

## Color Removal and COD Reduction of Dyeing Bath Wastewater by Fenton Reaction

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### Abstract

Wastewater produced from Al-Amel dyeing bathes was subjected to Fenton oxidation and three commercial disperse dyes were selected for this study. The selected dyes were, Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN, which used for dyeing cellulose fibers. At first, the optimum conditions for removing dyes from their aqueous solutions were determined and found to be 3 g/l H<sub>2</sub>O<sub>2</sub>, 120 mg/l ferrous sulfate hepta hydrate, pH 3 and retention time of about 100 minutes; these conditions achieve color removal of dyes reach 94% from their aqueous solution.

For the treated wastewater, it's found that color removal for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN was 84.66%, 77.19% and 79.63% respectively after retention time 160 minutes. Chemical oxygen demand (COD) measurements indicate that Fenton reaction shows a very good reduction of COD, this was 75.81%, 78.03% and 78.14% for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN respectively. These results strengthen the using of Fenton reaction as a preliminary treatment prior to biological treatment for this wastewater.

**Keywords:** Fenton reaction; Color removal; COD reduction

### Introduction

Al-Amel dyeing unit located at Mansoura city and concerned with dyeing fibers especially cellulose fiber, they use categories of commercial disperse dyes which cover a variety of colors. Wastewater produced from dyeing bathes drained directly to Sewerage network which increase organic pollutants in wastewater. In this study, Fenton's oxidation used for the reduction of COD and colors of the remaining disperse dyes in wastewater.

The problem of colored effluent has been a major challenge and an integral part of textile effluent treatment as a result of stricter environmental regulations. This is not only unsightly but dyes in the effluent may have a serious inhibitory effect on aquatic ecosystems [1-4].

Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Major pollutants in textile wastewaters are high suspended solids, oxygen consuming matter, heat, color, acidity and other soluble substances [5,6].

The effluent from the biological treatment still contains significant amount of colored compounds, microorganisms, recalcitrant organic compounds and suspended solids. Also, chemical oxygen demand (COD) cannot be removed effectively by biological treatment. Hence, advanced treatment is necessary to improve wastewater discharge quality and to reuse wastewater as process water [7].

Fenton process is one of advanced oxidation technologies which used for the degradation of organic compounds to simple products

which is biodegradable. Fenton's reagent is a mixture of H<sub>2</sub>O<sub>2</sub> and ferrous iron, which generates hydroxyl radicals according to the following reaction [6-11]:



In the presence of substrate, such as a target contaminant, the hydroxyl radicals generated are capable of detoxifying the contaminants via oxidation. Due to the formation of Fe<sup>3+</sup> during the reaction, the Fenton's reaction is normally accompanied by the precipitation of Fe(OH)<sub>3</sub> which is a coagulant helpful in removing suspended solids [10,11].

Clarke and Knowles [12] indicated that produced hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule. Carey [13] described a common pathway for the degradation of organics by the hydroxyl radicals as follows [12-15]:



Elham K and Mina F [15] studied the decolorization and degradation of Basic Blue 3 and Disperse Blue 56 dyes using Fenton Process, they found that more than 99% dye removal and 88% COD removal were obtained respectively for initial 10-100 mg/l dye solution in addition to Fenton's reagent at ambient conditions and pH 3.

## Materials and Methods

### Materials

All chemicals used were of the highest purity, sulfuric acid, ammonium hydroxide, hydrogen peroxide (30 % H<sub>2</sub>O<sub>2</sub> w/v), ferrous sulphate hepta hydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O), were produced by El-Nasr Pharmaceutical Company (Egypt), silver sulfate, mercuric sulfate and potassium dichromate were produced by Aldrich Chemical Co.

### Dye solutions and dye house wastewater

Optimum conditions for the removal of dyes was determined for their aqueous solutions of initial dye concentration 100 mg/l, and applied for dye house wastewater. All experiments were carried out at room temperature (25 ± 2°C).

### Color measurement

All color measurements were carried out by colorimetric method using a UV/Visible spectrophotometer [16,17]. The remaining hydrogen peroxide concentration was measured by using the iodometric titration method [18].

