in aqueous medium. The spectroscopic technique was adopted for the measurements of dye concentration. Moreover they were determined at 540 nm and 590 nm, respectively. Kinetics of the reaction was studied under the effect of concentration of reactive dyes, concentration of oxidant were followed under pseudo first order condition and found to influence the catalytic mechanism. The pH of the medium, vibrant response of several cations and anions and influence of ionic strength on the reaction kinetics were also monitored. Physical evidences for the degradation and mineralization of the dyes were evaluated by Lime water test, Ring Test and TLC test also confirmed the degradation of dye. Inhibitory effects of dyes were observed by CO_3^-, HCO_3^-, HPO_4^{2-}, Cl^-, I^- Al^{3+} and Na^+. Thermodynamic activation parameters in the oxidation reaction were studied and mode of mechanism was suggested on the basic of these parameters. This study explored the safe and eco friendly degradation of the textile dyes under Pseudo first order rate constant. It was observed that Fenton assisted degradation of the dyes under controlled conditions was found to be favorable for the treatment of textile wastewater. Moreover compared to other chemical methods it is effective and harmless to the environment.

Keywords: Catalytic mechanism, Ionic strength, Activation parameters, Advanced oxidation process, Reactive textile dyes.

Introduction

Reactive sulphonated dyes are extensively used in dyeing processes in textile industries while 70 % of them were remain in the effluents [1, 2]. Reactive dyes show a wide range of different chemical structures, due to substituted aromatic and heterocyclic groups. As reactive dyes are significantly soluble in water, their removal from wastewater is difficult by usually applied methods of coagulation and the activated sludge. Therefore, oxidation and adsorption are two major techniques that are used for wastewater treatment in the textile industry [3]. These dyes have the tendency to absorb light in the visible range of wave length, they are the color molecules capable of forming covalent bond between the dye molecules and fibers, which are usually cellulose fibers. The reactive dyes hydrolyze easily resulting in a high portion of unfixed reactive dyes, which have to be washed off during dying process about 70 % of un reacted dyes are present in the effluents [1]. The reaction between reactive dye and cotton fiber is complicated in the absence of alkali and the amount of alkali is the major factor in the fixation of reactive dye. Although water molecules participate the contestant role for the reaction with the dye, but cellulose fiber are mostly involved in this reaction basically due to the fact that the interaction of a reactive dye to fiber is exclusively immense than the attraction of it to the water. Moreover all the reactive dyes do not exhibit the same range of reactivity and less reactivity of dye might be due to the hydrolysis

which can mess up the dyeing. The reactive dye gets its reactivity by the assistance of alkaline medium which further enhances with the elevation of temperature [3].

Various treatment techniques for dyestuff though have been used by several researchers, our study focuses on the significance of modern advance oxidative and chemical technique for monitoring of the environmental impurities of dyestuffs which may have serious adverse toxic impact on our ecosystem as well as on environment.

The photoreduction of azo dyestuffs to hydrazine and amines [4] takes place in aquatic systems under less concentration of oxygen but it is slow process in the presence of high concentration of oxygen. Photooxidation of dyes lead to toxic aromatic amines and hydroxylation [5]. It imparts phototoxic properties to the resultantdye fragments that are dispersed in the environment and itself becomes a source of hazardous species. A high degree of stability to photochemical degradation is the normal requirement of the commercial dyestuff when applied to textile substrate which defy the photodegradation development. Practical consideration leads to conclusion that photodegradation does not play a safe and vital role in the environmental fate of dyestuffs.

Biodegradation is one of extensively used process of degradation of dyes. Dyestuffs are necessary to be resistant to change under aerobic conditions and they are in contact with body fluids. In addition to that they are highly resistant to aerobic biodegradation due to the strong electron-withdrawing characteristics of the azo group. Under anaerobic conditions the degradation takes place slowly by decolorization. Moreover this process results in the formation of toxic, mutagenic and carcinogenic aromatic amines that are resistant to further detoxification under low oxygen conditions. In addition to toxicity, the reactive textile dye wastewaters have undesirably high pH. Enzymes, certain bacteria, algae and fungi are used in these processes for declorization of azo dyes. The biodegradation of them mainly resulted into microbial reductive cleavage of the azo bond [6].
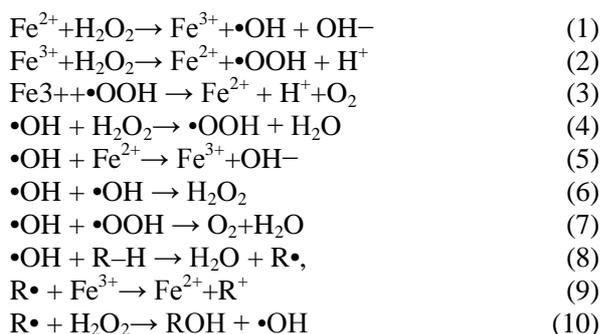
Adsorption technique is an expansive method for the treatment of wastewater from dyestuff production and is not feasible for bulk quantity treatment especially nano adsorptive methods. In addition adsorption technique is futile for many classes of dyes, for instance it is ineffective for Disperse, Vat and Sulphur dyes. Adsorption is favored by hydroxyl-, nitro – and azo- dyes. Presence of sulpho- groups in acid dyes reduce the possibility of adsorption process, whereas these groups do not influence the adsorption in case of reactive and direct dyes [7], which show responses to this method.

