A study of catalytic behaviour of aromatic additives on the photo–Fenton degradation of phenol red

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Abstract. The present study describes the photochemical degradation of phenol-red using photo–Fenton reaction. The progress of the reaction has been monitored spectrophotometrically. The effect of various organic additives e.g. hydroquinone, resorcinol and catechol on the rate of photodegradation has been observed. The effect of variation of various parameters such as pH, concentration of dye, Fe^{3+} ion and additives, amount of H_2O_2, and light intensity on the rate of photodegradation was also observed. A tentative mechanism of the reaction has been proposed.

Keywords. Photo–Fenton; spectrophotometrically; phenol-red; hydroquinone; resorcinol and catechol.

1. Introduction

Now-a-days nature is facing a serious problem of environmental pollution due to multifarious activities of human beings. One of the most pressing problems is water pollution. Photochemical degradation of dyes employing Fenton reagent provides a newer method for the treatment of waste water containing dye effluents. Fenton's reagent is an established reagent for the degradation of dye but the main drawback of the reagent is that the reaction becomes very slow after the consumption of Fe^{2+} ions, whose regeneration by Fe^{+3} ions is very slow, whereas in photo–Fenton reaction, Fe^{2+} ions are readily regenerated from Fe^{3+} ions with an additional requirement of light. This makes the process cyclic in nature and photochemical degradation proceeds smoothly. Thus ferric chloride was used instead of ferrous salts.

Fenton reaction is an effective method to treat organic pollutants in waste water.[1–4] Simple Fenton reaction involves the formation of hydroxyl and perhydroxy radicals.[5–7]

Degradation of various organic compounds e.g. 2,4-dichlorophenoxy acetic acid, *p*-dichlorobenzene and chlorobenzene; salicylic acid, poly(ethylene glycol), etc. by Fenton and photo–Fenton reagent

has been reported.[8–12] Degradation of malachite green by Fenton's reagent catalysed by various aromatic additives was examined by Chen *et al.*[13] Sedlak *et al.*[14] examined the photocatalytic effects of Fe(III) compounds on the hydroxylation of benzoic acid by hydrogen peroxide initiated by UV-radiation. Walling[15] studied intermediates in the reaction of Fenton's type reagents. A comparative study of Fenton's, photo–Fenton's and other related reagents on the degradation of various types of compounds e.g. dyes, resorcinol, etc. has been done.[16,17] Huang *et al*[18] reported the removal of citrate and hypophosphite binary components using Fenton, photo–Fenton and electro-Fenton processes. Methomyl degradation in aqueous solutions by Fenton's reagent and the photo–Fenton system is observed by Tamimi *et al.*[19] Optimizing the treatment of landfill leachate by conventional Fenton and photo–Fenton processes has been carried out by Hermosilla *et al.*[20] Papić *et al*[21] studied the decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes, whereas the treatment of wastewater by Fenton and photo–Fenton processes has been investigated by different groups of researchers.[22–24]

Although photo–Fenton reaction is a useful tool for the degradation of dyes as well as organic com-

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pounds but the major drawback is the slow rate of degradation, so it is important and necessary to find out some better and suitable modifications to increase the efficiency and applications of this reagent. Zakharov and Kumpman[25] observed the inhibiting and chemiluminescent properties of benzoic acid and acetyl salicylic acid in the presence of Fenton reagent. Sulphate, chloride and fluoride ions inhibit the process because these ions reduce the reactivity of ferric ions through coordination to form less reactive complexes.[26] Effect of fulvic acid on Fe (II) oxidation by hydrogen peroxide has been studied by Voelker and Sulzberger.[27]

The effect of quinones on the free radical processes of oxidation and fragmentation of hydroxyl-containing organic compounds has been investigated by Shadyro *et al.*[28] In the present work, the effect of various organic additives on the rate of photo–Fenton degradation of phenol red was investigated and the main emphasis is given to determine the conditions where these additives show the maximum rate of reaction. An attempt has also been made to explain their catalytic behaviour.

