

# Removal of some commercial dyes from their aqueous solutions and wastewater by using Fenton's reaction

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In this paper, advanced chemical Oxidation Technology (AOT), "Fenton's oxidation process" was applied for removal of four commercial dyes from their aqueous solutions and wastewater in batch experiments. Disperse blue 79, disperse red 167, disperse orange 25 and disperse violet 63 dyestuffs were used in this work. The different parameters that govern this process (concentration of hydrogen peroxide and ferrous sulfate, retention time and pH) were investigated and discussed to find the optimum conditions for complete and fast removal of dyes as a preliminary step prior to biological treatment. It was found that, removal of dyes was highly affected by pH (optimum pH was 3). Results revealed that dyes removal highly increases with the increase of both hydrogen peroxide and ferrous sulfate concentrations to certain critical value. It was found that the maximum removal of dyes from their aqueous solutions reached over 95 % after a retention time ranging from 60-80 minutes. Results indicate that the removal of COD was in the range 64-83 %.

في هذا البحث تم إستخدام إحدى الطرق المتقدمة للأكسدة لإزالة أربعة من الأصباغ التجاريه المستخدمه في صباغه المنسوجات القطنية والألياف الصناعية من محاليلها المائيه وكذلك من مياه الصرف الصناعي بإستخدام تفاعل فنتون في تجارب معملية. يعتمد تفاعل فنتون على وجود فوق أكسيد الهيدروجين مع كبريتات الحديدوز في وسط حمضي حيث ينتج شق الهيدروكسيد الحر الذي له القدره على تكسير وأكسدة المركبات العضويه وإزالة ألوانها من محاليلها المائيه ومن مياه الصرف الصناعي. ولقد اظهرت النتائج أن أفضل الظروف لإزالة هذه الأصباغ تكون عند رقم الأس الهيدروجيني 3 ، تركيز فوق أكسيد الهيدروجين 1 جم/لتر ، تركيز كبريتات الحديدوز 90 ملجم/لتر ، ويلزم زمن مكث قدره يتراوح بين 60 إلى 80 دقيقه لحدوث افضل إزاله للصبغات (أكثر من 95 %). كذلك تم قياس الأوكسجين الكيمايى المستهلك قبل وبعد عمليه الأكسدة كمؤشر للمحتوى العضوى، وأثبتت النتائج أنه تم إزالة حوالى من 64 % إلى 83 % من كميته الأوكسجين الكيمايى المستهلك.

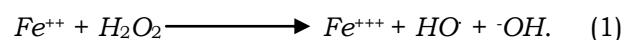
**Keywords:** Fenton reaction, Removal of dyes, Wastewater treatment and chemical oxygen demand reduction

## 1. Introduction

Pollution has not only deteriorated purity of water resources, but also has caused great economic loss and harm to human health. 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. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in textile wastewaters are high suspended solids, oxygen-consuming matter, heat, colour, acidity, and other soluble substances [1]. The color removal from textile industry and

dyestuff manufacturing industry wastewater represents a major environmental concern.

Fenton's reagent is a mixture of  $H_2O_2$  and ferrous iron, which generates hydroxyl radicals according to the following reaction [2- 4]:



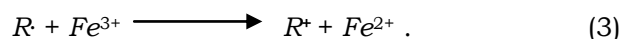
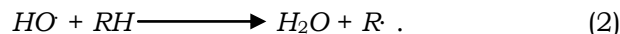
In the presence of substrate, such as a target contaminant, the hydroxyl radicals generated are capable of detoxifying the contaminants via oxidation. Various competing reactions, which involve  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $H_2O_2$ ,  $HO$  radicals, super-oxide radicals, and derived from the substrate, are also possible during Fenton's reagent treatment [5]. Due to the formation of  $Fe^{+++}$  during the reaction, the Fenton's reaction is normally accompanied by the precipitation of  $Fe(OH)_3$  [6].

Walter et al. [7] studied the photocatalytic oxidation kinetics and mechanism of Acid Blue 40 by Fenton's reagent. They found that the process is dependent on pH values. At pH 3, it follows the Langmuir-Hinshelwood model, while at higher pH values; no adequate kinetics model can be used.

Hung-Yee et al. [8] studied the photooxidation of two non-biodegradable azo dyes namely, Acid Red 1 and Acid Yellow 23. They found that the degradation rates of azo dyes in the presence of hydrogen peroxide with UV radiation and the decomposition rates of azo dyes in a UV/ $H_2O_2$  photo-oxidation reactor were much higher than these reactions obtained from using either hydrogen peroxide or UV radiation alone.

