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# Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment

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**Abstract**

A two stage sequential Fenton's oxidation followed by aerobic biological treatment train was used to achieve decolorization and to enhance mineralization of azo dyes, viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13), and Acid Orange 7 (AO7). In the first stage, Fenton's oxidation process was used while in the second stage aerobic sequential batch reactors (SBRs) were used as biological process. Study was done to evaluate effect of pH on Fenton's oxidation process. Results reveal that pH 3 was optimum pH for achieving decolorization and dearomatization of dyes by Fenton's process. Degradation of dye was assessed by COD reduction and reduction in aromatic amines (naphthalene chromophores) which was measured by reduction in absorbance at 200 nm. More than 95% of color was removed with Fenton's oxidation process in all dyes. In overall treatment train 81.95, 85.57, and 77.83% of COD reduction was achieved in RB5, RB13, and AO7 dyes, respectively. In the Fenton's oxidation process 56, 24.5, and 80% reduction in naphthalene group was observed in RB5, RB13, and AO7, respectively, which further increased to 81.34, 68.73, and 92% after aerobic treatment. Fenton's oxidation process followed by aerobic SBRs treatment sequence seems to be viable method for achieving significant degradation of azo dye.


*Keywords:* Fenton's oxidation process; Aerobic SBRs; Decolorization; Mineralization

## 1. Introduction

Wastewater from textile industry is one of the major sources of aromatic amines in to the environment [1]. There are more than 10,000 dyes used in textile industry and 280,000 t of textile dyes are discharged every year worldwide [2]. Degradation of dyes especially azo dyes, which contribute to about 70% of all used dyes, is difficult due to their complex structure and synthetic nature. Azo dyes are characterized by nitrogen to nitrogen double bond (–N=N–). The color of dyes is due to azo bond and associated chromophores [3], so disposal of dyes into surface water not only affects the aesthetic but cause also biotoxicity.

Due to the complex polyaromatic structure and recalcitrant nature, dyes are not possible to degrade by means of biological methods. Aromatic amines which are formed as metabolites of reductive cleavage of azo bond under anaerobic conditions are more toxic than intact dye molecules [4] and hence need further treatment. Textile wastewater exhibit low BOD to COD ratio (<0.1) indicating non-biodegradability of dyes [5]. The aerobic biological treatment processes can successfully degrade the organic matter present; nevertheless, these systems usually exhibit a relatively low color and nutrient removal potential [6].

Several physico-chemical methods like chemical precipitation [6], adsorption by activated carbon [7], natural absorbents, polycatalytic oxidation [8], ozonation, and Fenton's oxidation [9–12] have been investigated to treat azo dye containing wastewater.

Among these physico-chemical processes Fenton's oxidation is one of the oldest advanced oxidation process which is used successfully, as it is comparatively cheap and uses easy to handle reagents. Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron is effective for color and COD removal of dye effluent. Several investigators have demonstrated that AOPs are effective for complete color removal and partial degradation of organic matter [11,13].

For the decolorization of azo dye destruction of dye up to obtaining mineralization is not necessary because the removal of color is associated with the breaking of the chromophores,

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i.e. conjugated unsaturated bond (–N=N–) in molecules [14]. However, the end products formed are a concern due to their toxicity. Further some researchers have also suggests application of Fenton's oxidation process for treating recalcitrant toxic wastewater to achieve mineralization of toxic compounds [15].

Though AOPs are capable for dearomatization of dye stuff the main handicap lies is the high cost of reagent, energy and production of sludge which contain high amount of Fe (III), which needs to be managed by safe disposal methods [16]. Hence, there is need for further research for finding an efficient and economical treatment method for complete mineralization of textile azo dye.

Most of the previous researchers have focused on only one method of treatment, i.e. either biological process or advanced oxidation process for treating recalcitrant compound. Whereas the preferred method for treatment of recalcitrant compound is to use AOP (for partial degradation) followed by aerobic biological process [17–19].

From the above discussion it seems that mineralization of azo dye can be achieved using AOP–aerobic sequential treatment. Also Fongsatitkul et al. [20] reported that chemical treatment prior to biodegradation delivered the best performance for treating the dye effluent rather than only biological and biological prior to the chemical treatment.