2. Experimental

All solutions were prepared in doubly distilled water. 0.0886 g of phenol red was dissolved in 250.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M, which was used as stock solution. 30 mL reaction mixture was prepared by mixing all reagents one by one; whereas in case of hydroquinone system; the concentrations of dye, ferric chloride and hydroquinone were kept 8.33×10^{-5} M, 2.33×10^{-5} M and 2.00×10^{-4} M, respectively and 0.2 mL of H_2O_2 was added to the solution. For the typical run of catechol system, 30 mL reaction mixture was prepared, which contained 8.33×10^{-5} M dye, 2.33×10^{-5} M, ferric chloride and 1.67×10^{-5} M catechol and 0.1 mL of H_2O_2 was added to the solution. In case of resorcinol system, the 30 mL reaction mixture has 1.00×10^{-4} M dye, 2.33×10^{-5} M ferric chloride and 3.33×10^{-5} M resorcinol and 0.1 mL of H_2O_2 was added to the solution. These specified concentrations have been chosen on the basis of optimization of each reagent's concentration and these optimum values are the ones established constant when other parameter was changed.

For the irradiation the solution was placed under the 200 W tungsten lamp, which emitted the radia-

tions of visible range. The light intensities at various distances from the lamp were measured with the help of a solarimeter (CEL, Model SM 201). A water filter (a petridish, full of water) was used to cutoff thermal radiations. A digital pH meter (Systronics, Model 335) was used to measure the pH of the system. The pH of the solutions was adjusted by the addition of previously standardized 0.1 M sulfuric acid and 0.1 M sodium hydroxide solutions. All the solutions were kept at room temperature. The progress of the photochemical reactions was observed by measuring the absorbance at regular time intervals of 10 min with the UV-visible spectrophotometer (Systronics Model 106). Hydroquinone (E. Merck), resorcinol (E. Merck). $FeCl_3$ (E. Merck) catechol (CDH) and phenol red (Hi-media) was used as received commercially from the company specified in parenthesis. Hydrogen peroxide (E. Merck), concentration 30%, w/v) was been used.

3. Results and discussion

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals (10 min.) and the absorbance was measured at $\lambda_{max} = 430$ nm. It was observed that absorbance of the solution decreases with increasing time of exposure, indicating a decrease in concentration of phenol red.

The results are presented graphically in figures 1A–C. It was observed that absorbance of the solution decreases with increasing time of exposure, indicating a decrease in concentration of dye phenol red. A plot of $1 + \log [O.D.]$ or $2 + \log [O.D.]$ versus time was found to be linear and it follows pseudo-first order kinetics. The rate constant was measured with the expression:

$$k = 2.303 \times \text{Slope}.$$

It was observed that reaction was completed in two stages. The first stage has an induction period; may be for the generation of the $^\bullet OH$ radicals but during this time, a small decrease in O.D. has been observed, which may be attributed to simple photochemical degradation of dye. After this slow stage, a major decrease in O.D. has been observed, which seems to be the second stage of photo–Fenton degradation, where $^\bullet OH$ radicals act as oxidizing species for the degradation of dye. At the later stage of reaction, a lag period has also been observed, where the rate of reaction again slows down. The effect of
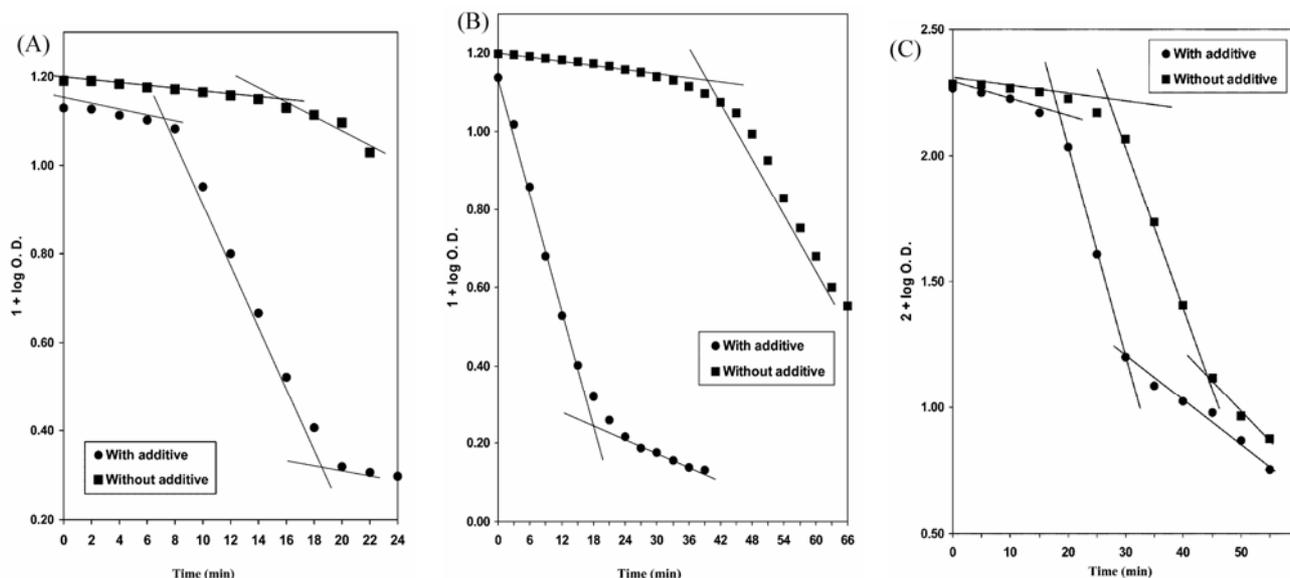
Figure 1. (**A**) A typical run hydroquinone system. (**B**) Catechol system. (**C**) Resorcinol system.