Decolorization of textile wastewater by photo-Fenton oxidation technology was studied by Shyh-Fang et al. [9]. The treated wastewater was simulated by using colorless polyvinyl alcohol (PVA) and reactive dyestuff of R94H. As a result, the hydroxyl radical ( $HO$ ) oxidation could effectively remove color, but the Chemical Oxygen Demand (COD) was removed in a slight degree. The color removal is markedly related with the amount of  $HO$  formed. The optimum pH for both the  $HO$  formation and color removal occurs at pH 3-5. Up to 96% of color can be removed within 30 min., under the studied conditions. Due to the photoreduction of ferric ion into ferrous ion, color resurgence was observed after 30 min.

Kuo [10] studied decolorizing dye wastewater with Fenton's reagent. Five types of simulated dye wastewater, separately prepared with disperse, reactive, direct, acid and basic dyes were decolorized with a hydrogen peroxide-ferrous ion system. The results are that the best pH value for decolorization is below 3.5, the average percent removal of COD is about 90%, and decolorization is above 97%. All the results of treating the dye wastewater of actual dyeing and finishing mills are similar to those in the laboratory. Kuo [10] also reported that the hydroxyl radicals generated from Fenton's reaction would attack the organic substrate RH like the unsaturated dye molecule. So, the chromophore or chromogen of the dye molecule would be destroyed and decolorized according to the following equations:



Besides, the most likely side reactions in the redox system are eqs. (5 and 6) as follows:



The dimerization as eq. (6) of such organic molecules as dyes, will be of advantage to decolorization.

Jesus et al. [11] studied the advanced oxidation of cork-processing wastewater using Fenton's reagent, they concluded that, COD removal ranged from 17 to 79% depending on the reagent dose and the stoichiometric reaction co-efficient.

Juan et al. [12] used a solar photocatalytic degradation of the azo dye Acid Orange 24 by means of a photo-Fenton's reaction promoted by solar energy. The dye degradation was monitored during the experimental runs through UV/Visible absorption as well as COD and TOC concentration determination and toxicity reduction. In most cases, discoloration higher than 85% was reached. In the case of the best reaction conditions, a discoloration of up to 95% and a 85% toxicity reduction occurred. In the same experiment, the removal of COD up to 88% and TOC up to 85% was reached.

Francesc et al. [13] studied the degradation of different commercial reactive dyes: a monoreactive dye (Procion Red H-E7B), a hetero-bireactive dye (Red Cibacron FN-R) and a Standard Trichromatic System, by using solar light assisted Fenton and photo-Fenton's reaction. The reaction efficiencies had been compared with the ones obtained for the same system in the dark or under the assistance of an artificial light source. The use of solar light is clearly beneficial for the removal of color, aromatic compounds, Total Organic Carbon (TOC), and the increase of the  $BOD_5/COD$  ratio.

Kositzi et al. [14] studied the photocatalytic organic content reduction of two selected

synthetic wastewater from the textile dyeing industry, by the use of heterogeneous and homogeneous photocatalytic methods under solar irradiation, at a pilot plant scale at the Plata forma Solar de Almeria. They found that photocatalytic decolorization as well as the DOC reduction in the case of nylon simulated wastewater is a slower process and leads to almost 54% mineralisation in both cases. The photo-Fenton's process in both types of wastewater was more efficient in comparison to the  $TiO_2$ /oxidant system.

In this work, Fenton's oxidation process was applied in order to obtain the effects of some operational parameters such as pH, retention time, dose of hydrogen peroxide and ferrous sulfate on the efficiency of color and COD removal of four commercial dyes. In the experiments, disperse blue 79, disperse red 167, disperse orange 25 and disperse violet 63 dye solutions and also wastewater discharged from Al-Amel dyeing unit, which is located at Sandoub near El-Mansura, Egypt were used.

## 2. Materials and methods

All chemicals used were of high purity, sulfuric acid, ammonium hydroxide, hydrogen peroxide (30%  $H_2O_2$  w/v), ferrous sulfate, were produced by El-Nasr Pharmaceutical Company (Egypt), silver sulfate, mercuric sulfate and potassium dichromate were produced by Aldrich Chemical Co. The concentration of hydrogen peroxide was checked by using the iodometric method [15]. All reactions were performed in a batch model using mechanical jar test fig. 1. Sulfuric acid and ammonium hydroxide were used for adjustment pH during the process. All experiments were conducted at room temperature ( $25 \pm 2$  °C). The processes were carried out in 1000-ml glass beakers with a 12-cm diameter. In these beakers ferrous sulfate and hydrogen peroxide in different proportions were added to the aqueous solution of each dye (initial concentration =100 mg/l). The whole mixture was stirred firstly, for 1 minute at 200 r.p.m, and then stirring was continued for additional 15 minutes at 25-30 r.p.m., after that the remaining dye concentration was determined spectrophotometrically [16],

at different time intervals up to 200 minutes (till the remaining concentration was reached to minimum constant value).