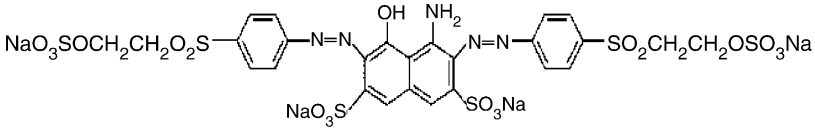
The main aim of the present study was to evaluate Fenton's oxidation process to achieve complete decolorization of azo dye and partial cleavage of aromatic amines to make them easily biodegradable. Further, degradation can be achieved by treating effluent of Fenton's treatment by aerobic SBRs. Three commercially available azo dyes, viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13), and Acid Orange 7 (AO7) were used as model dyes. Advanced oxidation process (Fenton's treatment) was evaluated for the effect of pH and effect of $H_2O_2$ dose on degradation of dyes. Fenton's treated dye solution was then fed to aerobic SBRs and the overall performance was evaluated.

## 2. Materials and methods

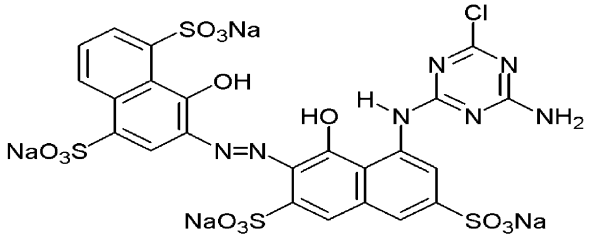
### 2.1. Materials

Commercially available azo dye, viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13), and Acid Orange 7 (AO7) were selected based on availability of structure and difficult to degrade. Fig. 1 shows the structure of dyes used. Dyes were purchased from local market and used without any further purification. Ferrous sulphate ($FeSO_4{\cdot}7H_2O$) (Sisco Research Lab, India), hydrogen peroxide (E-Merck, India, 50%, w/w) were used as received. Dextrose (E Merck) was used as a carbon source. pH of the solution was adjusted by using 1N $H_2SO_4$ and 1N NaOH. Fenton's reaction was performed in the polypropylene beaker of 11 operating capacity. Distilled water was used for preparation of all reagents and stock dye solution.

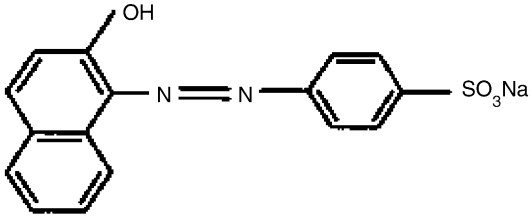
Aerobic biological treatment was accomplished by using four identical SBR systems, three for three different dyes and one for




(A) *Reactive Black 5*




(B) *Reactive Blue 13*




(C) *Acid Orange 7.*

Fig. 1. Chemical structures of the dyes used in the present study.

control (without dye). Polypropylene reactors of 1 l operating capacity were used as SBRs. Air pumps were used for the aeration of reactor.

### 2.2. Inoculum for bioreactors

Seed material was prepared by sieving the cow dung through a 355 μm sieve (mesh no. BS No. 44, ASTM 0.355 mm). The prepared slurry taken was 1% (w/v). Initial MLSS of the reactors was 1000 mg $l^{-1}$.

### 2.3. Methods

Total treatment was accomplished in two stage process, Physico-chemical process (Fenton's oxidation process, F.O. process) as stage 1 and aerobic biological treatment as (SBRs) as stage 2.

#### 2.3.1. Stage 1: physico-chemical process (F.O. process)

*2.3.1.1. Kinetic study.* Batch experiments of Fenton's oxidation process were performed in a polypropylene beakers having 1 l operating capacity at room temperature (25–30 °C) with Fenton dose of 72 mM of $H_2O_2$ and 1.05 mM of $Fe^{2+}$. Dye solution of 50 mg $l^{-1}$ concentration was prepared by diluting stock solution with tap water. Samples were taken from the reactor during the reaction at different time interval for analysis. Kinetic study was done to find out the effects of pH and effect of dose of Fenton's reagent on decolorization and mineralization rate of dye solution. As Fenton's oxidation stops at alkaline pH [9,12,20], reaction was stopped instantaneously by adjusting the reaction mixture to pH >7 before analysis.

*2.3.1.2. Fenton's oxidation process.* In the first stage, dye solution with initial concentration of 50 mg $l^{-1}$ was prepared by diluting stock solution in tap water, and pH was adjusted to 3 by using 1N $H_2SO_4$. Predetermined quantity of $FeSO_4$ and $H_2O_2$ were added to the reactor. Reaction was allowed to continue for 1 h after which pH of sample was adjusted to 7 by using 1N NaOH [9,12,20] and allowed to stand for 30 min. The supernatant was analyzed for color ($\lambda_{max}$), and at 200 nm and for COD. Precipitate of iron was separated from the reactor and clear supernatant was fed as influent to SBR. Effluent from AOP was analyzed for color removal, COD, and mineralization.

