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Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions

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Abstract

Degradation of dyes especially, azo dyes are difficult due to their complex structure and synthetic nature. The main objective of this study was to evaluate the Fenton-biological (aerobic) treatment train for decolorization and mineralization of azo dyes viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13) and Acid Orange 7 (AO7). The objective of Fenton treatment was only to decolorize the dyes (breakage of –N=N–), as it was considered that after breakage of –N=N–, the dyes will become amenable to biodegradation and can be further treated in aerobic biological system. Hence studies were carried out to optimize the lower Fenton's doses for decolorization of dyes. The optimum doses for decolorization (>95%) of all the three dyes were found out to be 15 mg L^{-1} of Fe^{2+} (0.27 mM) and 50 mg L^{-1} (1.47 mM) of H_2O_2 dose at optimum pH 3. Further it was also investigated that at lower doses, the main problem of Fenton process (sludge generation) can also be minimized. Later the mineralization of the dye (removal of aromatic amines) was achieved in the aerobic biological treatment system. Overall reduction of 64, 89 and 75% in the aromatic amines (at 254 nm), 88, 95 and 78% in naphthalene ring associated compounds (near 310 nm) and 49, 89 and 91% reduction in benzene ring associated compounds (near 226 nm) were observed for RB5, RB13 and AO7, respectively. Thus this treatment system seems to be quite effective and economical option for the treatment of recalcitrant compounds like dyes, as the cost in the chemical treatment is considered mainly due to chemicals thus at lower doses the operational cost is saved. Further, as the sludge generation was almost negligible at lower doses, thus the savings in cost of handling and disposal of hazardous sludge also adds to economy of treatment.

Keywords: Fenton's oxidation process; Treatment; Azo; Dye; Aerobic; Decolorization; Mineralization; Fenton sludge; Aromatic amine; Semi-batch reactor and advanced oxidation process

1. Introduction

Wastewater from textile industry is the major source of color and aromatic amines into the environment [1]. The color from textile industries is mainly due to dyeing process. There are more than 10,000 dyes used in textile industry and 280,000 t of textile dyes are discharged every year [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]. Color in the textile mill effluent is one of the most obvious indicators of water pollution and the discharge of highly colored synthetic dye effluents is aesthetically displeasing and can damage the receiving water body by impeding penetration of light [4,5]. Moreover, most of the azo dyes and degradation product of most of the dyes are cytotoxic [6] or carcinogenic [7]. Hence, the government legislation on discharge of dye effluents is becoming more and more stringent, especially in developed countries [8] and it is expected that this legislation will also become more stringent in the developing countries in near future. Hence, there is an urgent need to develop an economical treatment system for the treatment of wastewaters containing dyes.

Biological treatment processes are considered to be economical [9] but due to the complex polyaromatic structure, recalcitrant nature and low BOD to COD ratio (<0.1), wastewater-containing dyes are not possible to degrade by means of biological treatment unit [10]. However, some researchers have reported that partial mineralization of few dyes can be achieved by anaerobic followed by aerobic treatment [11–15] but the problem associated with anaerobic treatment

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of azo dyes is mainly it requires long hydraulic retention time (HRT) [16,17], long sludge retention time (SRT) [16,18]. The requirement of long HRTs and SRTs increases the volume of the reactors required and thus increases the cost of installation and also the requirements of additional carbon source [19], redox mediators [20] and skilled labour increases the operating cost of treatment. The researchers have also reported that some azo dyes are toxic to anaerobic biomass [20]. Thus in case of azo dyes, anaerobic treatment does not seem to be an economical as well as feasible treatment option. The aerobic biological treatment processes can successfully degrade the simpler biodegradable organic matter present in the wastewater, but these systems are not capable for the degradation of complex structured (recalcitrant) organic compounds such as azo dyes. The aerobic systems usually exhibit a relatively low color removal potential [21] and this removal is mostly due to the adsorption on to the biomass rather than biodegradation.

Due to above problems associated with biological treatment of azo dyes, several researchers have focused on various physicochemical methods like chemical precipitation [21], adsorption [22,23], membrane processes [24], electrochemical coagulation [25], advanced oxidation processes viz. catalytic oxidation [26,27], ozonation [28], radiolysis [29], sonochemical oxidation [27,28] and Fenton's oxidation [29–32] for treatment azo dye containing wastewater.

Though Fenton's reagent is capable for dearomatization of dyestuff, the main problems with this treatment are the generation of aromatic amines, high reagent costs and production of sludge which contain high amount of Fe (III), which needs to be managed by safe disposal methods. Hence, there is need for further research for finding an alternative 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 advanced oxidation processes (for partial degradation) followed by aerobic biological process [33–36]. Several investigators have demonstrated that Fenton's reagent is effective for complete color removal and partial degradation of complex organic matter [31,37].