Advanced oxidation processes (AOPs) have been recognized as an attractive option for water treatment, particularly in cases where the contaminated species are cumbersome to remove using the usual biological or physicochemical processes. They have precise advantages on the other remedies, like being of low cost, fast effective, fast decontamination, reusability and conveniently processed and are exceedingly capable of degrading textile dyes at atmospheric temperature and normal environmental conditions. This technique involves different possible reactions to produce $OH^.$ radicals which are highly reactive species and oxidizing agent [8]. In some cases Fe° is used as catalyst with persulphate (PS) for the degradation of azo dyes [9]. Among the most promising AOPs for water contaminated by organic molecules are, application of the Fenton's reagent (an aqueous mixture of Fe^{2+} and H_2O_2 that produces hydroxyl radicals $OH^.$) stands out due to its high oxidation power [10]. The rapid oxidation kinetics, relatively cheap and easily operated and maintained, which has been employed to treat a variety of industrial wastewaters containing aromatic amines, phenols, dyes, pesticides, toxic and biologically refractory organic substances etc. [4]. The complete degradation of dye results into mineralization and eventual formation of CO_2, H_2O, SO_4^{2-}, Cl^-, NO_3^- etc [12].

In the fenton reagent oxidation process (FROP), hydrogen peroxide acting as catalyst in the presence of ferrous sulfate and at pH 3-5 is called Fenton's Reagent. The Fenton's Reagent reacts to form hydroxyl radicals ($HO^.$), ferric iron

(Fe^{3+}), hydroperoxyl radicals (HO$_2^{\bullet}$) or superoxide radical anions (O$^{2-\bullet}$) [10].

The Fenton reaction is the reactions occur between hydrogen peroxide and Fe^{2+} in acidic aqueous medium (pH ≈ 3.00). The degradation of an organic compound by Fenton's reagent is safe and nonhazardous to the environment, there are evidences of the formation of the •OH radical as the principle active oxidant in the Fenton system by many techniques, such as electron paramagnetic resonance (EPR) spin-tapping technique [11]. The •OH radical can attack the chromophoric group of dye and initiate the oxidation of reactive dye by abstraction of hydrogen atom and electrophilic addition consecutively involving several degradation mechanisms, during which aromatic intermediates and inorganic ions are formed [12]. The Fenton reaction mechanism is shown by equations 1-10 [11]. During these steps H$_2$O$_2$ and hydroxyl free radical are regenerated.

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+\bullet OH + OH^- \qquad (1)$$
$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+\bullet OOH + H^+ \qquad (2)$$
$$Fe3++\bullet OOH \rightarrow Fe^{2+} + H^+ +O_2 \qquad (3)$$
$$\bullet OH + H_2O_2 \rightarrow \bullet OOH + H_2O \qquad (4)$$
$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} +OH^- \qquad (5)$$
$$\bullet OH + \bullet OH \rightarrow H_2O_2 \qquad (6)$$
$$\bullet OH + \bullet OOH \rightarrow O_2 +H_2O \qquad (7)$$
$$\bullet OH + R-H \rightarrow H_2O + R\bullet, \qquad (8)$$
$$R\bullet + Fe^{3+} \rightarrow Fe^{2+} +R^+ \qquad (9)$$
$$R\bullet + H_2O_2 \rightarrow ROH + \bullet OH \qquad (10)$$

The ferrous ions are relatively non toxic and inexpensive, among various transition metal catalysts. It is environmental friendly aspects and it has been widely studied to accelerate H$_2$O$_2$ oxidation for the decolorization of dyes. It is enormously fast and effective process and frequently applied for the treatment of industrial effluents with sound results. It is universally favored specifically for safe removal of azo dyes as the mineralization leads to non hazardous products.

Materials and Method

Our research spot highlighted the two textile dyes, Everzol Red 239 also known as Brilliant Red 239 and Reactive blue 19 also chimerically known as Remazol Brilliant blue

which are further proceeded to degradation by advance oxidative process. These dyes are extremely opposing to other oxidation process due to its aromatic anthraquinion structure which gives it high stability by resonance [13]. The chemical structures of reactive azo dyes, Everzol Red 239 and Reactive blue 19 is shown in Fig. 1.
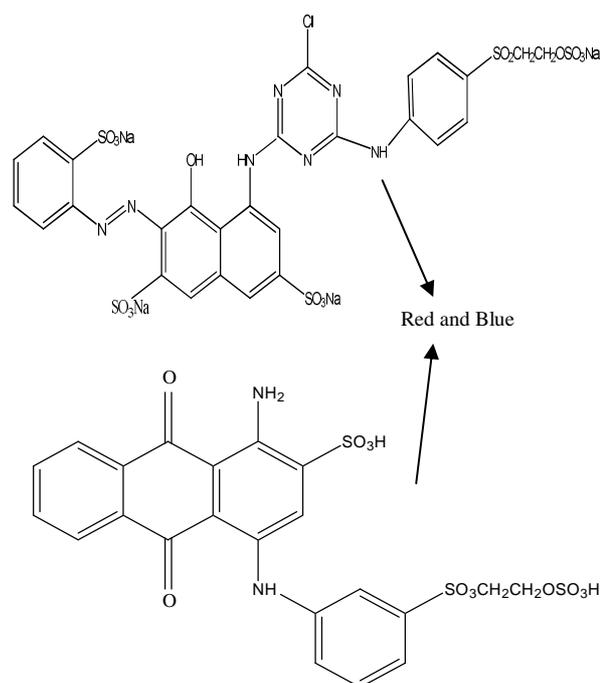

Figure 1. **Chemical Structures of Reactive Azo dyes, Everzol Red 239 and Reactive blue 19**

The textile dyes Reactive Red 239 and Reactive blue 19 of high purity were used in the present work. These dyes were provided by the courtesy of Farid Ahmed Vawda Industry and CO. All stock solutions and standard solutions were prepared from deionized water. The 5x10^{-4} M stock solution of dyes was prepared and its dilution was prepared by standard addition method. About 30% v/v solution of H$_2$SO$_4$ was used for maintaining pH of the reaction mixture. FeSO$_4$.7H$_2$O (E. Merck) solution 15 ppm concentration was maintained in all runs. H$_2$O$_2$ (E. Merck) 30% pure (9.7 M), stock concentration 7.35x10^{-3} M was used. All salts of extra pure quality (E. Merck) used were Na$_2$CO$_3$, CaCl$_2$, NaHCO$_3$, K$_2$HPO$_4$, CH$_3$COONa, KCl, CaSO$_4$, KNO$_3$, KI, MgSO$_4$, AlCl$_3$.6H$_2$O, NaCl. All the reagents used were of analytical grade.