### Chemical oxygen demand (COD) measurement

Chemical oxygen demand (COD) was measured by dichromate reflux method [18,19]. The remaining hydrogen peroxide after the process must be rejected or decompose before COD measurements this was achieved by adding Manganese dioxide Powder (MnO<sub>2</sub>) followed by centrifugation and filtration on 0.45 micrometer millipore filter paper to remove excess MnO<sub>2</sub> powder [3,12-14].

### Suspended solids (SS) and surfactants measurement

Suspended solids and surfactants were measured by Pastel UV ESCOMAM (France).

## Results and Discussion

### Optimum conditions for color removal of dyes from their aqueous solutions

Maximum wavelength for dyes were determined and listed in Table 1 and calibration curves for relationship between concentration and absorbance were established.

| Dye (commercial name) | Color  | Wavelength (nm) |
|-----------------------|--------|-----------------|
| Disperse Yellow 23    | Yellow | 380             |
| Disperse red 167      | Red    | 460             |
| Disperse Blue 2BLN    | Blue   | 570             |

Table 1: Color and maximum wavelength for the selected dyes

Fenton oxidation process was carried out at one liter glass beakers and we determine each optimum condition alone and all other additions were constant, i.e. for determining optimum pH we add constant dose from each of ferrous sulphate hepta hydrate and hydrogen peroxide and start the process. The whole mixture was stirred for 1 minute at 200 rpm followed by additional 15 minutes at

25-30 rpm and finally let the mixture for settling. After settling and precipitation, samples were withdrawn from supernatant for performing analysis at different retention time intervals.

**Effect of pH:** Fenton reaction is strongly affected by pH, since pH influences the generation of OH<sup>•</sup> radicals and affect the oxidation efficiency [3,12-15].

Figures 1-3 indicate that the remaining dye concentration was strongly affected by pH; results revealed that the optimum pH value for the maximum removal of the color of the tested dyes was pH 3. At pH values above 6 the degradation strongly decreases because, the ferrous catalyst may deactivate by the formation of ferric hydroxo complexes [11-15,20-23]. Also at higher pH values iron precipitates as hydroxide which reduces the transmission of light and consequently deactivates the Fenton oxidation process [11,20].

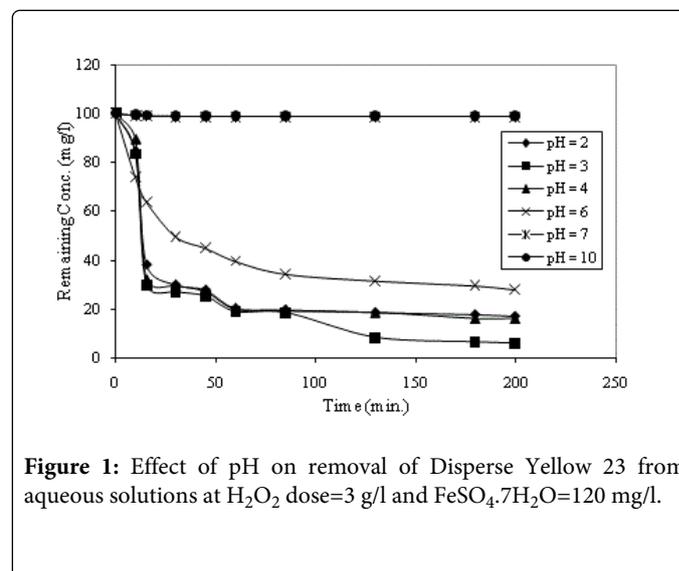


Figure 1: Effect of pH on removal of Disperse Yellow 23 from aqueous solutions at H<sub>2</sub>O<sub>2</sub> dose=3 g/l and FeSO<sub>4</sub>.7H<sub>2</sub>O=120 mg/l.