From the above discussion it seems that mineralization of azo dye can be achieved using Fenton's oxidation-biological sequential treatment. The same observation was made by Fongsatitkul et al. [36]. Fongsatitkul et al. [36] reported that chemical treatment prior to biodegradation delivered the best performance for treating the textile effluent rather than only biological and biological prior to the chemical treatment.

Fenton's oxidation is one of the oldest oxidation processes which is used successfully, as it is comparatively cheap and uses easy to handle reagent [38,39]. Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron is effective for color and COD removal of dye effluent [40]. In most of the previous research works using Fenton's reagent for the treatment of various dyes, the main objective was to mineralize and decolorize the dyes simultaneously and hence a higher doses of H_2O_2 and Fe^{2+} ions were used for the treatment of dyes. In most of the studies, the dye:H_2O_2:Fe^{2+} mass ratios (w/w/w) ranging between 1:0.25:0.08 and 1:48.96:1.16 were used [41–44]. At higher doses of the reagents (Fe^{2+} and H_2O_2), the operational cost of treatment increases and thus, in this study it was decided to optimize lower doses of reagents for only decolorization of dyes (breaking of –N=N–). 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, i.e. conjugated unsaturated bond (–N=N–) in molecules [43]. However the end products formed are of concern [36]. Further these end products (aromatic amines) can be possibly degraded biologically (after acclimatization) under aerobic condition [12,13,15,18–20], which is also considered to be an economical treatment. Thus a sequential Fenton's oxidation-aerobic treatment chain seems to be an economical alternative for the treatment for the wastewaters containing azo dyes. Thus, the operational cost of treatment can be reduced at lower doses as well as the problem of sludge generation can also be minimized and results in saving of sludge handling and disposal costs.

The main aim of the present study was to develop an economic and effective treatment scheme and to optimize the treatment scheme for wastewater containing azo dyes. As the main cost in the chemical treatment is considered to be of the chemicals, hence for economical reasons, Fenton's oxidation process at lower doses was used to achieve only decolorization of azo dyes and partial cleavage of aromatic amines, to make them amenable to biodegradation. Further, degradation of Fenton's treated effluent was achieved in aerobic SBRs.

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 as model dyes for study. Fig. 1 shows the structure of dyes used in the study. 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. pH of the solution was adjusted by using 0.5 M H_2SO_4 and 1 M NaOH. Fenton's reaction was performed in the glass beaker of 1 L 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 control (without dye). Polypropylene reactors of 1 L operating capacity were used as SBRs and aeration was provided using air diffusers.

2.1.1. Inoculum for bioreactors

The sludge used in the bioreactors was taken from an activated sludge plant degrading dairy industry wastewater. Initial MLSS and MLVSS of the sludge were 3000 and 2200 mg L^{-1}, respectively.

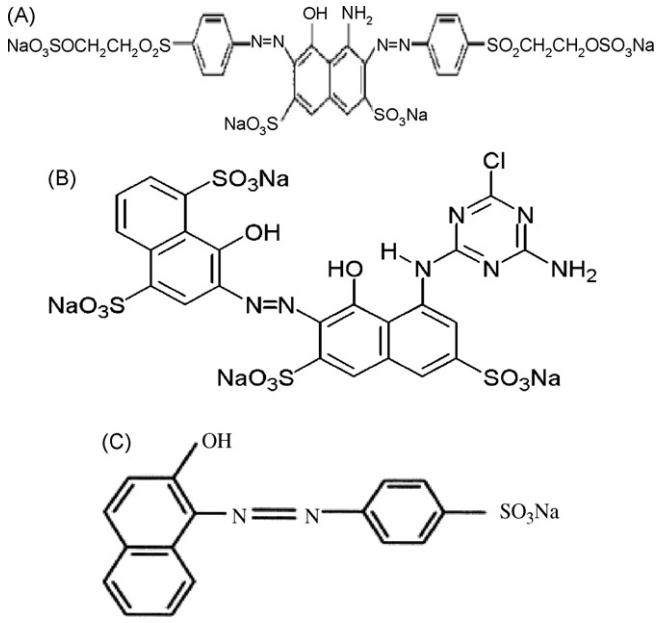

Fig. 1. Structures of different dyes used in study: (A) Reactive Black 5, (B) Reactive Blue 13 and (C) Acid Orange 7.

2.2. Methods

The overall treatment was accomplished in two stage process, advanced oxidation process (Fenton's oxidation process (FO process)) as stage I and aerobic biological treatment as (SBRs) as stage II.