Method of analysis

Spectral scanning of the dyes was done on spectrophotometer to determine maximum wavelength (λ_{max}) of Reactive Blue19 and Reactive Red 239. It was found to be 540nm and 590nm, respectively. After that determination of best concentration of ferrous sulfate and hydrogen peroxide was done for decolorization of dye. The selected range was determined, after that variation was preceded in that particular range to determine best concentration.

The decolorization efficiency was calculated as:

$$\text{Decolorization \%} = \frac{(Ao - At)}{Ao} \times 100 \qquad (11)$$

Where A_o and A_t are the initial absorbance of the dye at the time zero before the initiation of reaction and at reaction time (min), respectively.

All pH measurements were made by Hanna, pH 211 Microprocessor pH meter, adjusting the reaction mixture pH 3-5 by 30% v/v solution of H_2SO_4. The standard solution of Iron(II) sulphate heptahydrate was used as the source of Fe(II) catalyst in the H_2O_2 solution of 30% purity. Extra care was taken so that the pH does not exceed high, otherwise it was observed that the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen and consequently creating a hazardous situation instead of decolorizing the dye. Reaction rates with Fenton's reagent are synchronized to the rate of hydroxyl radical $OH^.$ generation which is in turn related to Ferrous II concentration. Fe: H_2O_2 ratios was 1:1 approximately was observed for the Fentons Reagent best performance. After addition of dye decolorization effect of the reaction mixture was monitored after 15 min as the reaction was fast and completed decolorization was observed within this time period. The rate of reaction was monitored at constant temperatures by Thermostatic Water Bath Tank of Model HH-4.

The rate of decolorization was analysed with Psuedo First order (PFO) kinetics by equations below:

$$At = Ao\ e^{-kobs.t} \qquad (12)$$

or $\ln \dfrac{At}{Ao} = - k_{obs}.t$

Exponential variation in the values of k_{obs} and Pseudo first order rate constant was observed by the increase in the term $\ln \dfrac{At}{Ao}$. Moreover the Pseudo first order plots of ln (At-Ao) against time were made and the slope of the plots gave the PFO rate constants k_{obs} [14]. The second order rate constant k_2 was calculated as represented in Equation 13.

$$\text{Rate of reaction} = -\frac{d[Dye]}{dt} = k_2\ [dye][Oxidant] \qquad (13)$$

Results and Discussions
Decolorization efficiency of everzol R and BrilliantB19 dye

The (Table 1) represents decolorization efficiency of Everzol R and Brilliant B19 dyes. Moreover the concentrations varied from 1×10^{-5} to 5×10^{-5}. It was observed that about 94.531% removal efficiency was observed for Everzol R. Whereas for Brilliant B19 removal efficiency was found to be 98.0%.

Table 1. **Decolorization Efficiency of Everzol R and Brilliant B19 Dye.**

[Everzol R] mol.dm^{-3}	dx/dt (mol.dm^{-3}s^{-1})	K_{obs} (s^{-1})	% Decolorization
1×10^{-5}	0.001	0.001	75.355
2×10^{-5}	0.001	0.001	83.175
3×10^{-5}	0.002	0.002	91.292
4×10^{-5}	0.002	0.002	92.865
5×10^{-5}	0.0025	0.002	94.531
[Brilliant B19]			
1×10^{-5}	0.0016	0.0521	77.90
2×10^{-5}	0.0033	0.0540	82.75
3×10^{-5}	0.0065	0.0774	88.85
4×10^{-5}	0.0094	0.1277	97.37
5×10^{-5}	0.0095	0.1288	98.00

The kinetics of the degradation of dyes was observed and the destruction of chromophore structure (- N = N- group) of the dyes underwent

oxidation easily, the decreased in colour intensity was observed within 15 min of treatment process. Moreover, the effect of dyes concentration on the initial rate of reaction is shown in (Table 2). The variations in pH, ionic strength, salts, concentration and chemical structures add complications in the decolorization process consequently minimizing its rate [6].

Table 2. **The Effect of Dyes concentration on the initial Rate of Reaction.**

[Dye] molL^{-1}	ln [Dyes]	Initial Rates (BB 19) Ms^{-1}	In (initial Rates)	Initial Rates (Ever.R) Ms^{-1}	In (initial Rates)
1x10^{-5}	-11.512	0.0016	-6.437	0.001	-6.907
2x10^{-5}	-10.819	0.0033	-5.713	0.001	-6.907
3x10^{-5}	-10.414	0.0065	-5.035	0.002	-6.214
4x10^{-5}	-10.126	0.0094	-4.667	0.002	-6.214
5x10^{-5}	-9.903	0.0095	-4.656	0.0025	-5.994

The rate law and rate of the reaction was established for the reactive azo dyes is represented as:

$$\frac{-d[Evezol\,Red\,239]}{dt} = k[Everzol\,red][Fe^{+2}]$$
$$[H_2O_2]^o \tag{16}$$

$$\frac{-d[Brilliant\,Blue19]}{dt} = k[Brilliant\;Blue19][Fe^{+2}]$$
$$[H_2O_2]^o \tag{17}$$

The PFO rate constants k_{obs} were determined on the basis of the excess concentration of Fenton reagent.