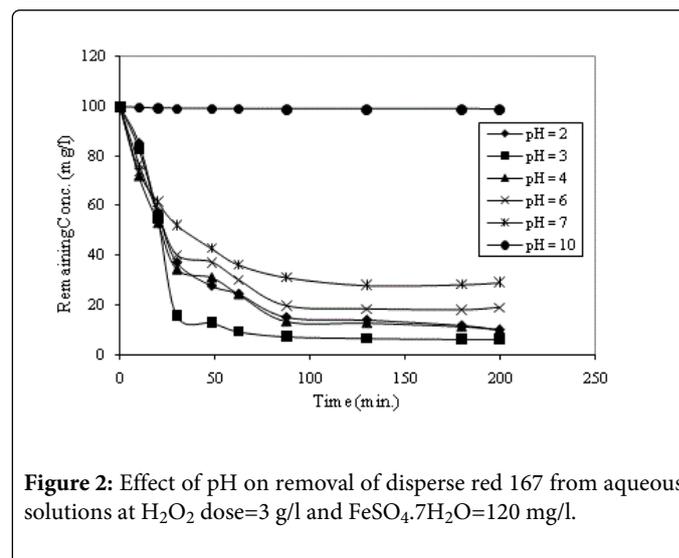


Figure 2: Effect of pH on removal of disperse red 167 from aqueous solutions at H<sub>2</sub>O<sub>2</sub> dose=3 g/l and FeSO<sub>4</sub>.7H<sub>2</sub>O=120 mg/l.

**Effect of hydrogen peroxide dose:** During Fenton's process at the optimum pH, the limiting factor for the process is hydrogen peroxide dose [8,10,14,19]; A significant enhancement of removal was noticed when hydrogen peroxide dose increases.

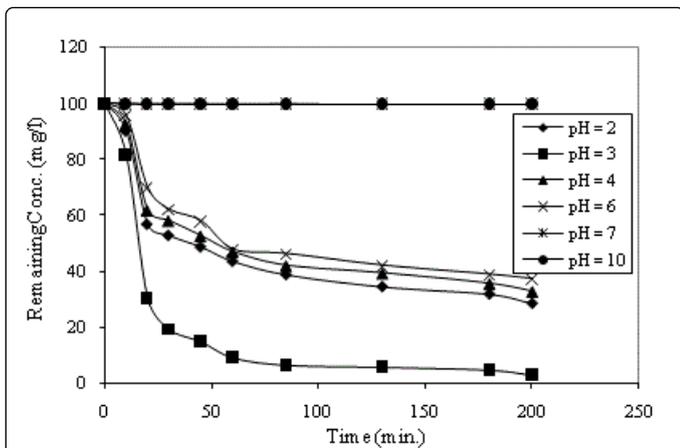


Figure 3: Effect of pH on removal of Disperse Blue 2BLN from aqueous solutions at  $H_2O_2$  dose=3 g/l and  $FeSO_4 \cdot 7H_2O=120$  mg/l.

Results obtained in Figures 4-6 indicated that the color removal of dyes from their aqueous solutions increases by increasing hydrogen peroxide doses. It can be noticed from results that, the percent of removal was about 94% at a dose 3 g/l of  $H_2O_2$  and after retention time 100 minutes. At higher doses than 3 g/l, there was a slight increase of dye removal.

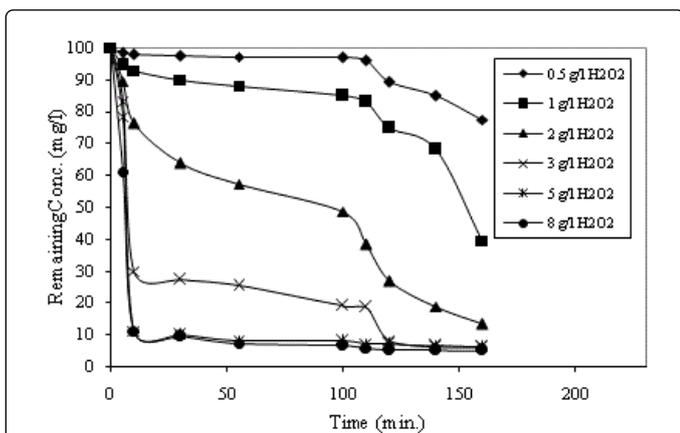


Figure 4: Effect of  $H_2O_2$  dose on removal of Disperse yellow 23 at pH 3 and  $FeSO_4 \cdot 7H_2O=120$  mg/l.