2.2.1. Fenton oxidation process (F.O. process)

2.2.1.1. Optimization studies for decolorization of dyes. Optimization studies were carried out to optimize the pH, low doses of H_2O_2 and Fe^{2+} ions for the decolorization of selected dyes. The studies were conducted in 1 L glass beaker. During pH optimization both H_2O_2 and Fe^{2+} ion doses were kept constant and pH was varied in range of 2–7. The dose optimization studies were carried out at optimum pH by varying one parameter and keeping the other constant.

2.2.1.2. Decolorization of dyes using Fenton's reagent. 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 0.5 M H_2SO_4. Predetermined quantity (lower optimum doses) of Fe^{2+} ions and H_2O_2 were added to the reactor. Reaction was allowed to continue for 30 min, after which pH of sample was adjusted to 7 by using 1 M NaOH [29,32,36] and allowed to stand for 30 min. The supernatant was analyzed for color (λ_{max}), aromatic amines, absorbance at benzene ring, absorbance at naphthalene ring and COD. Precipitate of iron was separated from the reactor and clear supernatant was fed as influent to SBRs. Fenton treated effluent was analyzed for color removal, residual H_2O_2, COD and mineralization.

2.3. Aerobic biological treatment (SBRs)

During the acclimation, reactors were fed with the tap water containing 0.4 g of dextrose providing 400 mg COD [45] as a carbon source for a period of 20 days. Every alternate day 0.5 L supernatant was withdrawn and 0.5 L feed was added to the reactors. After acclimation, Fenton's treated effluents were fed to the SBRs in the same manner as that of acclimation period for a period of 60 days. MLSS in the SBRs were maintained around 3000 mg L^{-1}.

2.4. Analytical methods

The UV–vis spectrum of azo dye samples were recorded from 200 to 800 nm using UV–vis spectrophotometer (JASCO-Model V-530). The maximum absorbance wavelength (λ_{max}) of RB5, RB13 and AO7 are at 596, 583, and 481 nm, respectively in visible range. In UV range aromatic amines, naphthalene and benzene rings gives absorbance at 254, 310 and 226 nm, respectively [41]. COD was measured by closed reflux titrimetric method as per procedure outlined in standard methods [46]. Residual hydrogen peroxide was measured according to iodometric titration with 0.02 mM $Na_2S_2O_3$ solution. Correction to the interference of H_2O_2 with COD measurement was applied as suggested by Talini and Anderson [47]. MLSS and MLVSS in the SBRs were measured as per procedures outlined by standard methods [46].

3. Results and discussion

3.1. Fenton's oxidation process

3.1.1. Optimization of pH for decolorization

All the studies were carried out at the dyes concentration of 50 mg L^{-1}. The aqueous pH has a major effect on the efficiency of Fenton's treatment. During the pH optimization study, the pH of the solution was varied in the range of 2–7. The reaction was carried out for 30 min under controlled pH condition with dose of Fe^{2+}: 20 mg L^{-1} (0.36 mM) and H_2O_2 dose of 100 mg L^{-1} (2.94 mM). Fig. 2 demonstrates the effect of pH on the decolorization of dyes. It is apparent from the figure that extent of decolorization decreases with increase in pH after pH 3, at pH 3

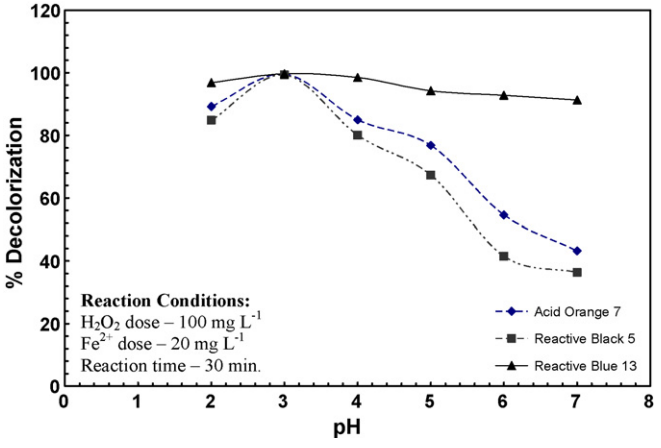

Fig. 2. Effect of pH on the decolorization of different dyes (reaction conditions—H_2O_2 dose: 100 mg L^{-1}, Fe^{2+} dose: 20 mg L^{-1}, reaction time: 30 min).

more than 99% color removal was observed for all dyes, whereas at the pH 7, 91%, 43% and 36% decolorization was observed for RB13, AO7, RB5, respectively. The lower degradation at pH 7 may be attributed to the generation of small amount of hydroxyl radical as compare to hydroxyl radicals generated at pH 3. However the decolorization of the RB13 dye depends on the breakage of chromophore of the dye by hydroxyl radical. It is likely that the chromophore of RB13 gets degraded by Fenton's reagent at pH 7 also. This is supported by the evidence that the RB13 dye molecule is decolorized at all the pH range (2–7), whereas for the other dyes (AO7 and RB5) the decolorization efficiency decreases as the pH increases. It was also observed during the study that at pH lower than pH 3, the degradation efficiency decreases; it may be due to scavenging of hydroxyl radical with H^+ ions as also reported by Neyens and Baeyens [48]. The observed maximum decolorization at pH 3 is in agreement with previous studies [1,29,42,43,49].