variation of various parameters on the rate of degradation was studied by comparing the rates of the second stage of the photo–Fenton reaction. Moreover, when the experimental conditions approach the optimum conditions, then the time taken by first stage (slow step/induction period) was found to reduce.

The organic additives accelerate the rate of reaction either by reducing the time taken in first stage i.e. $^{\bullet}OH$ radical generation becomes faster and/or increasing the rate of second stage. Moreover, at the optimum conditions of dye $FeCl_3 \cdot H_2O_2$ or additives, the rate of degradation becomes very fast and induction period was not observed in some cases.

3.1 *Effect of pH*

The effect of pH on additive catalysed photochemical degradation was investigated in the pH range 2·00–5·00. The results are reported in table 1. The rate of photo–Fenton degradation of phenol red was maximum at pH 2·50, 3·00, and 3·00 for hydroquinone, catechol and resorcinol system, respectively. The observations indicate that the rate of photo–Fenton reaction strongly depends on the pH of the system. In the system, the hydroxyl radicals are generated by reactions (7) and (9) of mechanism.

In reactions (4–5) of mechanism, Fe^{3+} ions are reduced to Fe^{2+} ions on reaction with additives. Reactions (7) and (8) also involve the reduction of Fe^{3+} ions to Fe^{2+} ions via reaction with H_2O and H_2O_2,

respectively. Fe^{2+} ions further reacts with H_2O_2 and $^{\bullet}OH$ radicals with the regenerations of Fe^{3+} ions. These $^{\bullet}OH$ radicals are involved in the photodegradation of the dye through oxidation process. At lower pH value (<2·0) the reactions (7) and (8) are comparatively slower. As the pH of the medium was increased, the rate of reaction also increases because reactions (7 and 8) of mechanism become faster. The increase in the rate continues up to pH 2·5, 3·0 and 3·0 for hydroquinone, catechol and resorcinol, respectively and the time taken by first stage decreased. Beyond these specific pH values for each additive, the reaction rate again decreases and time taken by first stage increased. This may be attributed to the retardation of reaction (9) in which Fe^{3+} ions are regenerated with the simultaneous formation of ^{-}OH ions.

It was observed that the pH of systems increases as the time of exposure increases for only those systems, which are having initial pH > 4·0. It shows that at the higher pH, ^{-}OH ions are formed instead of $^{\bullet}OH$ radicals and therefore; the rate of degradation lowers down due to less availability of hydroxyl radicals.

3.2 *Effect of hydrogen peroxide*

The effect of amount of H_2O_2 on the photochemical degradation of phenol red was also investigated. The results are reported in table 2. The rates were determined in the range from 0·0 to 0·7 mL. The rate of

Table 1. Effect of pH on the rate of reaction.