#### 2.3.2. Stage 2: aerobic biological treatment (SBRs)

During the acclimation, reactors were fed with the tap water containing 0.4 g of dextrose providing 400 mg COD [21] as a carbon source for a period of 73 days. Every alternate day 0.5 l supernatant was withdrawn and 0.5 l feed was added to the reactor. After acclimation, effluent from the AOP was fed to the SBR in the same manner as that of acclimation period for a period of 20 days with HRT of 96 h. SRT of reactors was maintained to 45 days. Effluent of SBR was analyzed for color removal, COD, and mineralization.

### 2.4. Analytical methods

The UV–vis spectra of azo dye samples were recorded from 190–900 nm using UV–vis spectrophotometer (JASCO-Model V-530). The maximum absorbance wavelength ($\lambda_{max}$) of RB5, RB13 and AO7 are at 596, 583, and 481 nm, respectively, in visible range. In UV range naphthalene chromophores gives absorbance at 200 nm [22], therefore concentration of azo dye in water was measured at $\lambda_{max}$ and degradation of naphthalene was determine from the absorbance at 200 nm. COD was measured by closed reflux titrimetric method as per procedure outlined in standard methods [23]. Residual Hydrogen peroxide was measured according to iodometric titration with 0.1N $Na_2S_2O_3$ solution. Correction to the interference of $H_2O_2$ with COD measurement was applied as suggested by Talini and Anderson [24].

## 3. Results and discussion

### 3.1. Stage 1: Fenton's oxidation process

#### 3.1.1. Effect of pH on decolorization

The aqueous pH has a major effect on the efficiency of Fenton's treatment. Fig. 2 demonstrates the effect of pH on the decolorization of dye. The reaction was done for 60 min under controlled pH condition with constant dose of $Fe^{2+}$ (1.05 mM) and $H_2O_2$ (576 mM). It is apparent from the figure that extent of decolorization decreases with increase in pH, at pH 3 almost >95% color removal was observed in all dyes, whereas at the pH 7, 91.3, 36.3 and 24.76% of decolorization was observed for RB13, AO7, and RB5, respectively. According to the data, it seems that decolorization of dyes varies with the type of dye. The observed decolorization, i.e. >95% at pH 3 is also supported by previous studies; Kuo [9] observed 97% of decolorization of dye

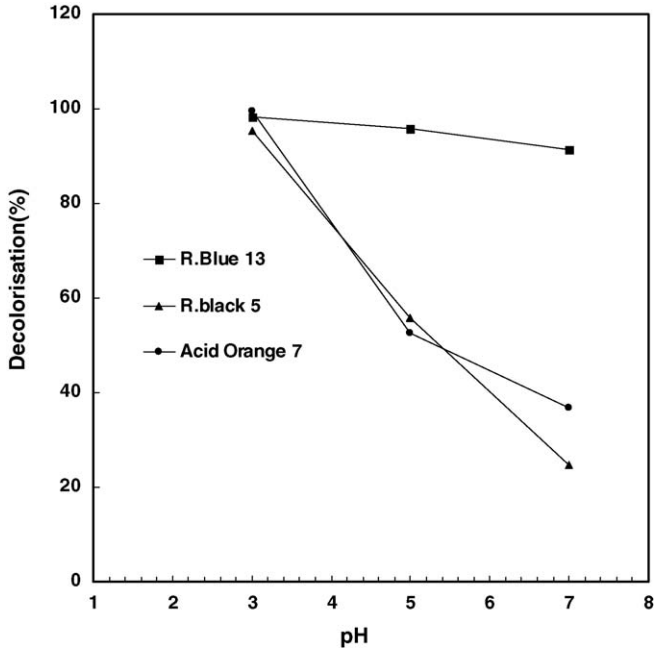



Fig. 2. Effect of pH on decolorization of azo dye. Reaction time 60 min, pH 3, $Fe^{2+}$ 1.05 mM, $H_2O_2$ 576 mM.

in 30 min. Malik and Saha [25] reported that the optimum pH was 3 for the decolorization of dyes. Meric et al. [14] showed that more than 99% of color removal was possible in the pH range of 3–3.5.