Generally, the removal rate of colour increases as the dose of hydrogen peroxide increases until a critical value; after this critical value, the removal may decrease or not significantly increase [4,20,21]. This is in agreement with the fact that an excess amount of hydrogen peroxide in the solution will slightly retard the destruction and removal of dyes [20-22]. This behavior may be due to auto-decomposition of  $H_2O_2$  to oxygen and water and the recombination of  $HO^*$  radicals [20-22]. Since  $HO^*$  radicals react with  $H_2O_2$  itself and contributes to  $HO^*$  scavenging capacity [6,11,20,22], so that  $H_2O_2$  should be added at an optimal concentration to achieve the best degradation.

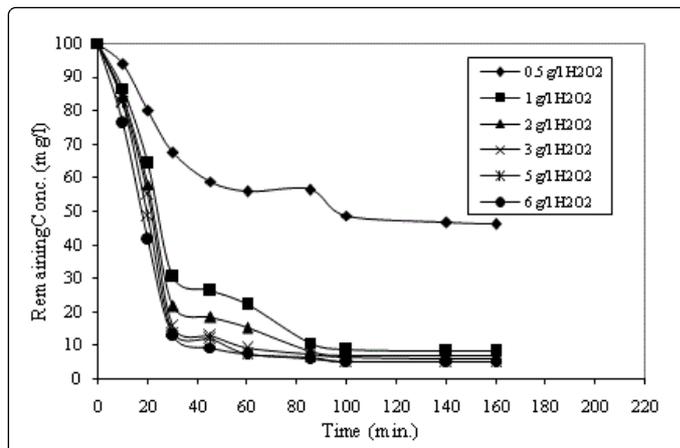


Figure 5: Effect of  $H_2O_2$  dose on removal of disperse red 167 at pH 3 and  $FeSO_4 \cdot 7H_2O=120$  mg/l.

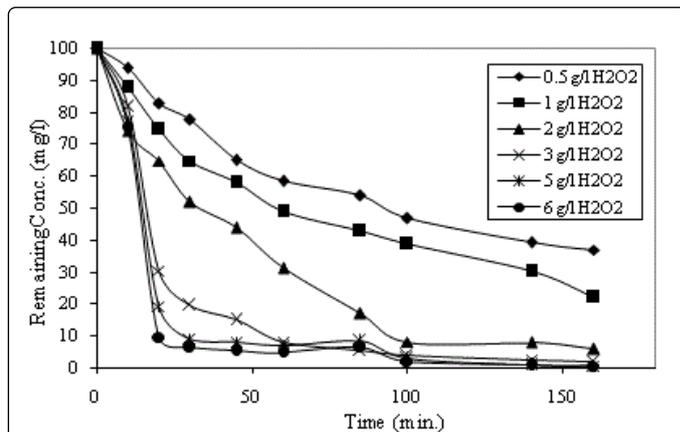


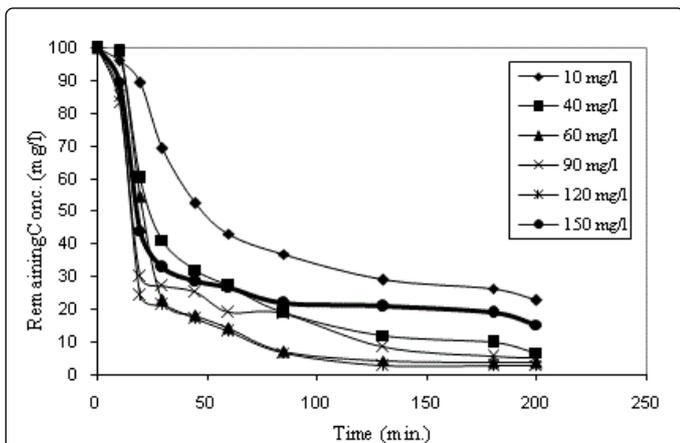
Figure 6: Effect of  $H_2O_2$  dose on removal of dye Blue 2 BLN at pH 3 and  $FeSO_4 \cdot 7H_2O=120$  mg/l.

The amount of  $H_2O_2$  used can be minimized to 1 g/l if the process carried out for longer time, 180 minutes with a considerable color removal; this will be of great interest for economic reasons.