$K_{obs} = k$ [Fenton reagent], where k is the second order Rate constant of the reaction.

Rate of reaction in terms of k_{obs} are given as below:

$$\frac{-d[Evezol\,Red\,239]}{dt} = k_{obs}\,[Everzol\,red] \tag{18}$$

$$\frac{-d[Brilliant\,Blue19]}{dt} = k_{obs}\,[Brilliant\,Blue\,19] \tag{19}$$

Order of reaction with respect to Brilliant B 19 and Everzol Red 239 has been found to be First order, as shown in (Fig. 2). The Order of reaction with respect to Fe^{+2} has been found to be First order, as represented in (Fig. 3). Furthermore the order of reaction with respect to H_2O_2 has been found to be zero order, as shown in (Fig. 4).
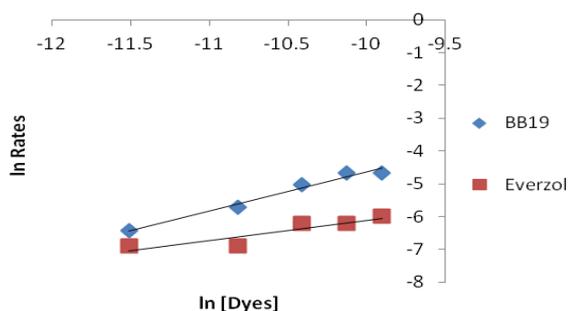

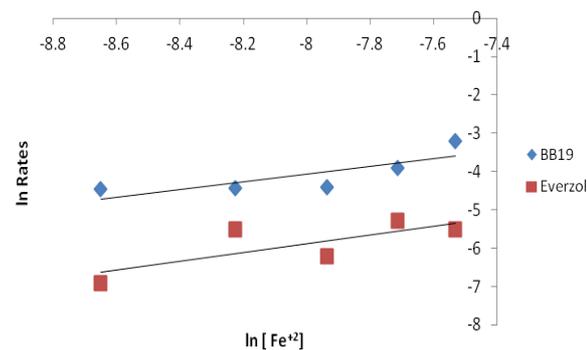*Figure 2.* **Plot of ln (Rates) versus ln [Dyes] at 303K Temperature**

Figure 3. **Plot of (ln Rates) versus ln[Fe^{+2}] at 303K Temperature**
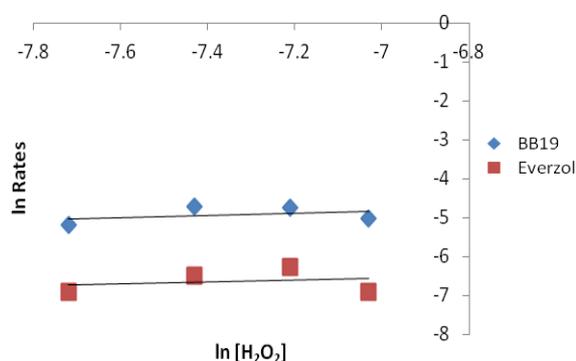

Figure 4. **Plot of ln[Rates] versus ln[H$_2$O$_2$] at 303K Temperature**

Kinetic order determination of dyes degradation and its mechanism

Keeping concentration of the fenton reagent constant and the initial dye concentrations varying initial rates were determined. A plot of ln (- Rates) and ln [Dye] was linear, and the slope of such relation determines the order of reaction with respect to dye concentration. The same pattern was evaluated for order with respect to Fentons reagent concentration by equations below:

- Rate of dye degradation = $k \, [Dye]^n[Fe^{+2}]^n [H_2O_2]^n$ (20)

$$ln \, (\text{-Initial Rate}) = ln k_{obs} + n \, ln[Dye] \qquad (21)$$

where n is order of reaction with respect to dye concentration. k_{obs} is the pseudo first order rate constant.

$$ln \, (\text{-Initial Rate}) = ln k_{obs} + n \, ln[\text{Fenton reagent}] \quad (22)$$

where n is order of reaction either respect to Fenton reagent.

Where n = 1.1, therefore order of reaction with respect to Brilliant Blue 19 is First Order. Moreover n = 0.6, the order of reaction with respect to Everzol Red 239 is approximately First Order as shown in (Fig. 2). The Table 1 describes the observations obtained by varying the concentrations of the dyes between 1×10^{-5}M to 5×10^{-5} M, at constant concentration of the oxidant (fenton reagent), showing that the rates of the decolorization of the dyes Everzol Red 239 and BB 19 by Fenton Reagent were highly dependent on the concentrations of the dyes. Thus it established that the PFO conditions have been maintained.

Effect of the concentration of ferrous ion on the Rate constant of the reaction

The concentration of Fe^{+2} and hydrogen peroxide act as pivotal factor responsible for the % decolorization. Their influence in term of concentration ratios of Fe^{+2} to H_2O_2 (fixed optimum) on the fast mineralization process was studied. All experiments were performed at constant pH 3 on account of the stability of these

reagents. The maximum decolorization efficiency was observed at concentration ratio of Fe^{+2} / H_2O_2 of 1:1 approximately. At optimum value the % decolorization was about 99 % as shown in (Table 3). It was concluded that degradation increased with increasing ratios of Fe^{+2} concentration. This fact is very well understood by the order of the reaction in terms of concentration of Fe^{+2} which has been found to be first order, as shown in (Fig. 3). Additionaly the effect of Fe^{+2} concentration on the initial reaction rate is represented in Table 4.