3.1.2. Optimization of H_2O_2 dose for decolorization

Many researchers [1,29,42,43,49] have shown that complete color removal is possible at pH 3. During the dose optimization studies the dyes concentration were kept constant at 50 mg L^{-1} and the pH of the dye solutions (pH 3) and Fe^{2+} dose of 20 mg L^{-1} (0.36 mM) were kept constant. The H_2O_2 concentrations were varied in the range from 25 mg L^{-1} (0.73 mM) to 150 mg L^{-1} (4.41 mM). The reactions were conducted for 30 min under controlled conditions. During the optimization studies, it was found that the decolorization increases with increase in H_2O_2 concentration up to a critical concentration of 100 mg L^{-1} (2.94 mM) for all three dyes. Further as H_2O_2 concentrations were increased, a decrease in decolorization of dyes were observed, which may be due to the hydroxyl radical scavenging effect of H_2O_2 according to equation (1)–(3) [1,3]. 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 of organic compounds was decreased as a result of the so-called scavenging effect. The same phenomenon was also observed by Tang and Huang [50] and Ramirez et al. [41]:

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

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

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

It was also found during the studies that the decolorization of dye solution at 50 mg L^{-1} (1.47 mM) and 100 mg L^{-1} (2.94 mM) of H_2O_2 dose does not vary much as shown in Fig. 3. The decolorization at 50 mg L^{-1} (1.47 mM) of H_2O_2 concentration were 98, 97 and 97% for RB13, AO7 and RB5, respectively and at 100 mg L^{-1} (2.94 mM) of H_2O_2 dose, decolorization was >99% for all the dyes. Hence, the optimum concentration of H_2O_2 was considered to be 50 mg L^{-1} (1.47 mM). At this concentration of H_2O_2 the cleavage of the azo bond, other aromatic rings and partial breakup of aromatic amines was achieved (as observed from UV spectrum), which was the aim of the Fenton's treatment during the study. Hence optimization studies for Fe^{2+} ion dose were carried out at this optimum H_2O_2 concentration.

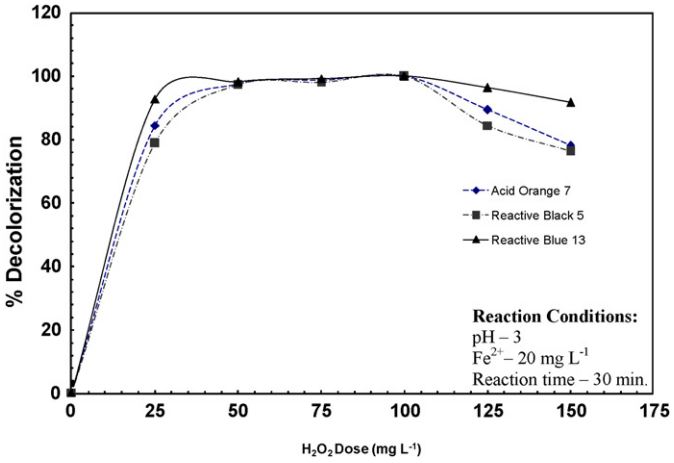

Fig. 3. Effect of concentration of H_2O_2 on the decolorization of different dyes (reaction conditions—pH 3, Fe^{2+} dose: 20 mg L^{-1}, reaction time: 30 min).

3.1.3. Optimizations of Fe^{2+} dose for decolorization

The optimization studies were carried out for the dyes concentration of 50 mg L^{-1} at optimum pH (pH 3) and lower optimum H_2O_2 doses by varying the concentration of Fe^{2+} ions in the range of 5 (0.09 mM) to 50 mg L^{-1} (0.9 mM). The reactions were conducted for 30 min under controlled conditions. The decolorization of dye solution was increased as the concentration of ferrous ion was increased up to a critical ferrous ion concentration and after this critical concentration the decolorization was observed to be decreased. The decrease in the decolorization may be due to the hydroxyl scavenging effect of ferrous ions as also reported by other researchers [41,50]. This decrease in decolorization at higher ferrous ion can be attributed to the reaction (4). The decolorization of dyes at different ferrous concentration is presented in Fig. 4. It was also found during the studies that the decolorization of dyes were maximum at ferrous ion concentration of 35 mg L^{-1} (0.63 mM) and after