Hydroquinone System			Catechol System			Resorcinol System		
[Phenol Red] = 8.33×10^{-5} M			[Phenol Red] = 8.33×10^{-5} M			[Phenol Red] = 1.00×10^{-4} M		
H_2O_2 = 0.2 mL			H_2O_2 = 0.1 mL			H_2O_2 = 0.1 mL		
$FeCl_3$ = 2.33×10^{-5} M			$FeCl_3$ = 2.33×10^{-5} M			$FeCl_3$ = 2.33×10^{-5} M		
[Hydroquinone] = 2.00×10^{-4} M			[Catechol] = 1.67×10^{-5} M			[Resorcinol] = 3.33×10^{-5} M		
Light intensity = 60.0 mW cm^{-2}			Light intensity = 60.0 mW cm^{-2}			Light intensity = 70.0 mW cm^{-2}		
pH	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	pH	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	pH	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)
1.50	0.34	10.1	2.25	0.20	5.1	1.50	0.19	34.0
2.00	1.24	8.3	2.50	0.93	3.8	2.00	0.26	32.3
2.50	2.88	8.0	2.75	1.77	2.6	2.50	3.12	25.5
3.00	2.16	8.6	3.00	1.98	0.0	3.00	3.34	18.0
3.50	1.11	10.1	3.25	1.93	1.6	3.50	3.01	31.4
4.00	0.58	10.4	3.50	1.61	2.4	4.00	1.78	55.3
4.50	0.49	10.7	3.75	0.29	4.1	4.50	1.37	59.5
5.00	0.26	11.1	–	–	–	–	–	–

Table 2. Effect of amount of hydrogen peroxide on the rate of reaction.

Hydroquinone System			Catechol System			Resorcinol System		
[Phenol Red] = 8.33×10^{-5} M			[Phenol Red] = 8.33×10^{-5} M			[Phenol Red] = 1.00×10^{-4} M		
$FeCl_3$ = 2.33×10^{-5} M			$FeCl_3$ = 2.33×10^{-5} M			$FeCl_3$ = 2.33×10^{-5} M		
[Hydroquinone] = 2.00×10^{-4} M			[Catechol] = 1.67×10^{-5} M			[Resorcinol] = 3.33×10^{-5} M		
pH = 2.50			pH = 3.00			pH = 3.00		
Light intensity = 60.0 mW cm^{-2}			Light intensity = 60 mW cm^{-2}			Light intensity = 70.0 mW cm^{-2}		
[H_2O_2] $\times 10^5$ M	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)		$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	
0.0	–	–	0.04	4.0		0.01	49.3	
0.1	1.67	14.3	1.98	0.0		3.34	18.0	
0.2	2.88	8.0	1.80	1.8		2.21	23.9	
0.3	2.61	12.0	1.30	3.4		1.95	28.5	
0.4	0.85	20.8	0.31	4.3		1.84	36.6	
0.5	0.23	24.0	0.24	4.4		1.43	37.8	
0.6	0.48	24.8	0.20	4.7		1.33	39.2	
0.7	0.27	32.0	0.15	5.3		0.82	43.2	

photo–Fenton degradation of phenol red was maximum at 0.2 mL, 0.1 mL and 0.1 mL for hydroquinone, catechol and resorcinol systems, respectively. Further increase in H_2O_2 concentration beyond these limits causes retardation of reaction. This may be explained on the basis that as the concentration of H_2O_2 is increased, the rate of reaction increases due to acceleration of reaction (9) of mechanism in which H_2O_2 reacts with Fe^{2+} ion and generates $^\bullet$OH radicals but a further increase in concentration causes the acceleration of reaction (10) in which H_2O_2 reacts with $^\bullet$OH radicals and as a consequence, a decrease in the rate of final reaction (13) has been observed.

3.3 *Effect of additives*

The effect of variation of concentration of additives on the photochemical degradation of phenol red was also investigated. The rates were determined in the range from 0.00–3.33×10^{-4} for hydroquinone, 0.00–8.33×10^{-5} for catechol and 0.00–2.33×10^{-4} for resorcinol systems.

The observed data show that rate of reaction was increased with the increase in concentration up to 2.00×10^{-4}, 1.67×10^{-5} and 3.33×10^{-5} M for hydroquinone, catechol and resorcinol, respectively. It was also observed that the time taken by first stage is decreased and at this concentration the values of induction period are 8.0, 0.0 and 18.0 min for hydroquinone, catechol and resorcinol, respectively. On further increase in concentration of additives, the rate of reaction decreases and the time taken by first stage is increased. The effect of aromatic additives is so important that these can significantly accelerate the Fenton reaction of phenol red even at very low concentrations. Moreover, the data show that these additives (hydroquinone, catechol and resorcinol) do not behave only as a catalyst, but also as a reactant, which were attacked by the hydroxyl radicals formed in the reaction process, and as a result, the rate of degradation decreases after maxima.