Some physical parameters of the commercial dyestuffs, which obtained from Al-Amel dyeing unit for dyeing fabrics and textiles at Sandoub near El- Mansoura, Egypt, are shown in table 1. Maximum wavelengths of dyes were determined spectrophotometrically. COD was measured according to Standard Methods [17].

## 3. Results and discussion

To achieve the best color removal of these dyes by Fenton's reagent the optimum conditions must firstly, be determined. These optimum conditions are the conditions at which the process achieves the best color removal for dyes from their solutions and consequently from wastewater.

### 3.1. Determination of optimum conditions for color removal of dyes from aqueous solutions

The most effective conditions were; pH value, hydrogen peroxide dose, ferrous sulfate dose, and retention time. Removal of these dyes from their aqueous solutions and from their wastewater was studied and discussed in the following:

#### 3.1.1. Effect of pH

Fenton's reaction is strongly affected by the pH value since it influences the generation of  $OH\cdot$  radicals and thus the oxidation efficiency [18, 19].

Figs. 2-5 show that the remaining concentration was highly affected by the pH value. The results revealed that the optimum pH value for the maximum removal of the color of the tested dyes was 3. Therefore, all the studied systems were firstly adjusted at pH 3. At pH values above 6 the degradation strongly decreases because, the ferrous catalyst is deactivated by the formation of ferric hydroxo complexes [20-22]. Also at higher pH values iron precipitates as hydroxide which reduces the transmission of



Fig. 1. Experimental set-up.

Table 1  
Color and maximum wavelength for the tested dyestuffs

Dye color index	Color	Wavelength (nm)
disperse blue 79	Blue	613
disperse red 167	Red	460
disperse orange 25	Orange	427
disperse violet 63	Violet	484

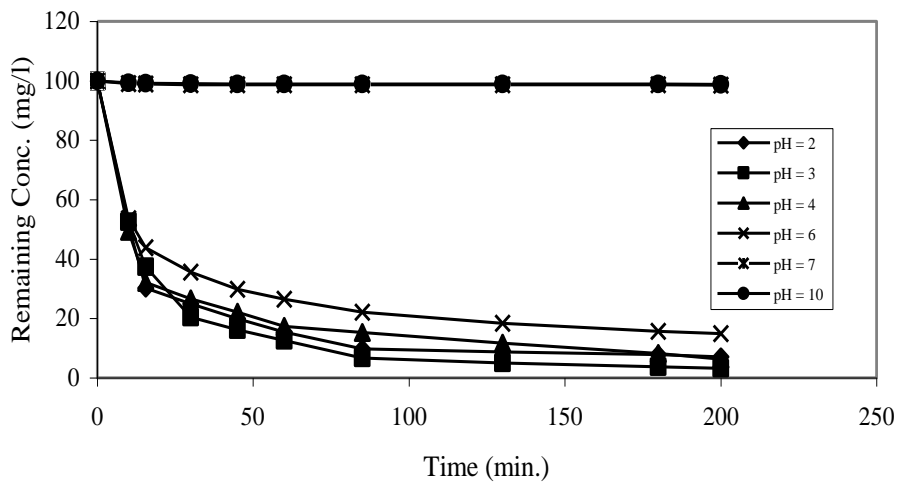


Fig. 2. Effect of pH on color removal of disperse blue 79 from aqueous solutions.

