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Effect of pre-treatment on dye degradation in aerobic reactor

Chitra Kalyanaraman*, K. Sri Bala Kameswari, S.V. Srinivasan, K. Thirumaran, J. Raghava Rao

Environmental Technology Division, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020, India,
Tel. +91 44 24916351; Fax: +91 44 24911589; emails: chitrakalyanaraman@yahoo.co.in (C. Kalyanaraman),
sribala_k@yahoo.com (K. Sri Bala Kameswari), srinivasansv@yahoo.com (S.V. Srinivasan), kthirumaran@gmail.com
(K. Thirumaran), jrrao@clri.res.in (J.R. Rao)

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ABSTRACT

Application of ozone and Fenton's reagent was investigated as a pre-treatment to improve the biodegradability of acid blue 113 (AB 113) dye used in the tanneries and subsequent treatment in aerobic reactor. Pre-ozonation of 5 min improved the BOD_5/COD ratio of AB 113 dye from 0.029 to 0.296 due to the partial oxidation of the dye molecules and resulted in the reduction in COD of 22%, with the generation of biodegradable organics. Fenton's oxidation as pre-treatment at the optimum dose of H_2O_2/COD ratio of 1.0 (w/w) and H_2O_2/Fe^{2+} ratio at 9.7 (w/w) resulted in 45% reduction of COD due to mineralization, with subsequent improvement in BOD_5/COD ratio from 0.029 to 0.411. Combined process of ozonation and aerobic treatment resulted in 55% removal of COD and the treated effluent had a BOD_5 and COD of 45 and 355 mg/L, respectively. Combined Fenton and aerobic treatment resulted in 82% removal of COD and 25 and 230 mg/L of BOD_5 and COD was observed in the treated effluent. FT-IR results also supported the finding that the application of ozonation and Fenton's oxidation effectively decolorizes the dye with partial mineralization and resulted in generation of biodegradable organics like acids, aldehydes, and ketones. High removal of the biodegradable organics in the aerobic reactor was observed for Fenton pre-treated AB 113 dye.

Keywords: Azo dye; Biodegradability; BOD5/COD ratio; Fenton's reagent; Ozonation

1. Introduction

Dyeing is one of the important steps in leather making as it is usually the first property of the leather to be assessed by the consumer. Practically, all commercial leather is dyed to improve the appearance and appeal of the finished product and also to make the leather adaptable for fashion styling. Proper dyeing of leather not only enhances its value as a commodity but also contributes to its general quality. The modern synthetic dyestuffs industry was initiated for the textile industry in 1856 and the leather industry started using the synthetic dyes half a century later [1]. Synthetic dyes include several structural varieties of dyes such as acidic, reactive, basic, azo, di-azo, anthraquinone based, and metal complex dyes. Azo dyes account for the majority (more than 3,000 different varieties) of all dyestuffs produced because of the ease and cost effectiveness of their synthesis, their stability, and the variety of colors available compared to natural dyes [2].

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*Corresponding author.

In the tanneries, dyeing process is carried out to produce level colors over the surface of each hide and skin. Typical dyestuffs used by the tanners are water-based acid dyes particularly for chrome tanned leather. Basic and reactive dyes are less commonly used in tanneries. Dyeing is one of the most expensive processes carried out in the tanneries due to the cost of the dyes. Due to this, exhaustion of dyes to the level of above 90% is typically achieved in the tanneries [3]. In the dyeing process, dyes are neither completely utilized nor recovered and as a result the effluent stream usually contains residual dyes. Improper discharge of dye effluent containing azo dyes and their metabolites in aqueous eco-systems is not only aesthetically unpleasant but also leads to acute toxic effects on aquatic flora and fauna, causing severe environmental problems worldwide [4].

For these reasons, dyes have attracted the most attention from conservationists and the general public. Conventional treatment systems cannot achieve decolorization due to the fact that textile dyes are intentionally designed to resist biological, photolytic, and chemical degradation [5]. A number of chemical and physical processes such as chemical precipitation, coagulation, electrocoagulation, elimination by adsorption on activated carbon are applied for color removal from textile effluents. These processes merely transfer the contamination from one phase to another and leave the problem essentially unresolved [6].

Azo dyes as the largest class of synthetic dyes are distinguished by the bonding of one or more azo group (–N=N–) to the aromatic rings. It has to be emphasized that due to their complicated and recalcitrant molecular structure, they are difficult to remove from wastewater using any common physical, chemical, and biological treatment method. The recalcitrant nature of azo dyes has been attributed to the presence of sulfonate groups and azo bonds, and these two features are generally considered as xenobiotic [7]. Therefore, it is essential to look for appropriate methods or techniques for the treatment of azo dye-containing wastewater to reduce their environmental impact.

To deal with wastewater that contains soluble organic compounds that are either toxic or non-biodegradable, application of various oxidation technologies was tried to mineralize or reduce the toxicity of the compounds. During chemical pre-treatment, partial oxidation takes place thereby producing/enhancing the biodegradable reaction intermediates for subsequent biological treatment process [8]. The enhancement of the biodegradability is related to cleavage of the azo bonds and aromatic rings and thus, the conversion of the dye molecules into simple and more degradable intermediates such as acetic acids, aldehydes, ketones, etc. [9].