Table 3. **Effect of Fe^{+2} concentration on dye degradation.**

Everzol R 239	[Fe^{+2}] ppm	dx/dt (mol. $dm^{-3}s^{-1}$)	K_{obs} (s^{-1})	% Decolorization
	10	0.001	0.003	91.20
	15	0.004	0.004	97.52
	20	0.002	0.002	86.24
	25	0.005	0.004	98.05
	30	0.004	0.002	93.32
	35	0.001	0.002	92.40

Brilliant B19	[Fe^{+2}] ppm	dx/dt (mol. $dm^{-3}s^{-1}$)	K_{obs} (s^{-1})	% Decolorization
	10	0.0116	0.0922	93.81
	15	0.0118	0.2109	99.73
	20	0.0120	0.2386	100.0
	25	0.0200	0.1989	92.61
	30	0.0400	0.1164	95.41
	35	0.0082	0.1600	95.57

Table 4. **Effect of Fe^{+2} concentration on the rate of Reaction.**

[Fe^{+2}] M	Ln [Fe^{+2}]	Initial Rates (BB 19) Ms^{-1}	In (initial Rates)	Initial Rates (Everzol) Ms^{-1}	In (initial Rates)
1.7×10^{-4}	-8.65	0.0116	-4.456	0.001	-6.907
2.6×10^{-4}	-8.22	0.0118	-4.439	0.004	-5.521
3.5×10^{-4}	-7.93	0.012	-4.400	0.002	-6.214
4.4×10^{-4}	-7.71	0.020	-3.900	0.005	-5.298
5.3×10^{-4}	-7.53	0.040	-3.200	0.004	-5.521

Influence of H_2O_2 on the dye degradation mechanism

The influence of H_2O_2 concentrations in this regard is also point to be elaborated in (Table 5 and 6). It was evident that increase in concentrations of hydrogen peroxide from 15 to 35 ppm slightly elevate the reaction rates. However at high concentrations of H_2O_2 the effect is reversed as it acts as to trap OH⁻ radical, (Equation 4). Thus producing less potent perhydroxyl radicals [11].

Table 5. **The Effect of concentration of H_2O_2 on dye degradation.**

	Everzol R 239		
[H_2O_2] ppm	dx/dt (mol.dm^{-3}s^{-1})	K_{obs} (s^{-1})	% Decolorization
15	0.001	0.001	67.87
20	0.0015	0.001	75.24
25	0.0019	0.002	83.47
30	0.001	0.001	80.82
35	0.001	0.001	62.59
	Brilliant B19		
[H_2O_2] ppm	dx/dt (mol.dm^{-3}s^{-1})	K_{obs} (s^{-1})	% Decolorization
15	0.0055	0.0200	45.72
20	0.0088	0.0406	72.35
25	0.0085	0.0334	65.37
30	0.0066	0.0234	51.88
35	0.001	0.0029	9.921

Table 6. **Effect of H_2O_2 on the initial Rate of Reaction of dye degradation.**

[H_2O_2] M	ln [H_2O_2]	Initial Rates (BB 19) Ms^{-1}	In (initial Rates)	Initial Rates (Everzol) Ms^{-1}	In (initial Rates)
4.4x10^{-4}	-7.72	0.0055	-5.20	0.001	-6.907
5.8x10^{-4}	-7.43	0.0088	-4.73	0.0015	-6.502
7.3x10^{-4}	-7.21	0.0085	-4.76	0.0019	-6.265
8.8x10^{-4}	-7.03	0.0066	-5.02	0.001	-6.907
1.0x10^{-3}	-6.90	0.001	-6.90	0.001	-6.907

The order of reaction related to hydrogen peroxide has been found to be zero order as evident from (Fig. 4). It shows that there is no direct influence of oxidant in the reaction mechanism. The Fe^{+2} ion is the key reagent which is responsible for the initiation of the production of OH⁻ radicals in acidic medium.
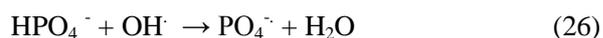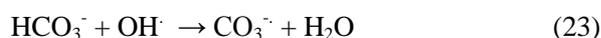
Response of electrolytes in the kinetics of the reaction

The presence of inorganic salts have multiple effects on the degradation process. Inhibitory effects for both dyes were observed among anions by CO_3^-, HCO_3^-, HPO_4^{2-}, Cl^- and I^- and among cations Al^{3+} and Na^+. Extraordinary high response towards decolorization was observed by Ca^{2+}, CH_3COO^- and NO_3^- ions. Whereas moderate effect was observed by Mg^{2+} ions as shown in (Table 7). The trend observed for anions $NO_3^- > CH_3COO^- > Cl^- \approx CO_3^- \approx HCO_3^- \approx HPO_4^{2-}$ & cations $Ca^{2+} > Mg^{2+} \approx K^+ > Na^+ > Al^{3+}$.

Table 7. **Effect of Salt concentration on the Rate and Decolorization Efficiency.**

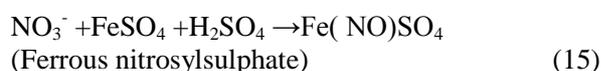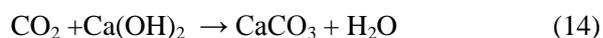| [Salts] 0.01M	Everzol 239			Brilliant B 19		
	K_{obs} s^{-1}x10^4	μ Rate x10^4	% Decolorization	K_{obs} s^{-1}x10^4	μ Rate x10^4	% Decolorization
CO_3^-	0.007	0.008	-0.69	16.0	16.0	3.590
HCO_3^-	0.5	0.6	26 HCO3	5.0	1.0	2.400
I^-	-	-	-	-	-	-
CH_3COO^-	0.1	0.1	34.75	-	-	-
HPO_4^{2-}	0.09	0.1	1.10	1.0	5.0	-23.90
NO_3^-	30.0	10.0	93.85	910.0	100.0	93.26
Na^+	3.0	3.0	37.62	59.0	40.0	36.84
K^+	30.0	10.0	95.70	688.0	86.0	87.50
Ca^{2+}	10.0	10.0	87.69	480.0	69000.0	75.00
Mg^{2+}	30.0	10.0	92.00	20.0	40.0	45.28
Al^{3+}	30.0	30.0	21.23	7.00	2.00	19.17