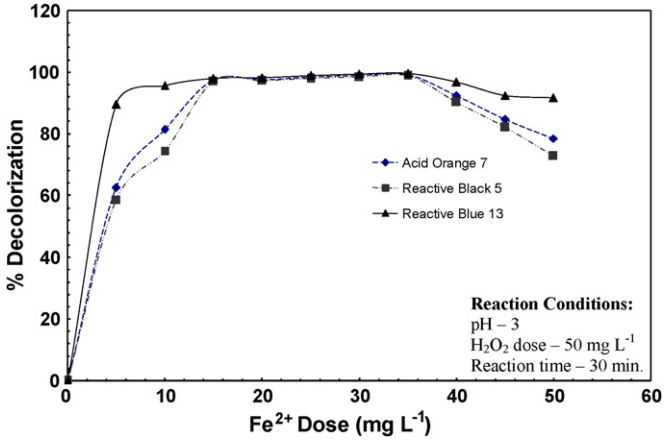

Fig. 4. Effect of concentration of ferrous ion on the decolorization of dyes (reaction conditions—pH 3, H_2O_2 dose: 50 mg L^{-1}, reaction time: 30 min).

this critical concentration, the decolorization decreases for all the studied dyes. But a significant phenomenon was observed at ferrous ion concentrations from 15 mg L^{-1} (0.27 mM) to 35 mg L^{-1} (0.63 mM). The decolorization of the dyes did not vary much between this concentrations range. The decolorization at 15 mg L^{-1} (0.27 mM) was about 97, 98 and 98% and at a concentration of 35 mg L^{-1} (0.63 mM) were more than 99% for AO7, RB5 and RB13, respectively, as could be seen in Fig. 4 also. Hence, the ferrous ion concentration of 15 mg L^{-1} (0.27 mM) was considered to be optimum for the cleavage of azo bonds and breakage of other rings

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

Hence from above optimization studies for decolorization, it was found that 15 mg L^{-1} (0.27 mM) of Fe^{2+} ion and 50 mg L^{-1} (1.47 mM) of H_2O_2 dose at pH 3 is required for >95% of decolorzation of dyes. The dye:H_2O_2:Fe^{2+} mass ratio (w/w/w) of 1:1:0.3 is required for 97, 98 and 97% for RB5, RB13 and AO7, respectively. However, previous studies, shows a higher dye:H_2O_2:Fe^{2+} mass ratio (w/w/w) for decolorization of the same dyes. Meric et al. [43] studied decolorization of RB5 and found that dye:H_2O_2:Fe^{2+} mass (w/w/w) ratio of 1:4:0.36 for 99% decolorization. Similar studies on RB5 shows >99% decolorization at dye:H_2O_2:Fe^{2+} mass ratio (w/w/w) of 1:48.96:1.05 by Tantak and Chaudhari [42]. For the Acid Orange 7 (AO7) dye, Tantak and Chaudhari [42] found a dye:H_2O_2:Fe^{2+} mass ratio (w/w/w) of 1:48.96:1.16 for more than 99% decolorization of dye. As for RB13, Tantak and Chaudhari [42], showed dye:H_2O_2:Fe^{2+} mass ratio (w/w/w) of 1:48.96:1.16. Thus at a lower optimization of doses of ferrous ion and hydrogen peroxide, operating cost (cost of excess chemicals) of the treatment can be saved as well as the problem of sludge generation can also be minimized. So the further studies were carried out at lower optimum doses of reagents.

3.1.4. Residual H_2O_2

Hydrogen peroxide, being a mild oxidant, might affect the subsequent biological process. Thereby residual H_2O_2 concentration was measured. An interesting fact was also noticed during studies that at the lower optimum doses, the H_2O_2 dose is consumed totally in the reaction and no residual H_2O_2 was found after the reaction. The H_2O_2 was almost completely consumed after the 8 min of the reaction for all three dye solutions and hence the Fenton's treated effluent is considered to be safe for the subsequent biological treatment after pH adjustment to 7. However, Tantak and Chaudhari [42] reported the residual H_2O_2 in the Fenton's treated effluent. It was also found during the studies that H_2O_2 dosage was consumed in the early stage of the Fenton reaction. It may be due to the reason that ferrous ion catalyses H_2O_2 to form hydroxyl radical quickly in the first stage of reaction, more decolorization occurs in the early stage of reaction as also observed by Malik and Saha [49] and Ramirez et al., [41]. The consumption pattern of H_2O_2 during Fenton oxidation for all three dyes is shown in Fig. 5. The results shows more than 50% decolorization in first minute and rest of the reaction occurs slowly, it takes 10 min for >90% of decolorization of dyes. The