Among the advanced oxidation processes (AOPs), application of Ozone and Fenton's reagent was investigated as a pre-treatment in this study to improve the biodegradability of the dye-containing wastewater. Ozone is a powerful oxidant for water and wastewater treatment. Ozonation is emerging as a potential process for color removal of dyes, since the chromophore groups with conjugated double bonds, which are responsible for breakdown of color by ozone either by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical forming smaller molecules, thereby decreasing the color of the effluents [10].

Fenton's oxidation is one of the oldest advanced oxidation processes which is used successfully, as it is comparatively cheap and uses easy-to-handle reagents. Fenton's reagent is a mixture of hydrogen peroxide and iron which is effective for color and COD removal with partial degradation of synthetic organic matter [11]. Fenton's reagent treatment eliminates the inhibitory species and increases the biodegradability of the treated water, which is measured as the ratio BOD_5/COD [12]. In this study, acid blue 113 (AB 113) was chosen as a representative model of non-biodegradable azo dye used in the tanneries. Considering the nature of the dye, chemical oxidation almost completely decolorizes the dye, but it also improves the biodegradability with some mineralization. The novel approach of the present study was to develop a sequential AOP followed by aerobic treatment for effective removal of dye in the prevailing conditions maintained in the aerobic treatment unit of tannery effluent treatment plants. AOP studies were carried out without adjusting the pH of the dye-containing wastewater and aerobic treatment studies were carried out in the prevailing conditions maintained in the aerobic treatment unit of tannery effluent treatment plants viz., F/M ratio, residence time.

2. Materials and methods

2.1. Characterization of acid blue 113 (AB 113) dye

AB 113 used for the study has the empirical formula of $C_{32}H_{21}N_5O_6S_2Na_2$ (Mol. Wt. 681.85). It was a commercial grade dye powder manufactured by M/s Clarient Industries located in Chennai, India. Synthetic dye solution was prepared with one gram AB 113 per liter of deionized water and the pH was adjusted to 3.5 using formic acid, which is similar to the practice in the dyeing process followed in the tanneries. Dye solution was characterized for physicochemical parameters pH

(Part 4500-H^+ method B), chemical oxygen demand (COD; Part 5220 method C), biochemical oxygen demand (BOD as BOD_5 at 20˚C; Part5210 method B), total kjeldhal nitrogen (TKN) (Part 4500_{org} method -B), phosphorus (Part 4500-P method E) as per standard methods 20th edition [13]. Samples were analyzed in triplicate and the average values are reported.

2.2. Application of advanced oxidation processes as pre-treatment

In the present study, ozonation and Fenton's reagent using H_2O_2 and Fe^{2+} were applied as pre-treatment to produce biodegradable reaction intermediates during chemical oxidation of AB 113. In the post-tanning process, pH of the final liquor was adjusted to 3.5 ± 0.1, using formic acid to facilitate proper fixing of the added post-tanning chemicals to the leather. At the end of the operation, the exhausted post-tanning wastewater has a pH of 3.5 ± 0.1. Considering this, all the experiments using AOP pre-treatment studies were done at the pH of 3.5±0.1. The biodegradability of wastewater is usually evaluated in terms of the BOD_5 to COD ratio. Hence, at regular intervals of time, the samples were collected, analyzed for color removal, BOD_5, and COD. The dye-containing wastewater refers to the synthetic solution of dye used for the study.

Ozonation experiments were carried out in a bench-scale glass reactor of diameter 60 mm and height 1,800 mm. Ozone was supplied through a ceramic diffuser fitted at the bottom. The laboratory ozone generator Model No. L6G from Faraday Instruments, India was used with pure oxygen as the feed inlet gas to produce 2 g/hr of ozone. Ozone concentration, before and after pre-treatment, was measured as per the procedure (Part 4500-O_3 B) given in standard methods 20th edition [13]. To verify the reproducibility of the experimental data, experiments were conducted and samples were analyzed in triplicate and the average values are reported.

The efficiency of the Fenton oxidation process depends on pH, concentration of H_2O_2, organic matter content, temperatur,e and Fe(II) concentration. For the pre-treatment using Fenton's reagent, known quantity of $FeSO_4$ and H_2O_2 (30%) was used at the pH of 3.5. Analytical grade chemicals needed for the experiments were procured from Merck. All solutions were prepared with deionized water obtained from a Millipore Milli-Q system.

2.3. Spectrophotometer analysis

Acid blue 113 (AB 113) is a water-soluble dye with λ_{max} at 560 nm. The dye decolorization and reduction in aromaticity at UV_{280nm} during pre-ozonation and Fenton's pre-treatment were monitored by following the change in the UV–vis spectra using a UV–vis spectrophotometer (model UV-2450), Shimadzu Corporation, Japan.

2.4. Experiment setup for aerobic biodegradation of dye

Experimental setup for the study, i.e. the preparation of activated sludge, addition of nutrients, elimination of interferences due to the presence of hydrogen peroxide and iron was done as per the procedure used elsewhere [8,14]. The batch reactor was operated with the F/M ratio of 0.15 and residence time of one day in line with the operating conditions maintained in the tannery CETPs and ETPs. All the experiments were conducted in duplicate.