### 3.1.2. Optimizations of $H_2O_2$ dose

Many researchers [1,9,14] have shown that complete color removal is possible at pH 3, but no study is available for effect of pH on dearomatization of dye. Umoren et al. [22] observed that UV spectrum of the dye showed the presence of naphthalene at wavelength of 200 nm. So in the present study reduction in absorbance at 200 nm is used as a surrogate to estimate reduction in the aromatic ring. It may be highlighted that degradation of chromophore ring (color forming group) by Fenton's reagent is quite effective. Further, the compound formed after treatment with Fenton's reagent is also a cause of concern. Hence the optimization of dose of $H_2O_2$ was based on the maximum reduction in the absorbance at 200 nm.

Experiments were carried out for duration of 1 h with initial dye concentration of 50 mg $l^{-1}$. The reaction was done at pH 3 with the constant dose of Fe (1.05 mM). The concentration of $H_2O_2$ was varied from 0 to 576 mM. From the data shown in Fig. 3, it can be seen that the maximum reduction in naphthalene group at 200 nm [22] occurred at dose of 72 mM. Less reduction in the absorbance is observed at 36 mM dose of $H_2O_2$. Further as $H_2O_2$ concentration increase, an increase in absorbance at 200 nm was also observed, which may be due to the hydroxyl radical scavenging effect of $H_2O_2$ according to Eqs. (1)–(3), [3,1]. According to Hsueh et al. [1] degradation rate of organic compounds increases as the $H_2O_2$ concentration increases until a critical $H_2O_2$ concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation rate of organic compounds was decreased as a result of so-called scavenging effect.

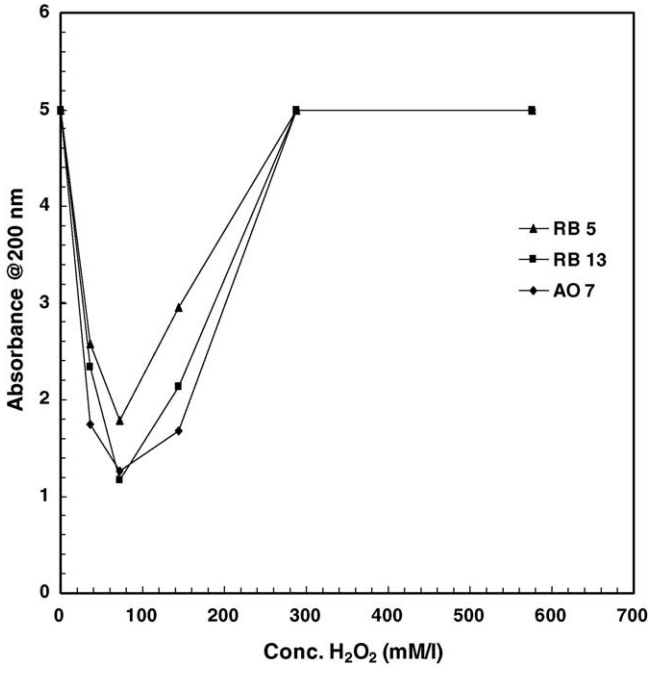



Fig. 3. Effect of concentration of hydrogen peroxide on dearomatization at pH 3. Reaction time 60 min, $Fe^{2+}$ 1.05 mM, $H_2O_2$ 0–576 mM.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet} \quad (1)$$

$$HO_2{}^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (2)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (3)$$

Based on this study dose of 72 mM of $H_2O_2$ was selected for conducting kinetic study of all dyes.

### 3.1.3. Kinetics

Kinetic studies for decolorization of dyes were done under the following experimental conditions: initial dye concentration 50 mg $l^{-1}$, Fenton's reagent ($Fe^{2+}$ 1.05 mM + $H_2O_2$ dose of 72 mM) with the pH varied from 3–7. The decolorization of dyes by Fenton's reaction was observed to be a function of time. For decolorization of the dye in the intial phase by Fenton's reagent, first order kinetic model has been suggested [26]. Hence, the kinetic data of first 4 min were fitted into the following equation:

$$\ln\left[\frac{C_t}{C_0}\right] = Kt$$

where $C_0$ and $C_t$ are concentration of the dyes at time 0 and at time $t$. $K$ is the first order rate constant in $min^{-1}$ and $t$ is the time in minutes. All of the values for the pseudo-first order reaction rate constant, $K$, were calculated from the linear regression of the pseudo-first order kinetic model. The coefficient of correlation ($R$) was in the range of 90–99%. The rate constants for all three model dyes at all pH are summarized in Table 1. From the data shown in Table 1 and from the Fig. 4, it is seen that the rate of decolorization decreased with an increase in pH. Kinetic results shows that Maximum color removal of 99.88, 99.96, and 99.98% was observed in RB5, RB13, and AO 7, respectively, at pH 3, while only 60.84, 91.89, and 71.87% of color removal was seen in RB5, RB13, and AO7, respectively, at pH 7, i.e. Maximum color removal was observed at pH 3 (Table 2), which is in agreement with the previous researchers [1,9,12,14,25,27,28]. From the same figure, it was seen that entire decolorization can be divided in two stages; decolorization in the first stage is more rapid than the second stage. The first stage follows first order kinetic model while the second stage follows the second order kinetic reaction. At pH 3 almost 97% of color removal occurred in first 4 min and around 99% reduction in color was observed in total period of 360 min. Most of the $H_2O_2$ dosage was consumed in the early stage of the Fenton reaction. Since ferrous ion catalyses $H_2O_2$ to form hydroxyl radical quickly in the first stage of