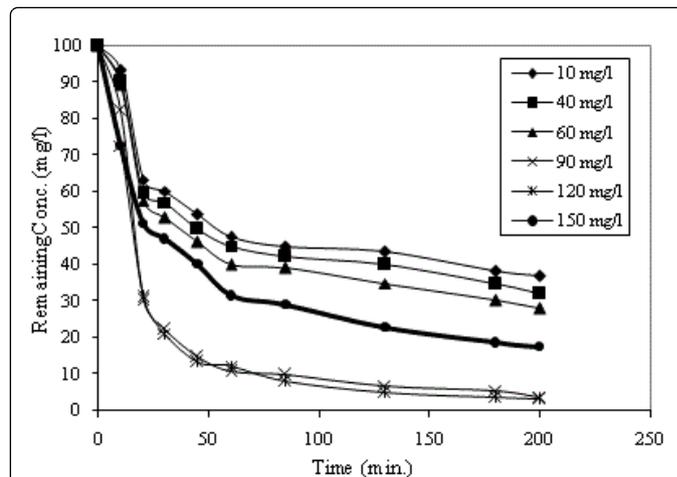
**Effect of ferrous sulfate hepta hydrate dose:** To obtain the optimal Fe (II) amounts, the processes were carried out with various amounts of iron salt under these conditions, pH=3, initial dye concentration 100 mg/l, and at hydrogen peroxide dose of 3 g/l.

Iron in its ferrous and ferric forms acts as a photocatalyst and requires a working pH below 4 to start the catalytic decomposition and enhance the removal of the tested dyes [20-24].

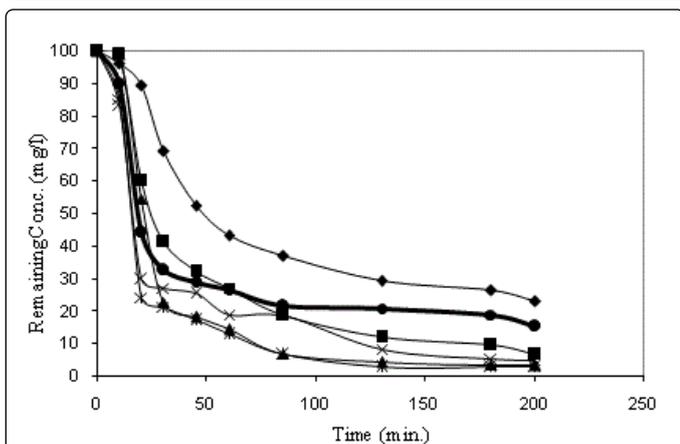
Results shown in Figures 7-9 indicate that the removal of the tested dyes in their aqueous solutions increases by increasing ferrous sulphate hepta hydrate dose to a certain limit at which the effect of ferrous salt is not significantly effective; this occur at doses higher than 120 mg/l.



**Figure 7:** Effect of ferrous sulphate hepta hydrate doses on removal of Disperse Yellow 23 at pH=3 and H<sub>2</sub>O<sub>2</sub>=3 g/L.



**Figure 9:** Effect of ferrous sulphate hepta hydrate doses on removal of Disperse Blue 2BLN at pH=3 and H<sub>2</sub>O<sub>2</sub>=3 g/L.



**Figure 8:** Effect of ferrous sulphate hepta hydrate doses on removal of Disperse Red 167 at pH=3 and H<sub>2</sub>O<sub>2</sub>=3 g/L.

| Parameter                         | Disperse Yellow 23 |               | Disperse Red 167 |               | Disperse Blue 2BLN |               |
|-----------------------------------|--------------------|---------------|------------------|---------------|--------------------|---------------|
|                                   | Raw waste          | Treated waste | Raw waste        | Treated waste | Raw waste          | Treated waste |
| pH                                | 8.98               | 2.91          | 9.16             | 2.88          | 8.78               | 2.95          |
| Remaining Dye concentration (ppm) | 153.21             | 23.5          | 170.38           | 38.96         | 163.67             | 33.96         |
| Total suspended solids (TSS, ppm) | 800                | 46            | 948              | 52            | 1160               | 43            |
| Chemical Oxygen Demand (COD, ppm) | 2452.3             | 593.22        | 2274.62          | 499.73        | 2388.7             | 522.1         |
| Surfactants (ppm)                 | 62                 | 36            | 158              | 18            | 84                 | 12            |