2.5. Fourier transform infrared spectrometry (FT-IR) analysis

FT-IR analysis was carried out in order to assess the functional groups present before and after aerobic treatment. The samples were filtered through 0.45 μm filter, lyophilized and the lyophilized samples were pelletized with potassium bromide (KBr) in the ratio of 1:50. The pellets were subjected to FT-IR analysis using transmission mode. The measurements were carried out in the mid-infrared range from 4,000 to 500 cm^{-1}, with ABB make MB 3000 model FT-IR.

3. Results and discussion

3.1. Characteristics of AB 113 dye

Characteristics of the acid blue (AB 113) dye are presented in Table 1. BOD_5/COD ratio of 0.029 indicated that AB 113 is not easily biodegradable. Generally, a compound is considered not easily biodegradable when its BOD_5/COD value is lower than 0.20. Dyes are designed to be recalcitrant under usage conditions such as exposure to sun light, washing, and microbial attack and these properties subsequently make the treatment process difficult.

3.2. Application of ozonation as pre-treatment

In ozonation processes, the nature of compounds present in water would determine the degree of reactivity with ozone. Compounds with specific functional groups (aromatic rings, unsaturated hydrocarbons) are prone to ozone attack while other compounds (saturated hydrocarbons, alcohols, aldehydes) are resistant to ozone attack [15]. Ozonation, as an effective

Table 1
Characteristics of acid blue (AB 113) dye

Sl.No	Parameter	Average value ± standard deviation
1.	pH	5.8 ± 0.05
2.	Chemical oxygen demand (COD), (mg/L)	680 ± 30
3.	Biochemical oxygen demand (BOD_5), (mg/L)	20 ± 5
4.	Total kjeldhal nitrogen (TKN) as Nitrogen (mg/L)	8 ± 2
5.	Phosphorus as P (mg/L)	2.5 ± 0.2
6.	BOD_5/COD ratio	0.029

oxidation process, has found application in the decolorization of synthetic dyes. It was reported that ozone effectively decomposed azo dyes in textile wastewater. The decomposition rate was considerably higher at acidic pH [16].

UV_{280} measurements can provide useful information, although not compound specific, because lower the aromatic content, lower is the toxicity of the treated wastewater. Change in the aromaticity of the wastewater during ozonation was monitored at 280 nm and decolorization of the dye color during ozonation is presented in Fig. 1. In three minutes contact time, some chromophores were still present and this was indicated in the visible region spectra. During ozonation, the absorbance peaks in the visible region of the dye decreased gradually with time and disappeared at 5 min of ozonation indicating the destruction of chromophore structure in the dye and the solution turned colorless.

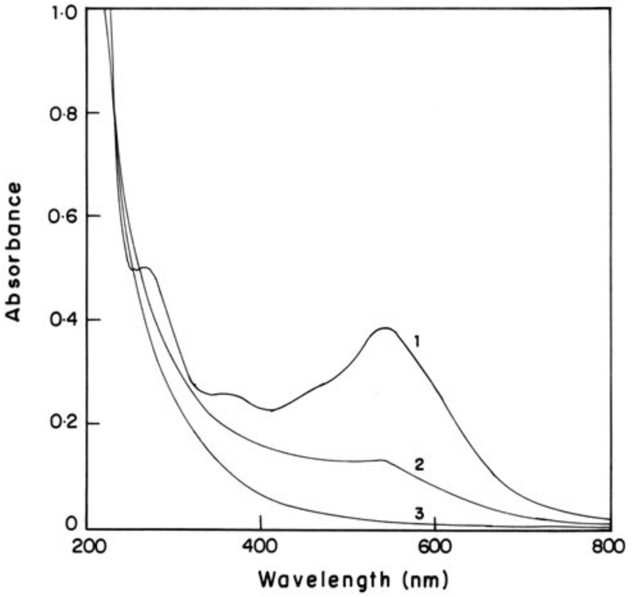

Fig. 1. Change in the color and aromaticity of the AB 113 during ozonation (1: without ozonation; 2: 3 min contact time; and 3: 5 min contact time).

In addition to decolorization, pre-ozonation of 5 min, improved the BOD_5/COD ratio of dye from 0.029 to 0.291 due to the partial oxidation of the dye molecules and the generation of biodegradable organics. During this step, partial mineralization took place and resulted in reduction in COD of 22%. Increasing the contact time beyond 5 min did not substantially increase the BOD_5/COD ratio. The reason was the resistance of the formed intermediate compounds to further ozonation. Thus, considerable amount of COD is attributed to these small organic molecules. Even though high color removal efficiency was observed, limited COD removal efficiency was obtained. This could be explained by incomplete oxidation of organic material and production of small organic molecular fragment along with destruction of dyestuff that not being completely oxidized [17].

At acidic pH, Ozone molecule is selective and attacks preferentially the unsaturated bonds of chromophores. For this reason, color removal by action of ozone is fast, but the mineralization is low. Typically, ozonation rarely originates complete mineralization to carbon dioxide and water, but leads to partial oxidation to organic acids, aldehydes, and ketones. Ozonation process has been suggested as a potential alternative for decolorization with low mineralization and improvement of biological degradation of textile effluents [18]. Hence, ozonation seems to be a suitable option for increasing the biodegradability of such wastewaters. The destruction of aromatic rings and unsaturated sites in organic molecules, and the resultant formation of acidic and alcoholic groups by ozonation may thus suggest an enhancement in biodegradability. It was further inferred that compounds that are already partially oxidized are generally considered to be more easily attacked by micro-organisms [19]. Hence, in the present study, pre-ozonation for 5 min was selected as the optimum contact time for increasing the BOD_5/COD ratio of dye to 0.291 from 0.029 at the pH of 3.5 ± 0.1.