Table 1
Pseudo-first order rate constant ($K$) for model dyes

| Dye | pH | | | | |
|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 |
| Reactive Black 5 | −0.3399 | −0.4547 | −0.3712 | −0.2731 | −0.2355 |
| Reactive Blue 13 | −0.3164 | −0.294 | −0.6698 | −0.2187 | −0.3437 |
| Acid Orange 7 | −1.0326 | −0.708 | −0.3146 | −0.5671 | −0.2644 |

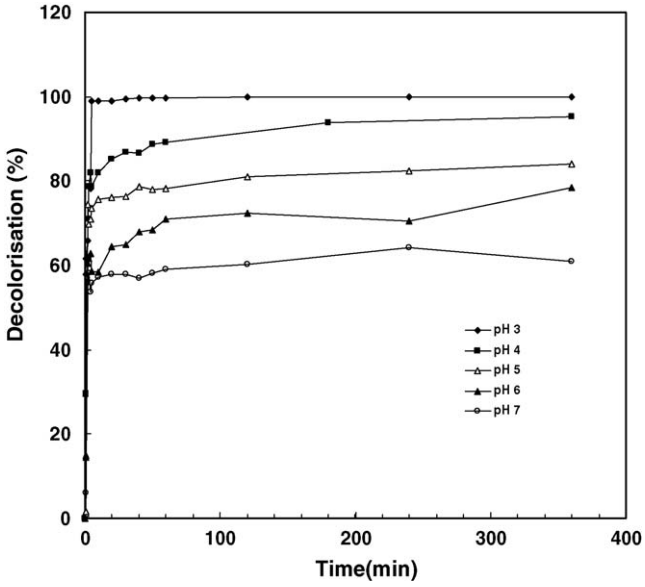



Fig. 4. Effect of pH on color removal. Initial dye concentration 50 mg $l^{-1}$, $Fe^{2+}$ 1.05 mM, $H_2O_2$ 72 mM, pH 3–7.

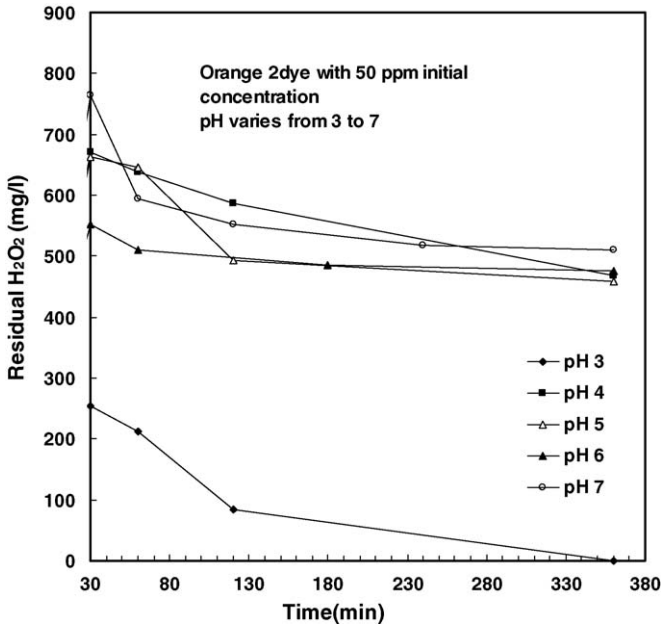



Fig. 5. Effect of pH on residual hydrogen peroxide. Initial dye concentration 50 mg $l^{-1}$, $Fe^{2+}$ 1.05 mM, $H_2O_2$ - 72 mM, pH 3–7.

reaction, more decolorization occurs in the early stage of reaction. Malik and Saha [25] showed that 70% degradation occurs in the first minute for both the dyes. The rest of the reaction occurs slowly, it takes 30 min for almost 97% of degradation. The probable reason for the decrease in reaction rate is that in the first stage ferrous ions react with hydrogen peroxide to produce a large amount of hydroxyl radical according to following reaction:

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (4)$$

Further ferric ions produced in the first stage react with hydrogen peroxide to produce hydroperoxyl radicals ($HO_2^{\bullet}$) and ferrous ions:

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+} \quad (5)$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (6)$$

Thus hydroxyl radical and hydroperoxyl radicals are formed in the first and second stage, respectively. Oxidation capability of hydroxyl radical is much more than the hydroperoxyl radicals.