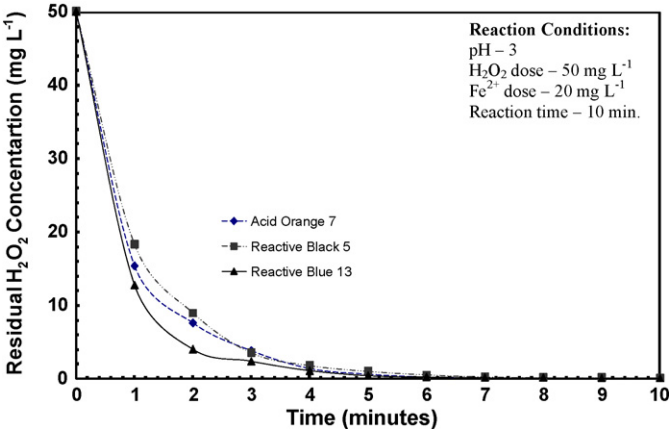

Fig. 5. Consumption pattern of H_2O_2 for different dyes during Fenton's oxidation process (reaction conditions—pH 3, H_2O_2 dose: 50 mg L^{-1}, Fe^{2+} ion dose: 20 mg L^{-1}, reaction time: 10 min).

probable reason for the decrease in reaction rate is that in the 1st stage ferrous ions react with hydrogen peroxide to produce a large amount of hydroxyl radical according to the following reaction:

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^{-} + Fe^{3+} \quad (5)$$

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

$$H_2O_2 + Fe^{3+} \rightarrow H^{+} + FeOOH^{2+} \quad (6)$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (7)$$

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.

3.1.5. Mineralization of dyes

Extent of mineralization of the dyes can be evaluated by measuring total organic carbon or COD (chemical oxygen demand) measurement or reduction in UV–vis spectrum. In this study, chemical oxygen demand measurements and reduction in the UV–vis spectrum were analyzed for evaluating the extent of mineralization of dyes. From the aforementioned sections it is clear that pH 3 is the optimum pH for the Fenton's oxidation process. The degradation of azo dye was evaluated for COD reduction of Fenton's treated sample. To determine the change in the COD, initial COD (pure dye solution) and the COD of a sample after the reaction were measured and COD reduction was determined.

A significant COD reduction of 63, 89 and 68% was achieved at a dye:H_2O_2:Fe^{2+} mass ratio of 1:1:0.3 for 50 mg L^{-1} of RB5, RB13 and AO7 dyes respectively, which indicates the partial mineralization of dyes. Kuo [29] reported approximately 90% chemical oxygen demand (COD) removal in 30 min. Malik and Saha [49] observed about 70% COD removal can be achieved in 60 min. The partial mineralization was monitored using UV–vis spectrum of the dyes. The reduction in the peak at 254 nm, which attributes to aromatic amines, was about 36, 76 and 45% for RB5,

RB13 and AO7, respectively. A significant reduction at naphthalene ring at 310 nm was also observed. The reduction was about 77, 67 and 53% for RB5, RB13 and AO7, respectively. However, in case of benzene ring at 226 nm, a significant increase in the absorbance was observed for RB5 dye and the increment was of 12%, this may be due to the breakage of other rings of RB5 and formation of benzene ring related compounds. However, in case of RB13 and AO7, a significant reduction of about 82 and 65% was observed. This significant reduction at all the aromatic rings shows partial mineralization of dyes.

3.1.6. Sludge generation

The production of sludge containing high amount of Fe (III) needs to be managed by safe disposal methods [38]. This is considered to be a major problem with the Fenton's oxidation process. A further interesting fact was noticed during the Fenton's treatment was that as the reaction was carried out at low ferrous ion dose, the amount of sludge generated during the study was negligible and thus the process at lower doses also solves the problem of safe disposal of sludge thereby adding to economy of treatment.

3.2. Sequential batch reactors

3.2.1. Start up of SBRs

During the startup, all SBRs were fed with tap water along with 400 mg L^{-1} of dextrose as the 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 the development of appropriate enzyme producing agents that are essential to induce biodegradation of toxic dye intermediates [36]. Stabilization of reactor was assessed by measurement of COD reduction. It takes almost 15 days for start up of the reactors, i.e. to achieve steady state COD reduction. After 15 days, almost similar COD removal of >90% was observed in the all four SBRs. The SBRs were operated with same feed for 20 days. The SBRs were now ready to fed with Fenton's treated effluent.