3.3. Application of Fenton's reagent as pre-treatment

Oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective decolorization and degradation of dyes, as well as for the destruction of a large number of hazardous and organic pollutants. Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by catalytic decomposition of H_2O_2 [20]. The mechanism of Fenton's oxidation involves basically the following steps:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \quad (5)$$

The major parameters affecting Fenton process are the solution's pH, amount of ferrous ions, concentration of H_2O_2, initial concentration of the pollutant, and presence of other ions. The optimum pH for Fenton's reagent processes ranges from 2 to 4. At pH higher than 4, the Fe^{2+} ions are unstable and they are easily transformed to Fe^{3+} ions, forming complexes with hydroxyl. Moreover, under alkaline conditions, H_2O_2 loses its oxidative power due to its breakdown into oxygen and water. For the pre-treatment using Fenton's reagent, known quantity of $FeSO_4$ and H_2O_2 (30%) was used at the pH of 3.5 ± 0.1. Addition of $FeSO_4$ typically contains residual H_2SO_4 (about 0.245%). This resulted in drop in pH to about 3.2 ± 0.1 from 3.5 ± 0.1. Addition of H_2O_2 resulted in further pronounced pH drop to 2.8 ± 0.1 due to the produced organic acids from the fragmentation of organic molecules by hydroxyl radicals [21].

Fenton oxidation as pre-treatment increases the biodegradability of wastewater and it requires less than the theoretical stoichiometric amount of H_2O_2. In the present study, optimization of H_2O_2 was carried out for different H_2O_2/COD ratios (w/w), ranging from 0.25 to 1.5. The Fe^{2+} dose was kept at 50 mg/L for all ratios of H_2O_2. A higher dose beyond the required quantity of H_2O_2 resulted in lesser removal efficiency of COD due to the auto-scavenging reactions of ${}^{\bullet}OH$ radicals. Effect of different H_2O_2/COD ratio on the mineralization and change in the biodegradability of AB 113 dye is presented in Fig. 2. The results from the figure indicated that using an amount of H_2O_2 higher than that corresponding to the theoretical stoichiometric H_2O_2 to COD ratio does not lead to any further improvement in mineralization.

The results indicated that H_2O_2/COD ratio (w/w) to 1.0 resulted in increase in BOD_5/COD ratio to 0.33 with COD reduction of 38% due to mineralization. Further increasing the H_2O_2/COD ratio (w/w) resulted in lesser removal of COD and decrease in BOD_5/COD ratio. Hence, optimization of Fe^{2+} dose was done by keeping the H_2O_2/COD ratio (w/w) to 1.0 and varying the concentration of Fe^{2+} from 50 to 100 mg/L. The results indicated that increasing the concentration of Fe^{2+} beyond the optimum concentration of 70 mg/L does not substantially improve the removal efficiency of COD and increase the BOD_5/COD ratio. The results of the optimization of Fe^{2+} are plotted in Fig. 3. Based on the results on pre-treatment using Fenton's reagent, the optimum dose selected was H_2O_2/COD ratio of 1.0 (w/w) and H_2O_2/Fe^{2+} was 9.7 (w/w) basis. Reaction time was optimized to one hour based on the removal efficiency of COD.

COD reduction slowed down after cleavage of chromophores during Fenton pre-treatment, probably

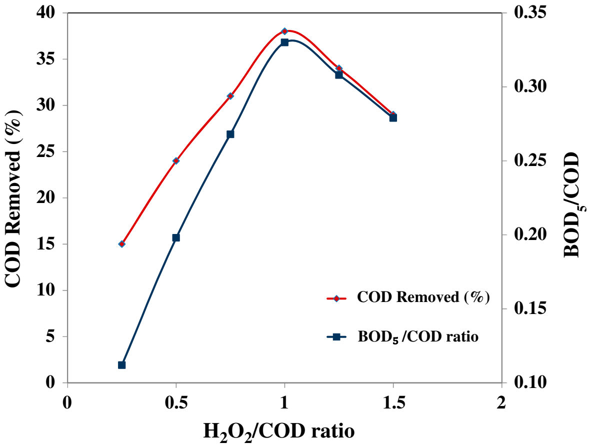

Fig. 2. Effect of different H_2O_2/COD ratio on the mineralization and change in the biodegradability of AB 113 dye.

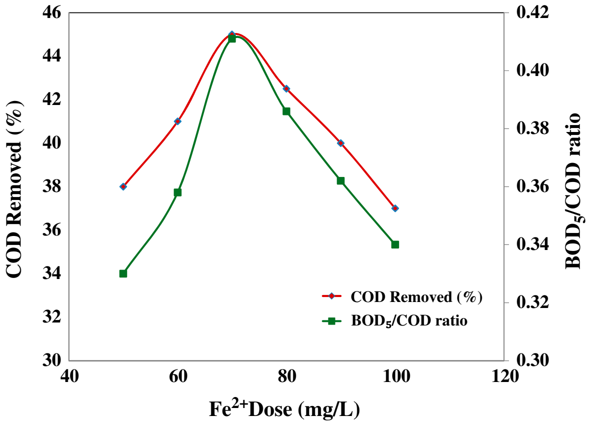

Fig. 3. Optimization of Fe^{2+} dose.