**Table 2:** Characteristics of wastewater and treated waste from dyeing bathes.

It can be seen that the percent of removal was about 94% at 120 mg/l ferrous sulphate hepta hydrate after reaction time about 100 minutes. In case of higher doses of ferrous sulphate hepta hydrate the efficiency of color removal decreases. This may be due to the increase of brown turbidity of Fe<sup>3+</sup> ions that hinders the absorption of light required for the Fenton process [11,20-24], so that ferrous sulphate hepta hydrate must be added in a critical dose, as well as it is necessary to use the smallest amount of iron in order to avoid the problems associated with its elimination.

### Treatment of wastewater of dyeing bath by Fenton

Some characteristics of raw wastewater discharged from dyeing bathes and treated wastewater were shown in Table 2. These results show a high concentration of dyes, high COD and high suspended solids in raw wastewater.

Wastewater was subjected to Fenton's reagent at the determined optimum conditions. Results shown in Figure 10, indicate that removal percent for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN were 84.67%, 77.19% and 79.63% respectively after a retention time of 160 minutes. This reveals the destruction of dye molecules and chromophore groups by free radical reactions produced from Fenton's [6-10,13].

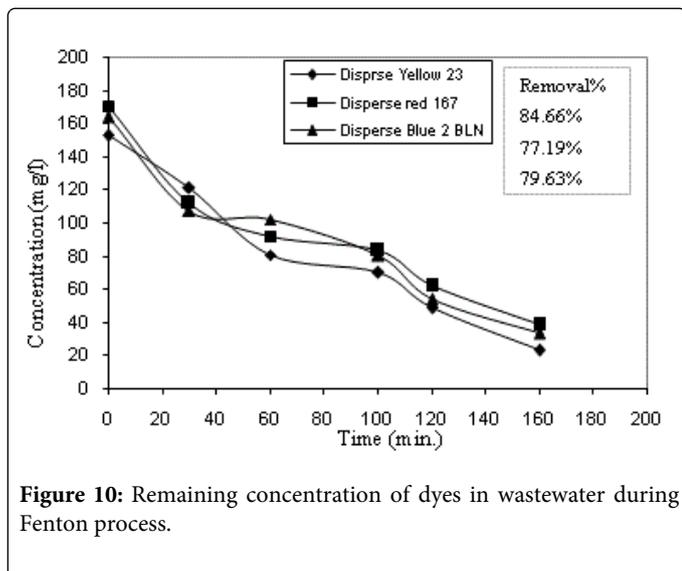


Figure 10: Remaining concentration of dyes in wastewater during Fenton process.

Removal percent in case of treated wastewater was lower than that in case of aqueous solutions at the same optimum conditions except retention time; this may be due to in case of real wastewater some chemicals e.g. sodium chloride and surfactants were added during the dyeing process which inhibit the Fenton reaction or lower the formation of free radicals which oxidize the dye molecules and require a higher retention time. Similar results were reported by Stanisław and Lucyna [24]; they reported that inhibition effect of NaCl presence in textile wastewater on discoloration has been found: the higher content of NaCl the poorer is discoloration degree. The emulsification effect of surfactants present in textile wastewater causes a decrease of discoloration rate [24].

### Evaluation of COD removal from wastewater of dyes

Fenton reaction has the advantage of both oxidation and coagulation processes due to the formation of  $Fe^{+++}$  ions. During the process, organic substances are oxidized by Fenton's reaction [6-12,24-31]; this leads to the degradation of dye molecules and reduce COD content.

COD measurements for treated waste water by Fenton reaction were shown in Figure 11, results indicate that COD reduction for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN were 75.81%, 78.03% and 78.14% respectively. These results in agreement with the degradation of these dyes by Fenton oxidation process.