### 3.1.4. *Effect of pH on dearomatization of dye and utilization of hydrogen peroxide*

When azo dye is treated with Fenton's reagent, it may be that, the reactant $H_2O_2$ added might not be sufficiently utilized. This would lead to residual $H_2O_2$ into treated dye waste. Hydrogen peroxide, being a mild oxidant, might affect the subsequent biological process. Thereby residual $H_2O_2$ was measured. From Fig. 5, it is seen that maximum utilization of $H_2O_2$ is observed at the pH 3, out of initial concentration of 72 mM of $H_2O_2$ only 0, 0.5, and 1 mM $H_2O_2$ was remain in RB5, RB13 and AO7

Table 2
Effect of pH on Fenton's process

| Dye | pH | Color reduction ($\lambda_{max}$) (%) | Dearomatization at 200 nm (%) | Residual $H_2O_2$ (mM) |
|---|---|---|---|---|
| Reactive Black 5 | 3 | 99.88 | 52.51 | 1 |
| | 4 | 95.25 | Negligible | 13.8 |
| | 5 | 84 | Negligible | 12.5 |
| | 6 | 78.38 | Negligible | 16.5 |
| | 7 | 60.84 | Negligible | 12.5 |
| Reactive Blue 13 | 3 | 99.96 | 20 | 0.5 |
| | 4 | 100 | Negligible | 78.5 |
| | 5 | 100 | Negligible | 9.5 |
| | 6 | 98.6 | Negligible | 10.5 |
| | 7 | 94.89 | Negligible | 12.5 |
| Acid Orange 7 | 3 | 99.98 | 64.09 | 0 |
| | 4 | 99.90 | Negligible | 13.52 |
| | 5 | 98.38 | Negligible | 13.5 |
| | 6 | 91.32 | Negligible | 14 |
| | 7 | 71.87 | Negligible | 15 |

Table 3
Reduction in the absorbance at 200 nm wavelength

| Reactor | RB5 | | RB13 | | AO7 | |
|---|---|---|---|---|---|---|
| | Absorbance | Reduction (%) | Absorbance | Reduction (%) | Absorbance | Reduction (%) |
| Pure dye solution | 2.47216 | | 1.2667 | | 5 | |
| AOP effluent | 1.06782 | 56 | 0.95654 | 24.5 | 1 | 80 |
| Aerobic effluent | 0.46106 | 81.34 | 0.39601 | 68.72 | 0.36528 | 92 |

after the reaction of 6 h. The main reason being that at a low pH, more $Fe(OH)^+$ is formed, which has much higher activity as compared to $Fe^{2+}$ in Fenton's oxidation. Also at the higher pH, $H_2O_2$ loses its oxidizing potential [25].

Kinetic study of dyes reveals that degradation of naphthalene (indicated by reduction in absorbance at 200 nm) is possible only at pH 3. Table 2 presents the data of reduction in naphthalene for all dyes. Approximately 52.51, 64.09, and 20% of degradation of the naphthalene group was observed in RB5, AO7, and RB13 dye, respectively, after a reaction period of 6 h.

### 3.1.5. COD reduction

Extent of mineralization of the dye by Fenton's process can be evaluated by measuring Total Organic Carbon or Chemical Oxygen Demand (COD) measurement. In this study Chemical Oxygen Demand measurements were conducted.

From the aforementioned sections it is clear that pH 3 seems to be the optimum pH for the Fenton's oxidation process. The degradation of azo dye was evaluated for COD reduction of F.O. treated sample. To determine the change in the COD of reaction medium, initial COD (pure dye solution) and the COD of a sample at different intervals during the reaction were measured and COD reduction was determined as follows:

$$\mathrm{COD_{removal}} = \frac{(1 - \mathrm{COD}_t)}{\mathrm{COD}_0} \times 100$$

where $\mathrm{COD}_t$ and $\mathrm{COD}_0$ are COD (mg $l^{-1}$) values at time ($t$) and at time (0), respectively. 55.5, 88.29, and 100% COD reduction is achieved in RB5, RB13, and AO7 dye, respectively, in 6 h, which indicates the partial mineralization of dyes. Kuo [9] reported approximately 90% chemical oxygen demand (COD) removal in 30 min. Malik and Saha [25] observed that at the optimal ratio of $[Fe^{2+}]$:$[H_2O_2]$:[dye] (initial concentration ratio) and at 30 °C with pH 3, 70% COD removal of can be achieved in 60 min.