due to the accumulation of advanced oxidation intermediates that are more resistant to further oxidation. In all cases, only partial COD removal was achieved at the end of the reaction due to the fact that after cleavage of the dye chromophores, the reaction slows down such that the highly complex-structured dye molecules are only partially degraded to relatively small organic fragments, such as carboxylic acids, aldehydes, ketones, and alcohols [5]. During Fenton's oxidation, using H_2O_2/COD ratio of 1.0 (w/w) and 50 mg/L of Fe^{2+} showed some of the chromophores were still present and this was indicated by the presence of color in the visible region. The absorbance peaks in the visible region of the dye disappeared at H_2O_2/COD ratio of 1.0 (w/w) and 70 mg/L of Fe^{2+} indicating the destruction of chromophore structure in the dye and resulted in the disappearance of color. Change in the aromaticity of the wastewater during Fenton's oxidation was monitored at 280 nm and decolorization of the dye color is presented in Fig. 4.

The effectiveness of Fenton and ozone oxidation has been compared for the wastewater generated by a textile finishing industry located in Istanbul. The results obtained indicate that Fenton oxidation removes COD to a major extent (59%) higher than ozone (33%), while color removal was about 90% in both the cases [22,23] examined the effectiveness of Fenton oxidation for the reduction of the organic content of the wastewater generated from a textile industry and results showed that the COD decreased by about 45% in Fenton oxidation In the present study, Fenton's reagent pre-treatment at the optimum dose of H_2O_2/COD ratio of 1.0 (w/w) and H_2O_2/ Fe^{2+} at 9.7 (w/w) resulted in 45% reduction of COD due to mineralization, with consequent improvement in BOD/COD ratio from 0.029 to 0.411.

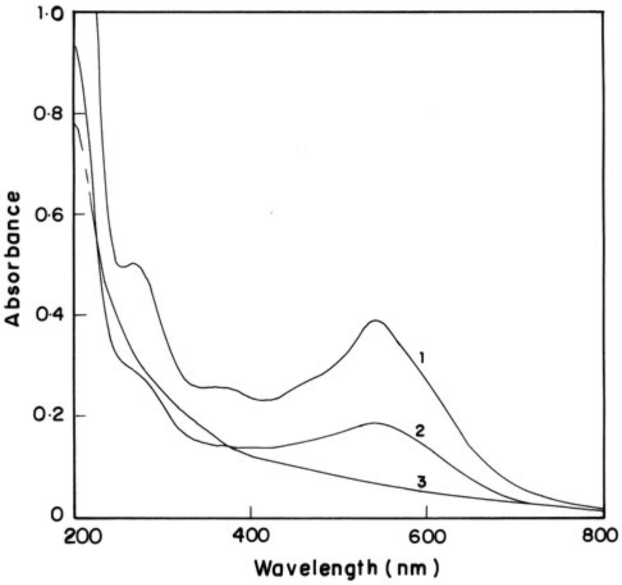

Fig. 4. Change in the aromaticity of the AB 113 during Fenton's reagent pre-treatment (1: without Fenton's oxidation; 2: Fe^{2+} dose of 50 mg/L; and 3; Fe^{2+} dose of 70 mg/L).

3.4. Batch aerobic reactor studies

3.4.1. Aerobic studies of AB 113 dye without AOP pre-treatment

Samples were collected at regular intervals of time and analyzed for BOD, COD and plotted in Fig. 5. The BOD_5 and COD removal efficiencies at 8 h contact time resulted in 16 and 11.47% removal. Further increasing the contact time to18 h resulted in BOD and COD removal of 24 and 22%. The BOD_5 and COD removal efficiencies during one day residence time reached 26.0 and 24%, which corresponds to the values of BOD_5 and COD of 15 and 510 mg/L in the treated wastewater. Further increasing the residence time to 30 h did not substantially improve the BOD_5 and COD removal efficiencies. Initial BOD_5 and COD of effluent were 20 and 680 mg/L indicating the recalcitrant nature of the wastewater and its resistance to biodegradation.

The chemical structure of the azo dyes include sulfonic acid groups that ensure both its solubility in water and its ability to dye wool, silk, nylon (polymide), cotton, cellulose acetate, and other kinds of fibers. However, the sulfonic acid group deactivates the structure with respect to an electrophilic attack and biological degradation that occur in conventional aerobic treatment units. Therefore, the treatment of

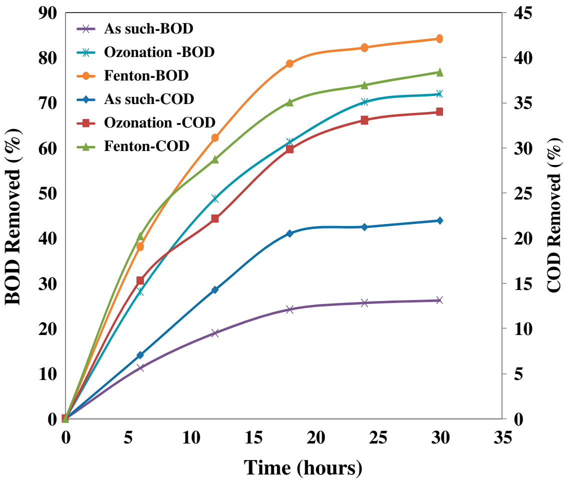

Fig. 5. Aerobic studies for AB 113 without and with AOP pre-treatment.

textile wastewater by conventional methods such as biological treatment is inefficient for color removal and degradation [16,24].