The Fenton degradation rates of phenol red with different aromatic additives is in the following order:

Hydroquinone > Catechol > Resorcinol.

This order is also quite consistent with their ability to be transformed into their corresponding quinine-like compounds. The catalysis by additives could be attributed to their reactions with ferric ions in which ferrous ion are generated with simultaneous transformation of hydroquinones to quinones. It is difficult to oxidise resorcinol directly by ferric ion into a quinine-like compound due to its molecular structure. However, hydroxyl radicals can attack resorcinol to generate hydroxyl substituted hydroquinone, which can promote the Fenton reaction although less efficiently as compared to hydroquinone (reactions 1–3).

With all the additives, initial induction period was observed. At a later stages of reaction, a lag period has also been observed for resorcinol, where rate of reaction again slows down.

(1)

(2)

(3)
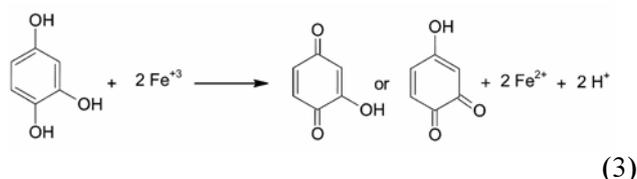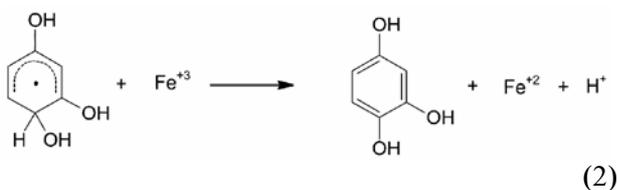
3.4 *Effect of ferric chloride concentration*

The effect of concentration of ferric ions on the rate of photochemical degradation of phenol red was observed by keeping all other factors identical. The results are summarised in table 3. It is clear from the data that the rate of photo–Fenton degradation increases on increasing concentration of ferric chloride and the time taken by first stage decreases. The rates were determined for ferric ion concentration up to concentration 2.33×10^{-5} M for all the systems. Because beyond this concentration, the rates were extremely fast and it was not possible to record the observations correctly due to experimental limitations. This increasing trend may be explained on the basis that on increasing the concentration of ferric chloride, the concentration of Fe^{2+} ions increases. This results in an enhanced generation of the $^{\bullet}OH$ radicals and as a consequence, the rate of photochemical degradation also increases.

3.5 *Effect of phenol red concentration*

The effect of phenol red concentration on the rate of its photo–Fenton degradation was observed and the results are summarized in table 4. The rate of photo–Fenton degradation was found to increase with increasing concentration of phenol red up to 8.33×10^{-5} M, 8.33×10^{-5} M and 10.0×10^{-5} M for hydroquinone, catechol and resorcinol system, respectively. Further increase in concentration beyond these limits results in decrease in the rate of degradation. This may be explained on the basis that on increasing the concentration of phenol red, the reaction rate increases, since more molecules of dye were available for degradation. But further increase in concentration causes retardation of reaction due to increase in number of collisions between dye molecules themselves whereas probability of collisions between dye and $^{\bullet}OH$ radicals will decrease. As a consequence, retardation in rate of reaction was observed. Unsuitable steric orientation is also one of the factors for a decrease in the rate of reaction.

Table 3. Effect of FeCl$_3$ concentration on the rate of reaction.

Hydroquinone System			Catechol System		Resorcinol System	
[Phenol Red] = $8 \cdot 33 \times 10^{-5}$ M			[Phenol Red] = $8 \cdot 33 \times 10^{-5}$ M		[Phenol Red] = $1 \cdot 0 \times 10^{-4}$ M	
H$_2$O$_2$ = 0·2 mL			H$_2$O$_2$ = 0·1 mL		H$_2$O$_2$ = 0·1 mL	
[Hydroquinone] = $2 \cdot 00 \times 10^{-4}$ M			[Catechol] = $1 \cdot 67 \times 10^{-5}$ M		[Resorsinol] = $3 \cdot 33 \times 10^{-5}$ M	
pH = 2·50			pH = 3·00		pH = 3·0 0	
Light intensity = 60·0 mW cm^{-2}			Light intensity = 60·0 mW cm^{-2}		Light intensity = 70·0 mW cm^{-2}	