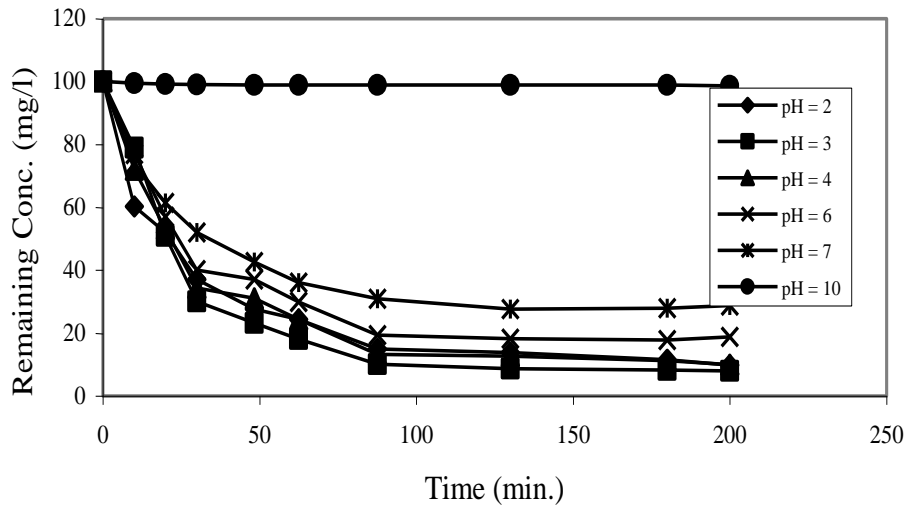


Fig. 3. Effect of pH on color removal of disperse red 167 from aqueous solutions.

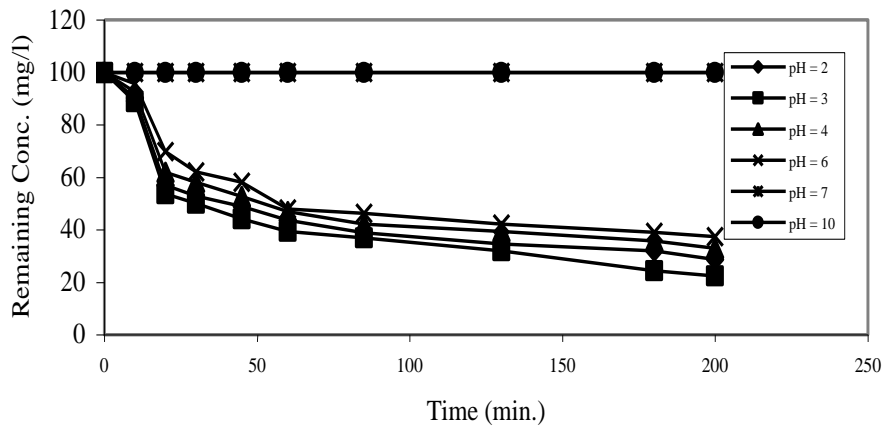


Fig. 4. Effect of pH on color removal of disperse orange 25 from aqueous solutions.

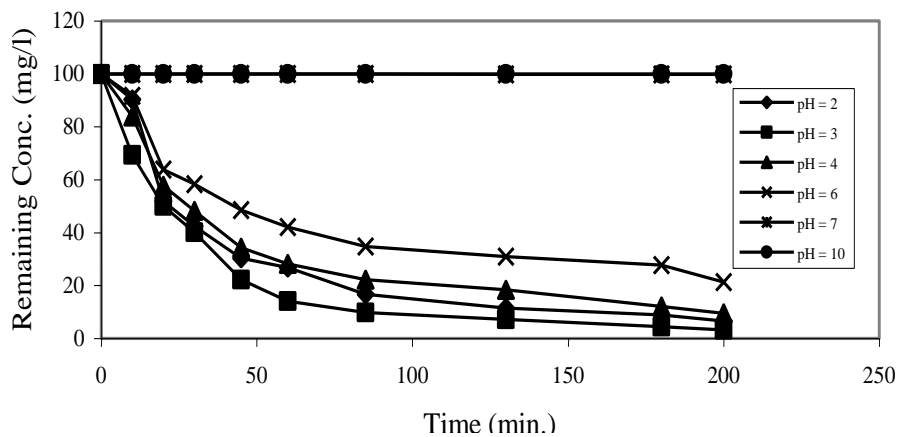


Fig. 5. Effect of pH on color removal of disperse violet 63 from aqueous solutions.

light and in turn, deactivates the Fenton oxidation process.

### 3.1.2. Effect of hydrogen peroxide dose

During Fenton's process the limiting reagent is hydrogen peroxide at the optimum pH [3, 21, 23]; A significant enhancement of removal was noticed when the hydrogen peroxide dose increases; up to 1 g/l. At higher doses there was a slight increase in the degradation of dyes.

Results obtained in figs. 6-9 indicated that the color removal of dyes from their aqueous solutions increases by increasing hydrogen peroxide doses. The effect of hydrogen peroxide is not significantly effective at doses higher than 1 g/l. Also it can be noticed from figures that, the percent of removal was over 95% at 1 g/l hydrogen peroxide after retention time 60-80 minutes. At higher doses than 1g/l, there was a slight increase of dye removal and destruction.