Studies of the partitioning of azo dyes in the activated sludge process have shown that most of the dyes pass through it unchanged, whilst some are adsorbed onto the mixed liquor solids and only a minority is degraded. Thus, conventional aerobic treatment cannot be relied upon for degradation of azo dyes [25]. The wastewater containing water-soluble dyes are generally not decolorized effectively by the aerobic biological treatment. Adsorption to the sludge is the primary removal mechanism for dyes in a biological wastewater treatment system and that factors inhibiting permeation of the dye through the microbial cell membrane reduce the effectiveness of biological degradation [26].

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 and this removal is mostly due to the adsorption on to the biomass rather than biodegradation [10]. The nature of the dye and its BOD_5/COD value of 0.029 indicated its recalcitrant nature. The biological treatment of dye also indicated the same and whatever the removal efficiency observed was only due to adsorption. Hence, this type of wastewater cannot be treated efficiently in a conventional biological treatment system without AOP pre-treatment.

3.4.2. Aerobic studies for ozone pre-treated AB 113 dye

Pre-ozonation increased the BOD_5/COD ratio from 0.029 to 0.296 with reduction in COD of 22% due to mineralization. BOD_5 and COD of ozonated dye were 157 and 530 mg/L indicating an increase in BOD_5 with some mineralization. The enhancement of the biodegradability is related to cleavage of the azo bonds and aromatic rings and thus, the conversion of the dye molecules into simple and more degradable intermediates such as acids, aldehydes, ketones, etc. [9]. During biological treatment, BOD_5 and COD removal efficiency in eight hours increased to 36.4 and 19.8 and it steadily increased and reached a value of 64.3 and 31.1% in 18 h contact time. BOD_5 and COD removal efficiencies in one day residence time in aerobic batch reactor further increased to 70.8 and 33% and resulted in 45 and 355 mg/L of BOD_5 and COD in the final treated wastewater. Further increasing the residence time to 30 h did not substantially improve the biodegradation. The results are given in Fig. 5.

Pre-ozonation improved BOD_5 and COD removal efficiencies in biological reactor from 26 and 24.3% to 70.8 and 33% indicating that produced biodegradable organics are effectively removed in the aerobic reactor with pre-treatment when compared with aerobic treatment of dye without pre-treatment. The partially oxidized organic matter produced after ozonation was presumably more amenable to aerobic biodegradation, thus, accounting for the observed enhancement of aerobic biodegradability. COD removal in the single-stage ozonation–biological treatment was 58% for Reactive Red 120 and it was due to the biodegradable compound produced during ozonation removed by the following biological treatment [27]. The continued presence of some residual organic matter in the effluent after final aerobic biodegradation is presumably of a refractory nature produced during ozonation [19]. The results of aerobic biodegradation studies of pre-ozonated dye indicated that even though ozonation improved the biodegradability, some of the produced intermediates resist further biodegradation and resulted in 55% removal of COD for the combined process. The treated effluent had a $BOD_5$and COD of 45 and 355 mg/L due to the lower removal of produced intermediates in the aerobic reactor.

3.4.3. Aerobic studies for Fenton's reagent pre-treated AB 113 dye

Fenton's reagent pre-treatment improved the BOD_5/COD ratio from 0.029 to 0.411, with COD removal efficiency of 45% due to mineralization. During aerobic treatment, BOD_5 and COD removal efficiencies increased to 46.6 and 21.9% in eight hours contact time and it further increased to 78.6 and 34.2% in 18 h contact time. It steadily increased, reaching BOD_5 and COD removal efficiencies of 83.3 and 37% in one day residence time. The final treated dye effluent had a BOD_5 and COD of 25 and 230 mg/L and was able to meet the discharge standards of BOD_5 and COD stipulated in India in one day residence time. The results are presented in Fig. 5.

The results clearly indicated that Fenton oxidation improves the biodegradability of dye and the intermediates formed are effectively degraded in the aerobic reactor. Fenton oxidation followed by aerobic biological treatment for decolorization and mineralization of azo dyes viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13) showed >99% reduction in color for all dyes with COD removal of 82, 89, and 84%. The results showed that Fenton oxidation was capable of significant mineralization of dyes with improvement in biodegradability, which was effectively removed in the aerobic treatment process [28]. The effect of Fenton's pre-treatment on the degradability and toxicity removal of a simulated acid dye bath effluent was studied in F/M ratio of 0.19 mg COD/mg MLVSS d^{-1} in activated sludge reactor showed that the inhibitory effect of the spent acid dye bath was totally eliminated with Fenton's pre-treatment under optimized reaction conditions [9]. The results of the present study for the dye indicated that sequential Fenton pre-treatment and aerobic treatment in one day residence time resulted in 82% removal of COD.

3.5. Evaluation of FT-IR spectra before and after aerobic treatment of AB 113 dye

The functional groups present in the dye (i) before and after aerobic treatment (ii) ozone pre-treated dye before and after aerobic treatment, and (iii) Fenton's reagent pre-treated dye before and after aerobic treatment are discussed below in detail.