## 3.2. Stage 2: sequential batch reactors

### 3.2.1. SBR acclimation

During the startup, all SBRs were fed with tap water with 400 mg $l^{-1}$ of dextrose as a carbon source. An acclimation period was necessary in order to gradually expose the microbial community to the potential inhibitory or toxic organic compound; this allows for the development of appropriate enzyme producing agents that are essential to induce biodegradation of dyes [20]. Stabilization of reactor was assessed by measurement of COD reduction. In this study, almost 73 days were required for start up of the reactors, i.e. to achieve steady state COD reduction. Continuous COD reduction of 81.5, 79.89, 80.9, and 80.53% was achieved in RB5, RB13, AO7, and control reactor during the acclimatization period of SBR

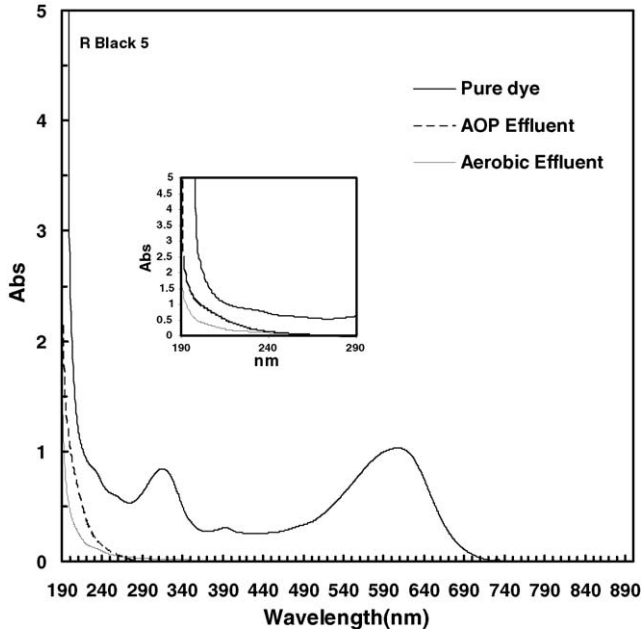



Fig. 6. UV–vis absorbance spectra of Reactive Black 5.

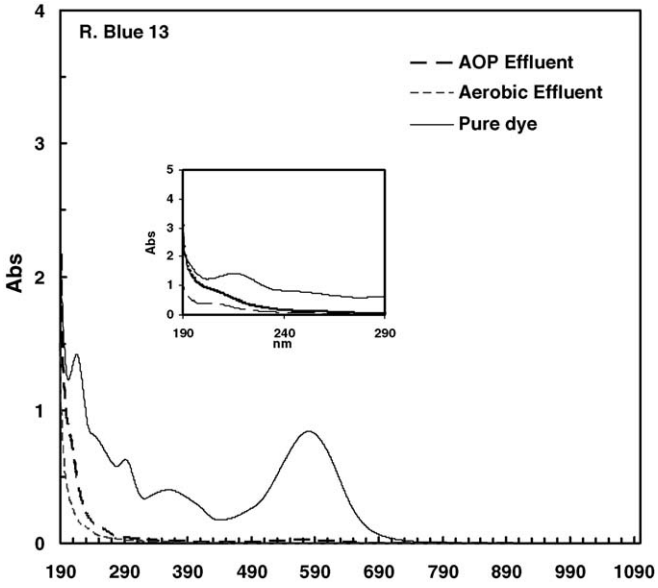



Fig. 7. UV–vis absorbance spectra of Reactive Blue 13.