Generally, the removal rate of organic compounds increases as the dose of hydrogen peroxide increases until a critical value; after this critical value, the removal may decrease or not significantly increase [3, 21, 24]. The optimum hydrogen peroxide dose was found to be 1 g/l. 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 [19, 21]. This behavior may be due to auto-decomposition of  $H_2O_2$  to oxygen and water and the recombination of  $HO$  radicals. Since  $HO$  radicals react with  $H_2O_2$ , itself contributes to

the  $HO$  scavenging capacity [3, 6, 25], so that  $H_2O_2$  should be added at an optimal concentration to achieve the best degradation. We can conclude that, on using iron as a catalyst it is essential to use the smallest amount of iron in order to avoid the problems associated with its elimination.

### 3.1.3. Effect of ferrous sulfate dose

Iron in its ferrous and ferric forms acts as a photocatalyst and requires a working pH below 4 to start the catalytic decomposition and the removal of the tested dyes [26, 27]. To obtain the optimal Fe (II) or Fe (III) 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 1 g/l. The results shown in fig. 10-13 indicated that the destruction of the tested dyes in their aqueous solutions increases by increasing ferrous sulfate dose, the effect of ferrous sulfate is not significantly effective at doses higher than 90 mg/l. It can be seen from figures that the percent of removal was over 95% at 90 mg/l ferrous sulfate after reaction time 60-80 minutes. In case of higher doses of ferrous sulfate the efficiency of color removal decreases. This may be due to the increase of brown turbidity of  $Fe^{3+}$  ions that hinders the absorption of light required for the photo-Fenton process [17], so that ferrous sulfate must be added in a critical dose to achieve the best removal.

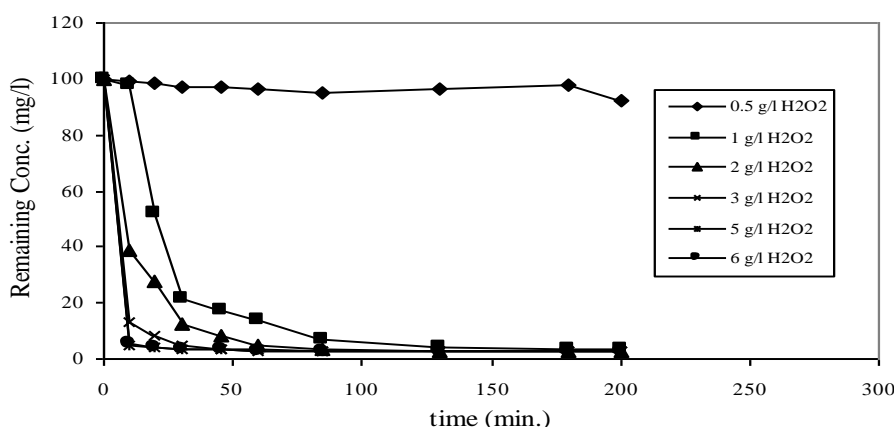


Fig. 6. Effect of hydrogen peroxide dose on removal of dye disperse blue 79.

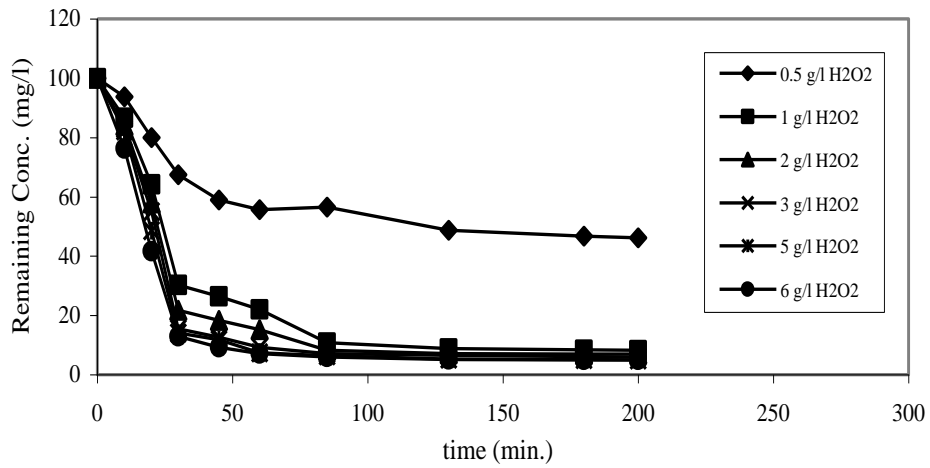


Fig. 7. Effect of hydrogen peroxide dose on removal of dye disperse red 167.