3.5.1. FT-IR analysis of AB 113 dye before and after aerobic treatment

FT-IR spectrum of the dye before and after aerobic treatment is shown in Fig. 6. Spectrum of the dye before aerobic treatment showed the following peaks. The prominent absorption band around 3,455 cm^{-1} can be associated with O–H, N–H, and aromatic =C–H stretching [29]. The peaks in the region 1,600–1,430 cm^{-1} could be due to C=C aromatic ring stretching. Several aromatic C–H out-of-plane bending vibrations in 670–900 cm^{-1} and in-plane bending vibrations in the region 950–1,275 cm^{-1} were observed. N=N stretching due to azo bond was observed in 1,500 and 1,450 cm^{-1}. SO_2 symmetric and asymmetric stretching were observed in the zone of 1,290–1,390 and 1,120–1,190 cm^{-1} [30].

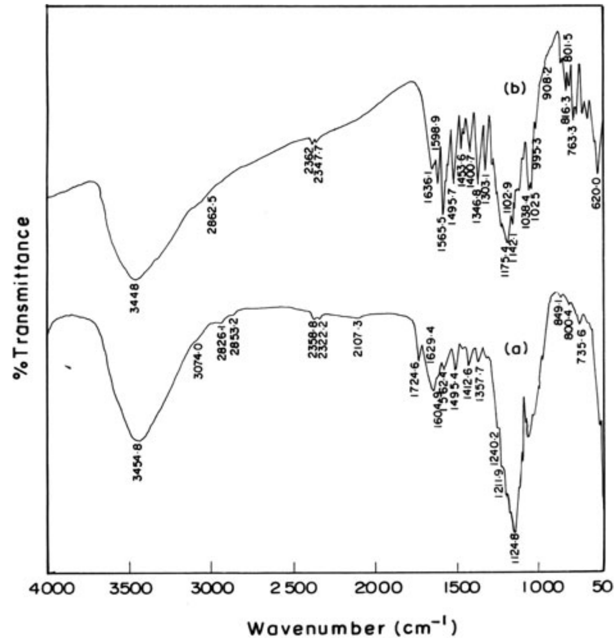

Fig. 6. FT-IR spectrum of the AB 113 before (b) and after (a) aerobic treatment.

FT-IR results after aerobic treatment showed that almost all the compounds present in it are not effectively degraded. The presence of aromatic ring stretching was observed in the fingerprint region. In particular, the peak around 1,495 and 1,450 cm^{-1} due to the azo bond was still present in the treated effluent, indicating that the degradation was not carried out efficiently by the aerobic micro-organisms. These results clearly indicated that pre-treatment by AOP is needed for increasing the biodegradability for effective removal of dye in the aerobic reactor.

3.5.2. FT-IR analysis of ozone pre-treated AB 113 dye before and after aerobic treatment

FT-IR spectrum of the ozone pre-treated dye before and after aerobic treatment is shown in Fig. 7. The prominent absorption band around 3,400 cm^{-1} can be associated with O–H, N–H, and C–H stretching vibrations. Two sets of bands in the region, with one set

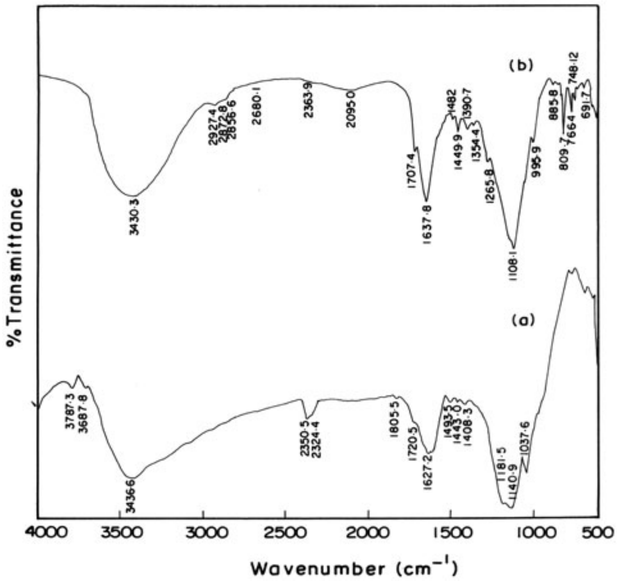

Fig. 7. FT-IR spectrum of the ozone pre-treated AB 113 before (b) and after (a) aerobic treatment.

around 1,600 cm^{-1} and the other around 1,500 cm^{-1}, are consistent with the stretching of aromatic ring. Ozonation resulted in breaking the azo bond and this was supported by the absence of peak and disappearance of color due to the breaking of chromophore. Peak at 1,638 cm^{-1} may be due to the presence of aryl carboxylic acid or quinine [31]. Conjugated aldehydes, ketones, and esters also show peaks in this region [32]. The C=O stretching was observed at 1,707 and 1,354 cm^{-1}. N–H bending of aromatic amines also show peaks in the region of 1,360 to 1,250 cm^{-1}. N–H bending of aliphatic amines is observed in the region of 1,020 to 1,220 cm^{-1} [33]. Peaks observed in the region 2,935–2,915 cm^{-1} and 2,850 cm^{-1} were due to stretching of C–H bond. Peak observed in the region of 2,340 cm^{-1} was characterized by dissolved CO_2 [34]. C–H stretching of alkanes was observed at 2,925 and 2,859 cm^{-1}. During ozonation, part of the organics in the wastewater was mineralized and new intermediate compounds were produced, which were reflected in the peak when compared without AOP pre-treatment. The results indicated that complex dye molecules were attacked by the ozone and new compounds like aromatic carboxylic acid, aldehyde, aromatic and aliphatic amines were generated due to ring opening and mineralization [35].