Fenton oxidation occur at acidic pH close to 3, this must be followed by raising pH again to neutral conditions to help in coagulation and precipitation of ferric ions ( $Fe^{+++}$ ); this can be achieved by using calcium hydroxide.

After Fenton process suspended solids greatly reduced, this due to the coagulant effect of Ferric iron ( $Fe^{+++}$ ) which is a good coagulant helpful in removing suspended solids after precipitation. This will adapt wastewater to biological oxidation; also the remaining hydrogen peroxide when decompose increasing dissolved oxygen [6,9,23-31].

We can theoretically suggest a pathway for using Fenton's process as a preliminary treatment to biological oxidation as shown in the following; this can be investigated experimentally in a future studies.

Flow diagram for biological treatment of dye house wastewater is shown in Figure 12.

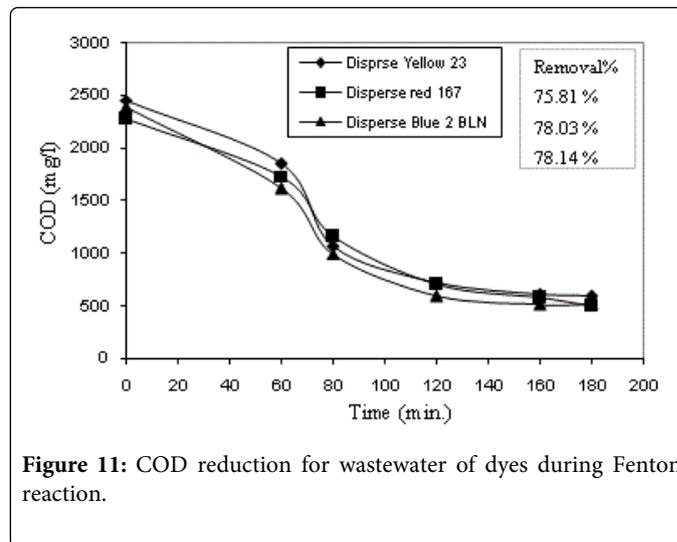


Figure 11: COD reduction for wastewater of dyes during Fenton reaction.

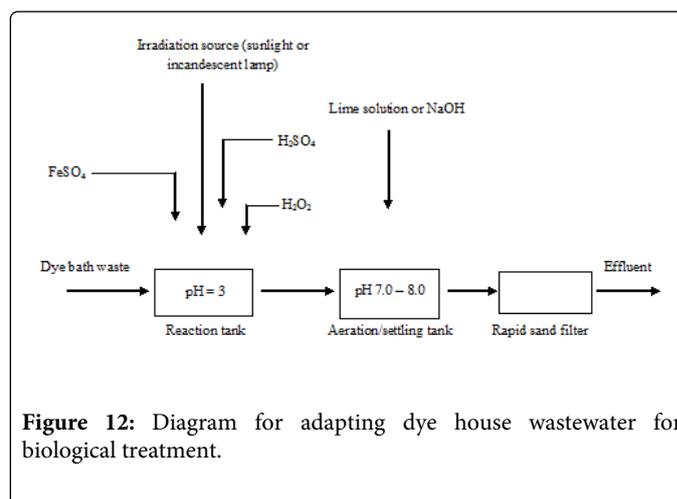


Figure 12: Diagram for adapting dye house wastewater for biological treatment.

### Conclusions

The optimum conditions for removing dyes from their aqueous solutions were determined and found to be 3 g/l  $H_2O_2$ , 120 mg/l ferrous sulfate hepta hydrate, pH 3 and retention time of about 100 minutes; these conditions achieve color removal of dyes reach 94% from their aqueous solution.

The color removal for the treated wastewater for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN were 84.66%, 77.19% and 79.63% respectively. This reinforces the ability of using Fenton reaction for removing colors of these dyes from their wastewater.

Reduction percent in COD for dyes from their wastewater were 75.81%, 78.03% and 78.14% for Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN respectively. It's necessary to inhibit the effect of remaining  $H_2O_2$  by adding manganese oxide and filtration before measuring COD.

Fenton reaction not only leads to color removal of the dyes from wastewater but also leads to a significant COD reduction; this adapts the treated wastewater prior to biological treatment.

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