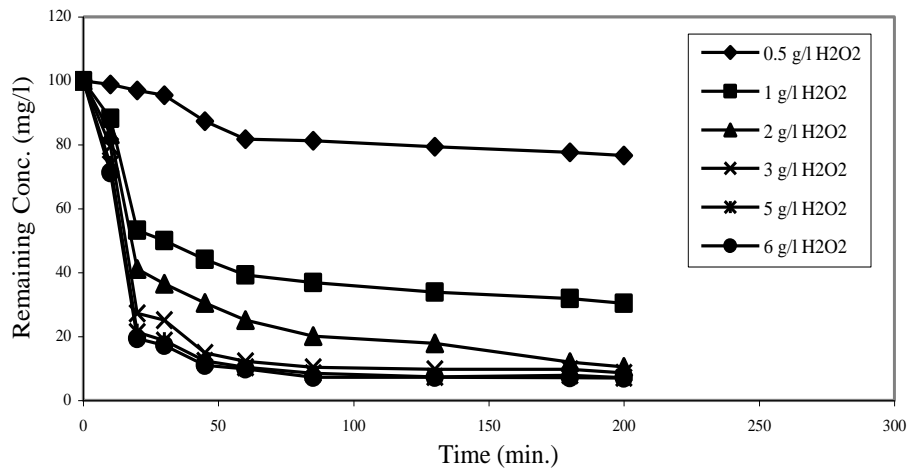


Fig. 8. Effect of hydrogen peroxide dose on removal of dye disperse orange 25.

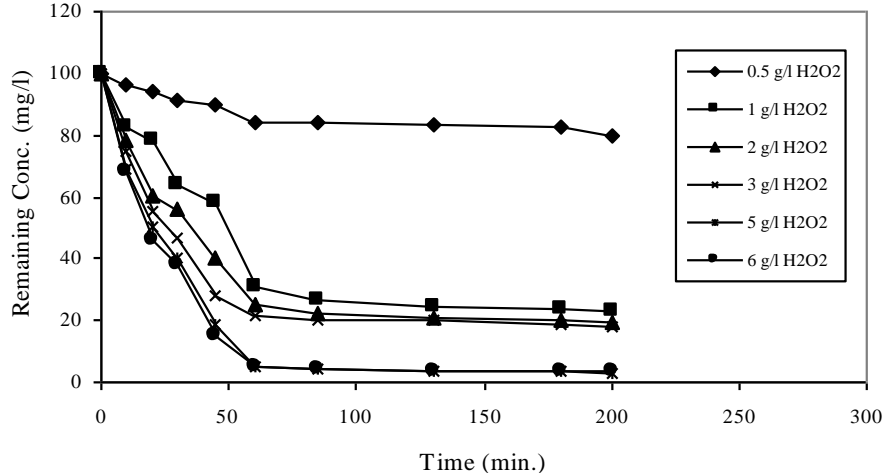


Fig. 9. Effect of hydrogen peroxide dose on removal of dye disperse violet 63.

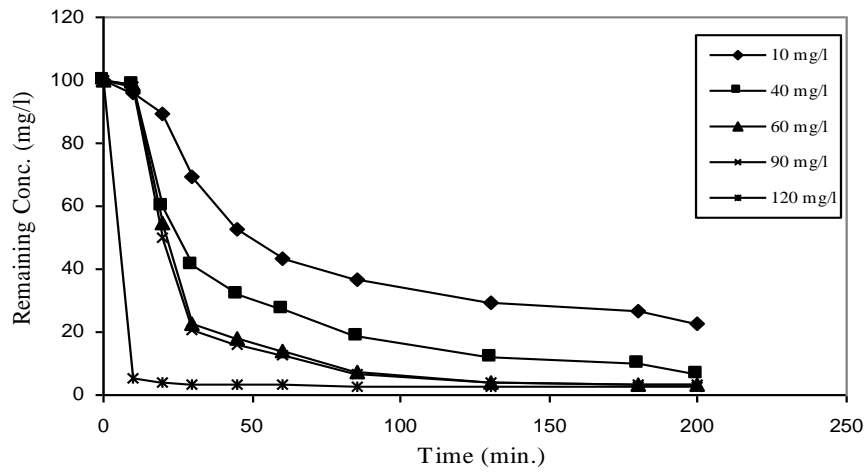


Fig. 10. Effect of ferrous sulfate doses on color removal of disperse blue 79.