[FeCl$_3$] × (10^5 M)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)
0·00	0·016	128·6	–	–	1·37	58·0
0·33	0·16	25·6	0·16	6·8	3·21	40·0
0·67	0·42	24·8	0·46	3·8	2·92	30·0
1·00	0·56	24·0	0·79	2·9	2·45	22·1
1·33	0·91	22·4	0·99	2·5	2·55	20·0
1·67	1·23	14·3	1·16	2·2	2·87	19·0
2·00	2·32	10·4	1·38	1·4	3·20	18·6
2·33	2·88	8·0	1·98	0·0	3·34	18·0

Table 4. Effect of concentration of phenol red on the rate of reaction.

Hydroquinone System			Catechol System		Resorcinol System	
H$_2$O$_2$ = 0·2 mL			H$_2$O$_2$ = 0·1 mL		H$_2$O$_2$ = 0·1 mL	
FeCl$_3$ = $2 \cdot 33 \times 10^{-5}$ M			FeCl$_3$ = $2 \cdot 33 \times 10^{-5}$ M		FeCl$_3$ = $2 \cdot 33 \times 10^{-5}$ M	
[Hydroquinone] = $2 \cdot 00 \times 10^{-4}$ M			[Catechol] = $1 \cdot 67 \times 10^{-5}$ M		[Resorcinol] = $3 \cdot 33 \times 10^{-5}$ M	
pH = 2·50			pH = 3·00		pH = 3·00	
Light intensity = 60·0 mW cm^{-2}			Light intensity = 60·0 mW cm^{-2}		Light intensity = 70·0 mW cm^{-2}	

[Phenol Red] × 10^5 M	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)
6·66	0·56	12·5	1·72	3·8	3·28	23·8
8·33	2·88	8·0	1·98	0·0	2·16	22·1
10·00	0·96	9·3	1·56	3·2	3·34	18·0
11·66	0·74	11·2	1·35	3·7	1·91	27·2
13·33	0·65	11·4	1·30	4·3	1·84	28·9
15·00	0·64	11·6	1·26	4·6	1·81	31·5
16·66	0·47	11·7	1·17	5·2	1·85	33·2

3.6 *Effect of light intensity*

The effect of light intensity on the photo–Fenton degradation of phenol red was investigated. The results are reported in table 5. The data indicate that as the light intensity was increased the rate of reaction also increases and maximum rate of reaction for hydroquinone and catechol systems have been found at 60·0 mWcm^{-2} and at 70·0 mWcm^{-2} for resorcinol system. Further increase in the intensity results in a decrease in the rate of reaction may be due to thermal reactions.

4. Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of phenol red by photo–Fenton's reagent in the presence of aromatic additives.
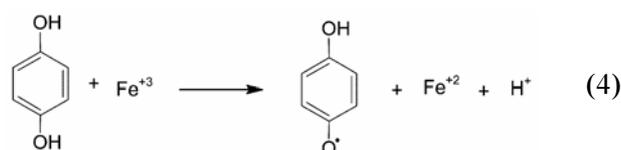
Table 5. Effect of light intensity on the rate of reaction.

Hydroquinone System			Catechol System			Resorcinol System		
[Phenol Red] = 8.33×10^{-5} M H_2O_2 = 2.0 mL $FeCl_3$ = 2.33×10^{-5} M [Hydroquinone] = 2.00×10^{-4} M pH = 2.5			[Phenol Red] = 8.33×10^{-5} M H_2O_2 = 0.1 mL $FeCl_3$ = 2.33×10^{-5} M [Catechol] = 1.67×10^{-5} pH = 3.00			[Phenol Red] = 1.00×10^{-4} M H_2O_2 = 0.1 mL $FeCl_3$ = 2.33×10^{-5} M [Resorcinol] = 3.33×10^{-5} M pH = 3.00		
Light intensity (mW cm^{-2})	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	$k \times 10^3$ (s^{-1})	Time taken by first stage (min)		$k \times 10^3$ (s^{-1})	Time taken by first stage (min)	
10.0	0.68	16.9	1.18	6.1		2.42	31.6	
20.0	0.74	16.2	1.67	5.3		2.51	20.3	
30.0	1.06	15.4	1.71	3.7		2.79	19.5	
40.0	1.69	12.9	1.75	3.1		2.94	19.2	
50.0	2.25	9.5	1.76	2.8		2.99	18.9	
60.0	2.88	8.0	1.98	0.0		3.25	18.5	
70.0	2.43	8.9	1.93	2.1		3.34	18.0	
80.0	2.21	10.6	–	–		3.07	22.6	