3.2.2. Treatment of Fenton treated effluent in SBRs

The SBRs were fed with Fenton's treated effluents for 60 days. Degradation of dye was checked by COD reduction and mineralization was checked by UV–vis spectrum analysis. The steady state conditions were achieved after 40 days for all dyes. At steady state conditions, COD removal of 82, 89, and 84% were achieved in the Fenton treated RB5, RB13, and AO7 dye effluents respectively, as shown in Fig. 6. However, Fongsatitkul et al. [36] found more than 90% of COD reduction in chemical plus biological treatment sequence for simulated textile wastewater. Furthermore, transformation of absorbance in UV range has been seen in the spectrum of SBR effluent. The reduction of about 43, 61 and 55% of aromatic amines (254 nm), 50, 86 and 53% at naphthalene ring (310 nm) and 55, 38 and 76% at benzene ring (226 nm) was observed for RB5, RB13 andAO7 dyes respectively, which shows a significant mineralization of all the three studied dye.

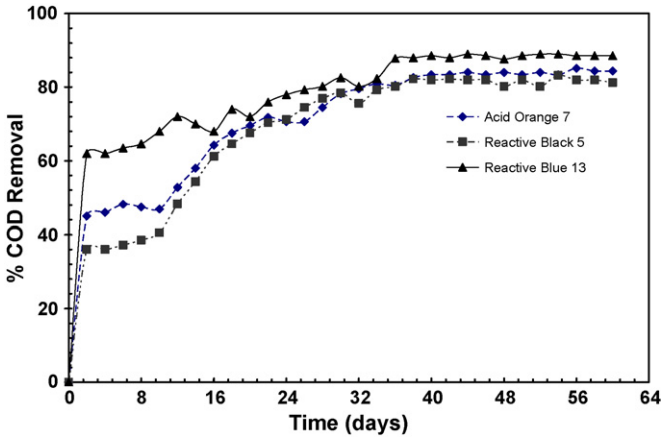

Fig. 6. Reduction in COD of Fenton's treated effluent along with dextrose (400 mg L^{-1}) for different dyes in aerobic SBRs.

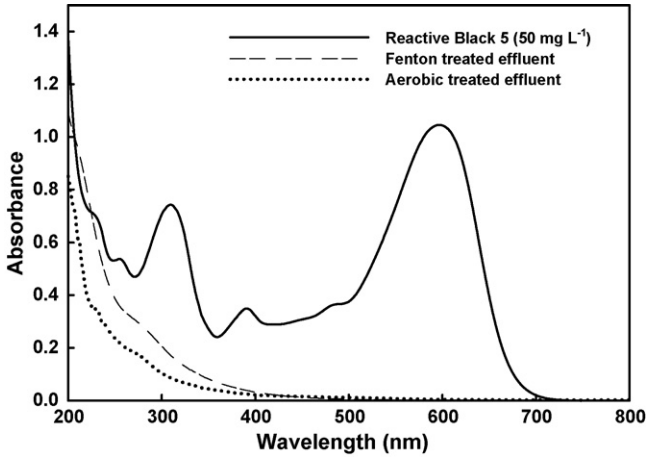

Fig. 7. UV–vis spectrum of RB5 showing original dye (50 mg L^{-1}), Fenton's treated effluent and aerobic treated effluent.

3.3. Overall treatment scheme performance

The overall treatment chain performance can be seen in Figs. 7–9, which show comparative UV–vis spectrum of original

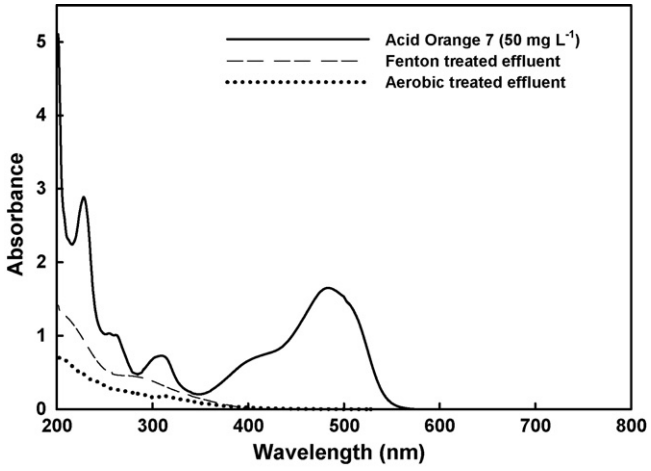

Fig. 8. UV–vis spectrum of AO7 showing original dye (50 mg L^{-1}), Fenton's treated effluent and aerobic treated effluent.