Aerobic treatment of pre-ozonated dye showed weak absorption in the peaks of 1805 and 1,720 cm^{-1}. The presence of peaks may be due to C=O stretching of carbonyl groups present in acids, saturated aldehydes, and ketones (Mistry 2009). C=O stretching of carboxylic acid was observed at 1,627 cm^{-1}. Peak due to O–H stretching was observed at 3,437 cm^{-1}. Peak at 1,140 cm^{-1} showed the stretching of C–O–H bond [30]. Peak at 1,140 and 1,037 cm^{-1} may be due to S=O stretching. The results indicated that final aerobic-treated solution contains aliphatic carbonyl compounds.

3.5.3. FT-IR analysis of Fenton's reagent pre-treated AB 113 dye before and after aerobic treatment

FT-IR spectrum of the Fenton's reagent pre-treated dye before and after aerobic treatment is shown in Fig. 8. The prominent absorption band around 3,400 cm^{-1} was due to O–H stretching and C–H stretching vibrations. C=C stretching due to ketone, aldehyde, and carboxylic acid was observed at 1,727 cm^{-1}. C=O stretching of carboxylic acid was observed at 1,633 cm^{-1}. Conjugated aldehydes, ketones, esters, and carboxylic acids also show peaks in this region [32]. N–H bending of aliphatic amines was observed in the region of 1,020–1,220 cm^{-1} [33]. N–H stretching of aromatic amines was not observed. Peak observed in the region of 2,340 cm^{-1} was characterized by dissolved CO_2 [34]. The results indicated that new compounds like carboxylic acids, aldehyde, esters, ketones, and aliphatic amines were generated during pre-treatment.

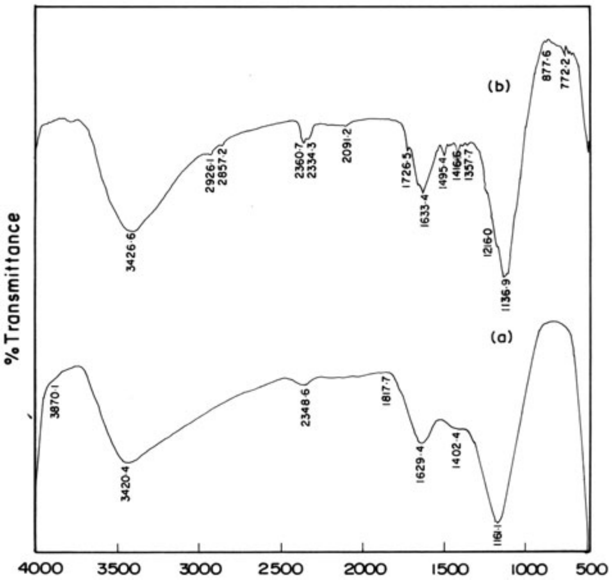

Fig. 8. FT-IR spectrum of the Fenton's reagent pre-treated AB 113 before (b) and after (a) aerobic treatment.

The spectrum of the aerobic-treated dye was simple, indicating the presence of simple organic compound. Aerobic treatment of Fenton's reagent pre-treated dye showed the disappearance of the peaks for the aromatic compounds. C=O stretching of carboxylic acid was observed at 1,629 cm^{-1}. Peak due to O–H stretching was observed at 3,420 cm^{-1}. Peak at 1,161 cm^{-1} showed the stretching of C–O–H bond. Based on FT-IR analysis, it was clear that AOP pre-treatment improved the biodegradability and the biodegradable compounds are removed effectively in the aerobic reactor. This result is also supported by the BOD_5 and COD removal efficiencies in the aerobic treatment.

4. Conclusions

The aerobic systems usually exhibit a relatively low color removal potential for dye-containing wastewater. BOD_5/COD ratio of 0.029 indicated the recalcitrant nature of dye which prevented the degradation in the aerobic reactor. The low BOD_5 and COD removal efficiency observed was only due to the adsorption over the microbes and resulted in carrying color and organics into the effluent. Pre-ozonation improves the biodegradability by increased BOD_5/COD ratio from 0.029 to 0.296 with reduction in COD of 22% due to mineralization. $BOD_5$and COD removal efficiencies in one day residence time in aerobic batch reactor was 70.8 and 33% and resulted in 45 and 355 mg/L of BOD_5 and COD in the final treated wastewater. Even though ozonation improved the biodegradability, some of the produced intermediates resist further biodegradation and resulted in only 55% removal of COD for the combined process. Fenton pre-treatment resulted in increased biodegradability from 0.029 to 0.411 with reduction in COD of 45% due to mineralization. Aerobic treatment of Fenton pre-treated dye resulted in effective degradation of produced organic compounds and resulted in BOD_5 and COD of 25 and 230 mg/L in the treated effluent. The results of the present study for the dye indicated that sequential Fenton pre-treatment and aerobic treatment in one day residence tim**e** resulted in 82% removal of COD in the combined process.

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