$$\text{(5)}$$

$$\text{(6)}$$

$$Fe^{3+} + H_2O_2 \xrightarrow[\text{visible}]{h\nu} Fe^{2+} + {}^{\bullet}OH + H^+ \tag{7}$$

$$Fe^{2+} + H_2O_2 \xrightarrow[\text{visible}]{h\nu} Fe^{2+} + HO_2^{\bullet} + H^+ \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^-OH \tag{9}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{10}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + {}^-OH \tag{11}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{12}$$

$$\text{Dye} + {}^{\bullet}OH \rightarrow \text{Colourless degradation products.} \tag{13}$$

The aqueous solution of ferric ions on exposure to light generates a proton and ${}^{\bullet}OH$ radicals and it is reduced to ferrous state. These ferrous ions further react with H_2O_2 producing hydroxyl ions and hydroxyl radicals and oxidised back to ferric ions. These generated hydroxyl radicals are the most probable active species in the degradation of dye.

Aromatic compounds can play an important role in catalysing the Fenton reaction, when these are transformed into hydroquinone like intermediates by the attack of ${}^{\bullet}OH$ radicals. In addition, their efficiency to promote the Fenton reaction is closely related to their easiness to be transformed into hydroquinone-like intermediates. Hydroquinone-like compounds accelerate the Fenton reaction by increasing the regeneration of ferrous ion (e.g. (4), (5)), which might be the slow reaction in the mechanism of the simple Fenton reaction. Further, the hydroquinones-like compounds are continuously regenerated from quinone or semi-quinone by reacting with $HO_2^{\bullet}$ radicals and disproportion reaction, thus continuously promote the rate of reaction.

$$HO_2^{\bullet} + \text{Quinone} \rightarrow \text{Semiquinone} + O_2 \tag{14}$$

$$HO_2^{\bullet} + \text{Semiquinone} \rightarrow \text{Hydroquinone} + O_2 \tag{15}$$

$$2\,\text{Semiquinone} \rightarrow \text{Hydroquinone} + \text{Quinone.} \tag{16}$$
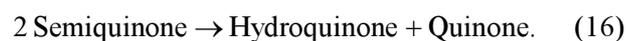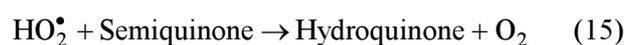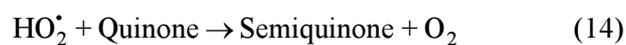
These hydroxyl radicals will degrade the phenol red. The participation of ${}^{\bullet}OH$ radicals as an active oxidising species was confirmed by using hydroxyl radical scavengers, e.g. isopropanol, where the rate of photodegradation was drastically reduced.

Further, this method has more advantages over other methods. It does not add to pollution anymore. The active oxidising species i.e. the hydroxyl radicals will dimerize to give hydrogen peroxide, which may degrade ultimately to water and oxygen.

5. Conclusion

photo–Fenton reactions are the most effective methods for the treatment of wastewater. In dark, the rate of Fenton reaction is slow, whereas with the irradiation of reaction mixture acceleration in the rate of degradation of dye was observed. Due to the presence of light, the rate of regeneration of ferrous ions in the system increases through the photo–Fenton reaction and this process becomes cyclic. Aromatic compounds can play an important role in catalysing the Fenton reaction. Their efficiency to promote the Fenton reaction is closely related to their tendencies to be transformed into hydroquinone-like intermediates. These aromatic additives accelerate the rate of reaction by increasing the regeneration of ferrous ions in the system. The whole process is represented diagrammatically in figure 2.
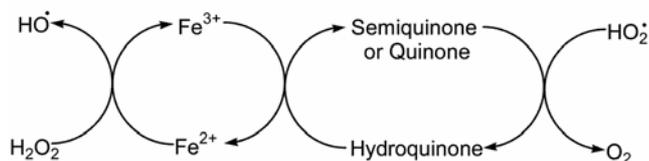
The order of efficiency of the additives in the degradation of phenol red is:

Hydroquinone > Catechol > Resorcinol.

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