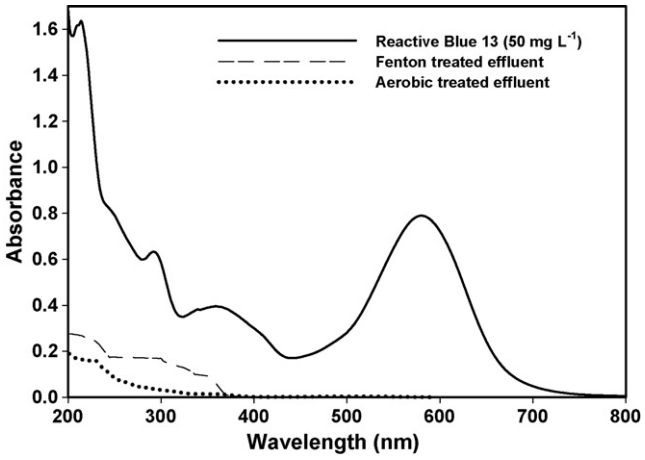

Fig. 9. UV–vis spectrum of RB13 showing original dye (50 mg L^{-1}), Fenton's treated effluent and aerobic treated effluent.

dyes (50 mg L^{-1}), Fenton treated effluents and aerobic treated effluents (50th day) for RB5, AO7 and RB13, respectively. The influent spectrum of RB5, RB13 and AO7 shows the maximum peaks (λ_{max}) at 596, 581 and 483 nm, respectively. These λ_{max} values in the visible region, accounts for color of respective dye. The aromatic amines, naphthalene and benzene ring associated compounds gives absorbance in UV region at 254, 310 and 226 nm, respectively [41]. The decolorization and mineralization of dyes was analyzed by the decrease in absorbance in visible and UV regions respectively.

The UV–vis spectrum of Fenton's treated effluents for all three dyes shows >95% reduction in absorbance at λ_{max} (refer Figs. 7–9), which depicts a significant color removal of the dyes (breakage of –N=N– chromophore). The spectrum of Fenton treated effluents also shows significant reduction in absorbance at 254 nm (aromatic amines) and 310 nm for all three dyes (refer Figs. 7–9), which shows the partial mineralization of all three dyes after Fenton treatment. At 226 nm (benzene ring associated chromophore), the reduction in the absorbance was observed for AO7 and RB13 dyes (refer Figs. 8 and 9). However an increase in the absorbance for the RB5 dye (refer Fig. 7) was observed, which may be due to transformation of aromatic amines and naphthalene ring associated compound to the benzene ring associated compounds. This change in absorbance of the spectrum of Fenton treated effluents in visible and UV regions for all three dyes may be considered as the partial mineralization of the dyes after Fenton treatment.

Furthermore, the degradation of the remaining aromatic amines, naphthalene and benzene ring associated compounds were carried out in the aerobic SBRs. The effluents from the aerobic SBRs shows >99% decrease in absorbance at λ_{max} for all the three dyes (refer Figs. 7–9), which represents almost complete color removal of the dyes. The aerobically treated effluents also show a significant reduction in the absorbance in UV region. The reduction in absorbance was also observed at 254 nm (aromatic amines), 310 nm (naphthalene ring associated compounds) and 226 nm (benzene ring associated compounds) for all the three dyes (refer Figs. 7–9).

The overall treatment chain (Fenton oxidation followed by aerobic biological treatment) showed >99% reduction in color (refer Figs. 7–9). The overall reduction in absorbance in UV region was about 64, 89 and 75% at 254 nm (aromatic amines), 88, 95 and 78% at 310 nm (naphthalene ring associated compounds) and 49, 89 and 91% at 226 nm (benzene ring associated compounds) for RB5, RB13 and AO7 dyes, respectively (refer Figs. 7–9). The reduction in COD (refer Fig. 6) and the absorbance at different aromatic rings (refer Figs. 7–9) show that Fenton's oxidation-aerobic system is capable of significant mineralization of azo dyes.

4. Conclusion

From the study, it was found that the low dose of reagents for Fenton's treatment of azo dyes is quite effective in decolorization and partial degradation of aromatic amines and other aromatic rings. When treatment was done at lower doses, residual H_2O_2, which subsequently affect adversely in biological treatment, was not found in Fenton's treated effluent. As the cost in the chemical treatment is considered mainly due to chemicals thus at lower doses operating cost of the treatment can be saved. It was also found that, as the process is carried out at lower ferrous ion dose, the sludge generation was almost negligible. Thus the sludge handling and disposal cost can also be saved. Later the mineralization of the dye (removal of aromatic amines and other aromatic rings) can be achieved in the aerobic biological treatment system, which is considered to be economical. Thus the overall treatment chain of Fenton's oxidation followed by aerobic treatment seems to be quite effective and economical option for the treatment of recalcitrant compounds like azo dyes.

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