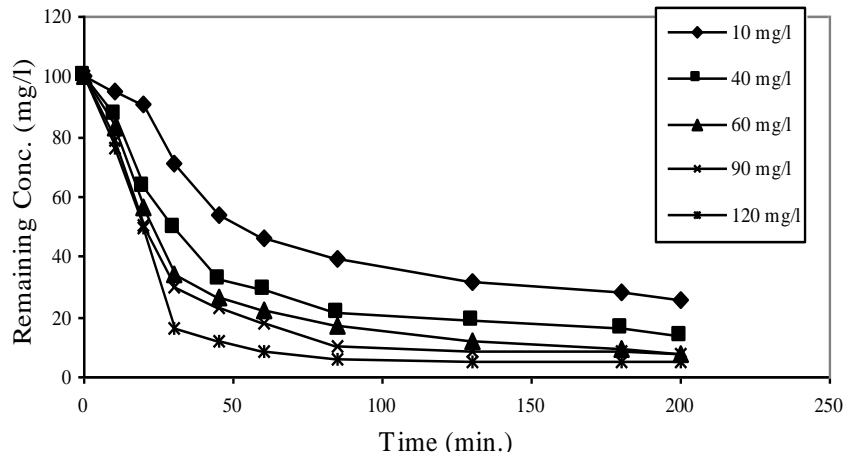


Fig. 11. Effect of ferrous sulfate doses on color removal of disperse red 167.

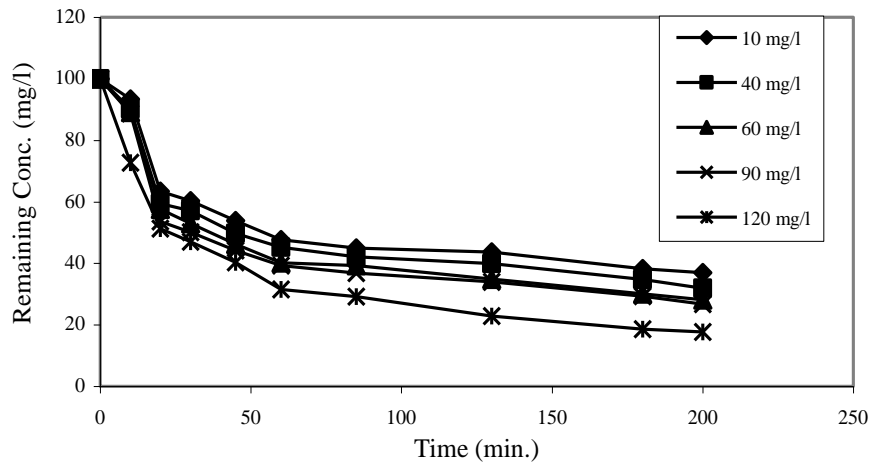


Fig. 12. Effect of ferrous sulfate doses on color removal of disperse orange 25.



3.1.4. Effect of retention time

To determine the effective retention time for the best removal of these dyes by Fenton's reaction, the process was carried out at hydrogen peroxide dose = 1g/l, initial dye concentration = 100 mg/l, ferrous sulfate dose = 90 mg/l, and pH = 3. Samples were drawn at different intervals along the reaction time.

It was found that the maximum removal of some dyes from their aqueous solution reached over 95 % after a retention time ranging from 60-80 minutes as shown in fig. 14. Moreover, the removal and degradation rate was reduced very fast within 10 minutes, but the reaction became slower, because the hydrogen peroxide is already consumed. This

is in accordance with findings in literature [21, 23, 24].

3.2. Application of Fenton oxidation process for removal of color of dyes from effluents of dyeing baths

Wastewater resulting from Al-Amel dyeing unit was subjected to Fenton's reagent under the previously determined optimum conditions (pH = 3,  $H_2O_2$  = 1g/l and  $FeSO_4$  = 90 mg/l). It is shown from fig. 15 that, the color removal and degradation of dyes from their wastewater was over 95%.

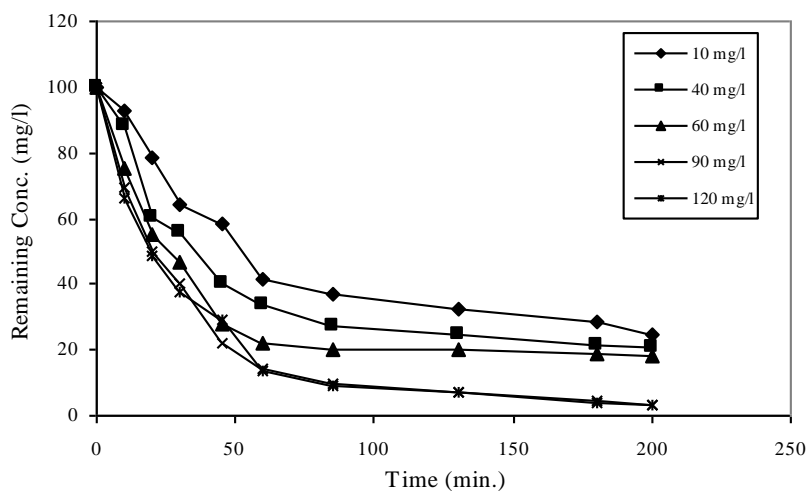


Fig. 13. Effect of ferrous sulfate doses on color removal of disperse violet 63.