It was found that as the electrolytes act as sustaining species in the reaction mechanism especially potassium salts of nitrate and chlorides as KNO_3 and KCl also sodium salts of acetate as CH_3COONa. The degradation rates were high in

NO_3^-, $CH3COO^-$ and Cl^- medium among anions. Therefore we used potassium nitrate, potassium chloride and sodium acetate as helping species in our reaction. Among cations the role of calcium in decolorization was exceptional whether as salt of $CaCl$ or $CaSO_4$, calcium ions have strong catalytic effect in degradation of Everzol Red 239 and Brilliat B 19 in acidic medium. The anions including CO_3^-, HCO_3^-, HPO_4^- and I^-, role were not supporting in this reaction as they trap the OH^- radicals in acidic medium ,thus suppressing rate of reaction [15], as represented in equations 23-26. The anion radicals CO_3^-, OHI^- and PO_4^- are not so active species compeer to OH^- radical.

$$HCO_3^- + OH^- \rightarrow CO_3^- + H_2O \qquad (23)$$

$$CO_3^- + OH^- \rightarrow CO_3^- + H_2O + O^- \qquad (24)$$

$$I^- + OH^- \rightarrow OHI^- \qquad (25)$$

$$HPO_4^- + OH^- \rightarrow PO_4^- + H_2O \qquad (26)$$

Physical evidences for the degradation and mineralization of the Dyes

The mineralization of the dyes was investigated by Lime water test [16]. Moreover, the reaction mixture after Fenton treatment was tested with lime water, which turned milky also the brisk effervescence were observed during the course of reaction which confirms the mineralization and further degradation of the dyes occur into Co_2 and water. Presence of NO_3^- ions were confirmed by ring test. $FeSO_4$ solution in acidic medium [16].

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (14)$$

$$NO_3^- + FeSO_4 + H_2SO_4 \rightarrow Fe(NO)SO_4$$
(Ferrous nitrosylsulphate) $\qquad (15)$

The TLC test also confirmed the dye degradation. Therefore the detachment of chromophore group from the dye structure is determined. Both dyes are soluble in methanol. The spots of the dyes are visible without UV light on TLC plate. There was no spot of the dyes in the reaction mixture was appeared after 15 minutes with or without UV light on TLC plate. This is clear indicated that complete degradation of dyes occurred using Fentons Reagent.

Significance of temperature and effects of thermodynamic parameters on dye degradation

The temperature variations were studied in the temperature range of 293-333K as shown in (Table 8). It was observed that the degradation of the textile dyes increased with temperature within 15 minute of oxidation by Fenton reaction. It clearly shows the applicability of Arrhenius theory to our present reaction [17] as shown in Fig. 5 and 6. Moreover the dye decolorization basically enhanced due to the elevated interaction between H_2O_2 molecules and Fe^{2+} ions and hence causes more production of OH^- radicals. The thermodynamic parameters Ea, ΔG, $\Delta H^{\#}$ and $\Delta S^{\#}$ were calculated by using Arrhenius equation and Eyring Polany's equation [18] as represented by Equation 27-28 respectively. The negative values of free energy change shows the reaction is spontaneous and moderate value of Energy of activation for Everzol Red 239. It shows that its degradation was energetically successful and low value for Brilliant B signifies that the reaction was fast sustainable in natural environment.

$$\ln k = \ln A \frac{Ea}{-20303R} \frac{1}{.T} \qquad (27)$$

$$\ln \frac{k}{T} = \frac{\Delta H\#}{-R} \frac{1}{.T} + \ln \frac{kB}{h} + \frac{\Delta S\#}{R} \qquad (28)$$

h, Plancks constant = 6.626×10^{-34} Js
k_B, Boltzmann constant = 1.38×10^{-23} JK^{-1}

Table 8. **Thermodynamic activation parameters.**

Everzol Red 239	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}	Ea KJ mol^{-1}	Brilliant B 19	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}	Ea KJ mol^{-1}
	3.868	-197	-9.972	14.26		0.354	-177	-19.2	6.117

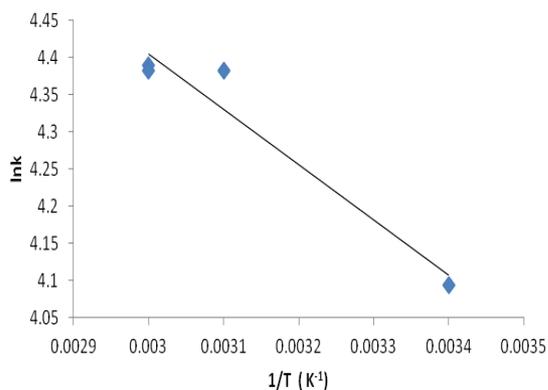*Figure 5.* Plot of ln k versus I/T for Everzol Red dye
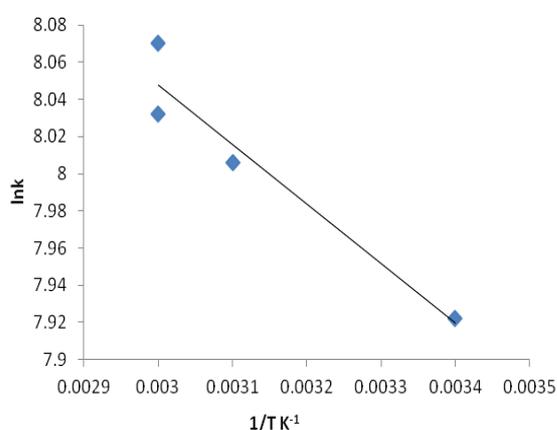