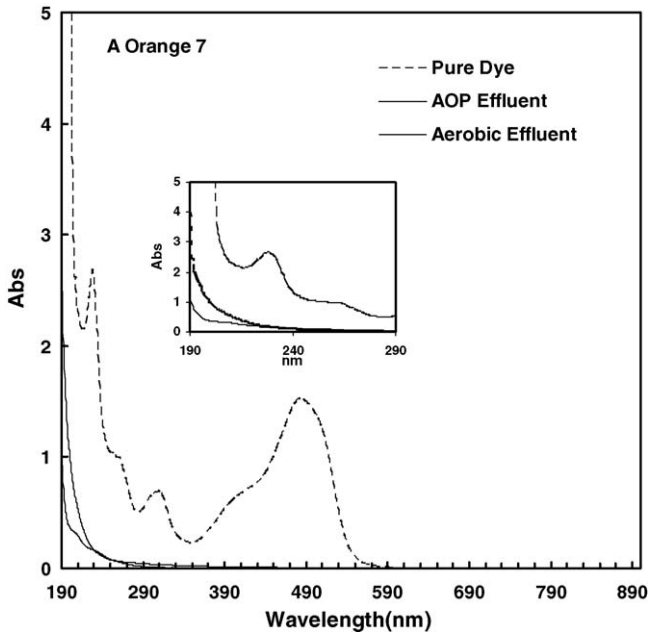



Fig. 8. UV–vis absorbance spectra of Acid Orange 7.

### 3.2.2. Degradation of azo dye

The SBRs were fed with Fenton's effluent for 20 days. Degradation of dye was checked by COD reduction and reduction in naphthalene group was checked by UV–vis spectra analysis. COD reduction of 81.95, 85.57, and 77.83% was achieved in the RB5, RB13, and AO7, respectively. The data in Table 3 shows that 81.34, 68.73 and 92% of reduction in naphthalene group was achieved in RB5, RB13, and AO7, respectively. As per Fongsatitkul et al. [20] more than 90% of COD can be achieved in chemical plus biological treatment sequence.

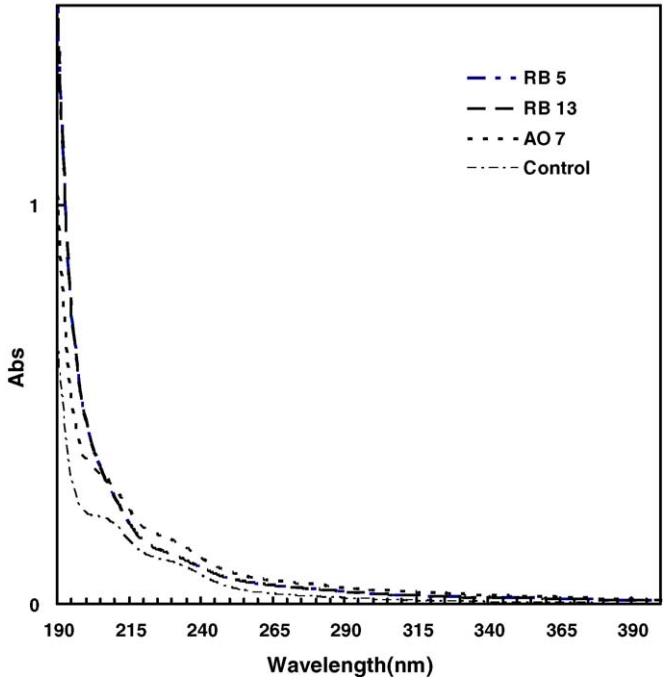



Fig. 9. Comparison of Spectrum of different dye with no dye reactor effluent.

### 3.3. UV–vis spectra analysis

Figs. 6–8 show the UV–vis spectra for different dyes. The influent spectra of RB5, RB13, and AO7 peak at 596, 581, and 483 nm which account for color and absorbance at 200 nm in UV range accounts for naphthalene chromophore [22].

Spectrum of Fenton's effluent shows no absorbance in visible region depicts complete removal of color, however, absorbance at 200 nm is observed indicating formation of aromatic amines (naphthalene). Furthermore, transformation of absorbance at 200 nm has been seen in the spectrum of SBR effluent. In AOP–aerobic sequential treatment 81.34, 68.73, and 92% reduction in absorbance at 200 nm is achieved in RB5, RB13, and AO7 (Table 3; Figs. 6–8), respectively, indicate significant mineralization of azo dye.

Fig. 9 shows the comparisons of the effluent of aerobic reactors that contain dye solution and the effluent from control. From the figure, it is seen that partial mineralization was achieved in the AOP–aerobic sequential process.

## 4. Conclusion

Two stage Fenton oxidation and aerobic biological treatment chain achieved efficient decolorization and mineralization of hydrolyzed azo dyes, viz. RB5, RB13, and AO7. Results indicate that Fenton's oxidation process is not only effective for decolorization of dyes but degradation of aromatic amines is also possible at pH 3. More than 95% of color was removed with Fenton's oxidation process for all dyes. In overall treatment train 81.95, 85.57, and 77.83% reduction in COD and 81.34, 68.73, and 92% reduction in naphthalene group was achieved in the RB5, RB13, and AO7, respectively, indicative of partial but significant mineralization of azo dye.

## References

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