Figure 6. Plot of ln k versus 1/T for Brilliant B 19 dye

Thermodynamic parameters for the dye brilliant blue and everzol red Ddyes

The thermodynamic activation parameters are shown in the (Table 8). The negative values of entropy of activation for Everzol R as shown in (Fig. 7) and for BB 19 in (Fig. 8) and for combine system shown in (Fig. 9), represent that this reaction has associated mechanism [19]. The dye and oxidizing agent forms an activated unstable complex in transition state which has an ordered structure, more than that of reactant i.e Activated complex is highly structurally organized and unstable. The positive value of enthalpy of activation $\Delta H^{\neq} = + 3.868$ KJmol^{-1} for Everzol R as shownin Fig. 7 and, $\Delta H^{\#} = 0.354$ KJmol^{-1} for BB 19. The Figure 8 shows that this reaction is endothermic and catalytically assisted, and it is also temperature dependent.
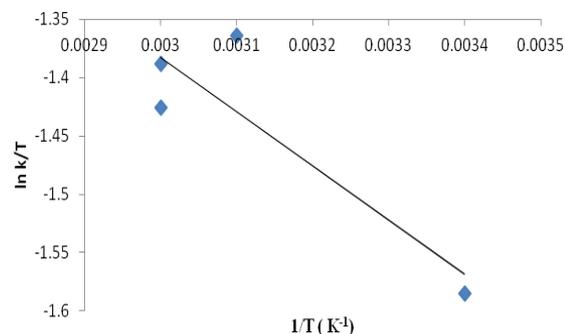

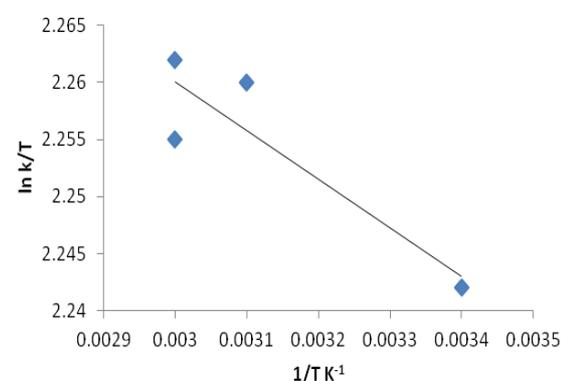*Figure 7.* Plot of ln (k /T) versus I/T for Everzol Red 239 dye

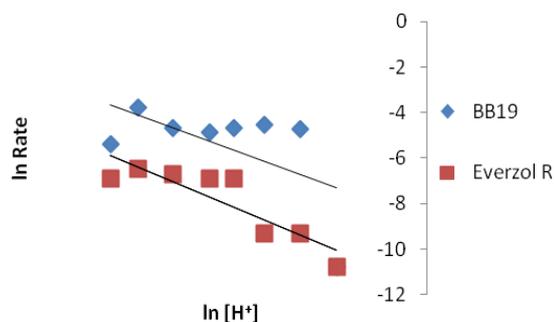*Figure 8.* Plot of ln (k/T) versus I/T for Brilliant B 19 dye

Figure 9. Plot of ln(Rate) versus ln [H$^+$] concentration for both dyes systems

Effects of variations in pH on observed rate constants of the reaction

Dye Fenton reaction was performed in acidic conditions pH value is between 1-4, where pH plays the major role. This reaction has been found to be possible only in acidic pH. At pH 3 the % decolorization was observed to be highest and is 100 % as shown in (Table 9). It indicated fact that

at acidic pH ferrous ions are stable, since the variation in concentration of $OH^{.}$ radical is responsible for dye degradation. At high pH values greater than 4, the reaction is inhibited due to the precipitation of iron (III) as $Fe(OH)_3$ [20], Equation 29, therefore the consequent decrease of Ferric ions decrease the formation of ferrous iron, Equation 2. Moreover at alkaline pH, H_2O_2 is less stable. It has been observed that at pH below 3, $OH^{.}$ radicals can be trapped by protons in the medium [8], Equation 30.

$$Fe^{+3} + OH^{-} \rightarrow Fe(OH)_3 \quad ppt \qquad (29)$$
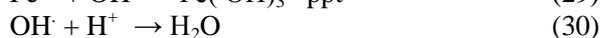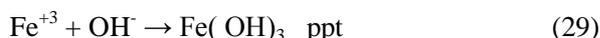$$OH^{.} + H^{+} \rightarrow H_2O \qquad (30)$$

Table 9 summarizes the results for the experiments at varying concentrations of hydrogen ions for a fixed temperature 303K. The PFO rate constants and rate of degradation is in terms of pH is given as, Equation 31 [18].

$$\text{Rate of degradation of dye} = k\,[H^{+}]^{n}\,[Dye]\,[Fe^{+2}]\,[H_2O_2] \qquad (31)$$

Where n, is the order of reaction with respect to the hydrogen ion concentration and has been found to be equal to n = 0.7 for Everzol R and n= 0.63 for BB 19 by plotting ln (Rate) vs. ln[H^{+}] as shown in Fig. 9. This result implies that rate of degradation of dyes by Fentons reaction was dependent nearly on the first power of hydrogen ion concentration. Furthermore it was also found that as pH of medium approach towards alkalinity the rate of the reaction decreased.

Effect of variation of ionic strength (CaCl₂) in the reaction rate

The reaction rates have observed to be influenced by ionic strength [21, 22]. The reaction rates have slight enrichment with increasing ionic strength as shown in Table 10. The ionic strengths were maintained by $CaCl_2$ salt. It was observed that for both the dyes system at low concentration of $CaCl_2$ and low ionic strength of the medium, the rate of the dye degradation was high but as the ionic strength increased the rate of the reaction declined. Table 10, show that large concentration of Cl^{-} ions inhibited the reaction by removing $OH^{.}$ radicals. The Equation 32, shows that since hypochloride radical anion is less reactive compared to hydroxyl radical hence reaction is evidently obstructed. The rate of reaction increased by the catalytic effect of Ca^{+2} ions as proposed by our study, as Ca^{+2} ions might have drawn near, coordinated with the transient activated complex before the oxidation process and accelerated the electron transfer mechanism.

$$Cl^{-} + OH^{.} \rightarrow OHCl^{-} \qquad (32)$$

Table 9. **Effect of variation of pH on the reaction rates.**

pH	[H⁺]	Everzol Red 239			Brilliant blue 19		
		dx/dt $(mol.dm^{-3}s^{-1})$	K_{obs} (s^{-1})	% Decolorization	dx/dt $(mol.dm^{-3}s^{-1})$	K_{obs} (s^{-1})	% Decolorization
1.0	0.1000	0.00002	0.00002	01.300	0.00005	0.0384	31.91
1.4	0.0398	0.00009	0.00008	07.100	0.0088	0.0479	57.96
1.8	0.0158	0.00009	0.00008	38.190	0.0104	0.0625	78.73
2.1	0.0070	0.00100	0.00300	94.070	0.0093	0.1175	98.11
2.4	0.0039	0.00100	0.00300	95.000	0.0078	0.0379	79.62
2.8	0.0016	0.00120	0.00300	97.750	0.0082	0.0812	91.17
3.0	0.0007	0.00150	0.00350	97.720	0.0220	0.0887	100.0
3.5	0.00032	0.00100	0.00200	84.540	0.0046	0.0790	39.05

Table 10. **Effect of variation of ionic strength (Using Salt Cacl₂) on the reaction rate.**

		Brilliant Blue			Everzol Red 239		
Ionic Strength	*[CaCl₂] mol.dm⁻³*	*dx/dt mol.dm⁻³s⁻¹*	*K_obs s⁻¹*	*% Decolorization*	*dx/dt mol.dm⁻³s⁻¹*	*K_obs s⁻¹*	*% Decolorization*
0.03	0.01	6.9	0.0485	75.3012	0.0002	0.002	87.692
0.09	0.03	9.5	0.0614	82.96703	0.0001	0.001	73.253
0.15	0.05	6.5	0.0346	65.0165	0.00015	0.0012	78.5156
0.21	0.07	1.4	0.005	2.371542	0.00012	0.001	75.4509

Determination of the second order Rate constant k of the reaction

The apparent rate constant k $_{obs}$ determines the value of actual rate constant k of the reaction, as represented by Equation 32.

$$K_{obs} = k [Fe^{+2}] \qquad (32)$$

Since H_2O_2 variation is not effecting the reaction rate and actually it is iron II concentration which is controlling the production of hydroxyl radicals .

The value of second order Rate constant k, of the reaction were estimated as:

The k about 12.55 mol⁻¹ Ls⁻¹ for Brilliant Blue, shown in (Fig. 10). While for Everzol red dye k was 1.053×10^3 mol⁻¹ Ls⁻¹ as shown in (Fig. 11).
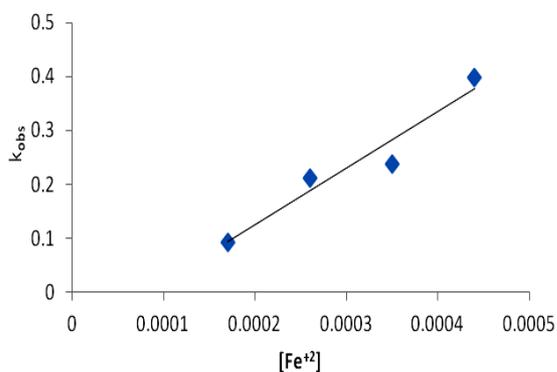
Figure 10. **Plot of k$_{obs}$ versus [Fe^{+2}]for Brilliant Blue Dye System**
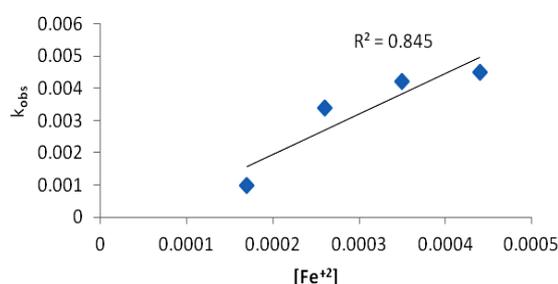
Figure 11. **Plot of k$_{obs}$ versus [Fe^{+2}]for Everzol Red 239 Dye System**

Conclusion

This study focused on the safe and eco friendly degradation of the textile dyes Everzol red and Brilliant B 19 under Pseudo first order conditions. The degradation too fast for Brilliant B rather than for Everzol Red as evident by the second order rate constants values of the reaction. The reaction clearly indicates dependency on the concentration of ferrous II ion as compared to hydrogen peroxide which is the main oxidant. In principle it was observed that Fe^{+2} ions are controlling the production of hydroxyl radicals which act as an active oxidant. The pH of the scheme plays fundamental role as it directly initiates OH⁻ radicals formation. Optimum pH observed in this prospect is 3, which is moderately acidic, the reaction is inhibited in basic medium. The effect of temperature is tremendous as obvious by the positive value of enthalpy of activation. We presume that the Fenton assisted degradation of the reactive textile dyes under controlled conditions could resolve our textile wastewater dilemma as this simple chemical method is effective and harmless to our environment.

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