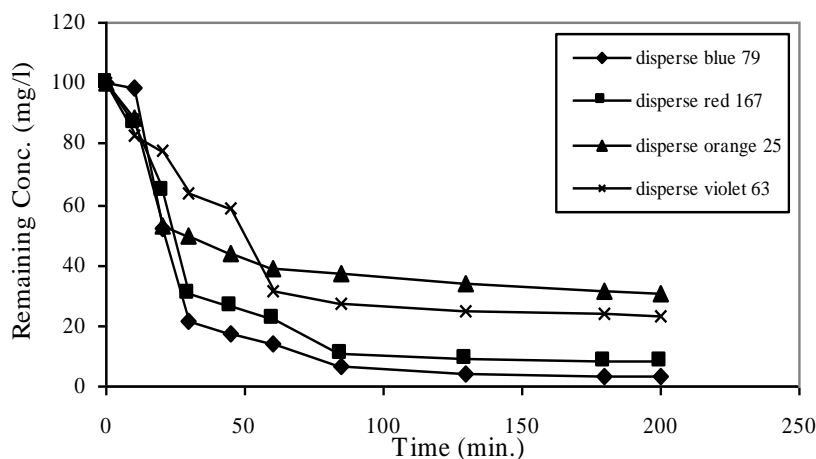


Fig. 14. Determination of critical time for the tested dyestuffs at optimum conditions.

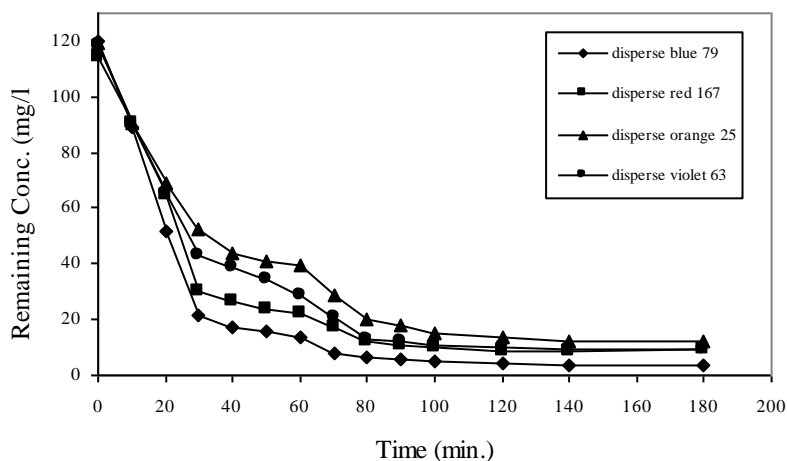


Fig. 15. Removal of dyes from wastewater at optimum conditions.

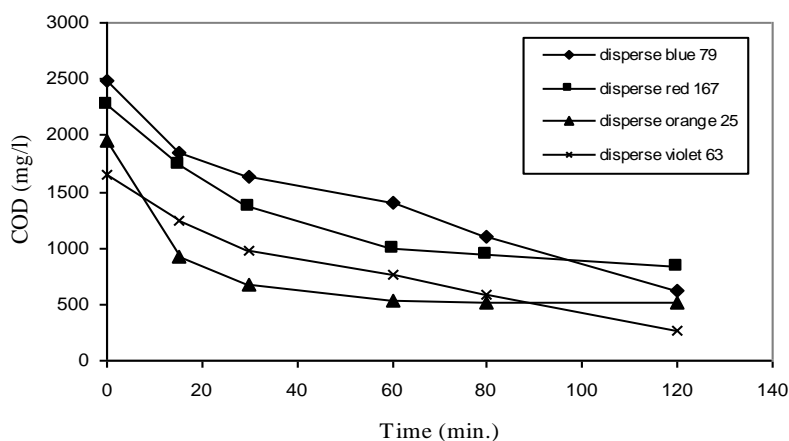


Fig. 16. Effect of time on COD removal from wastewater of dyes.

### 3.3. Evaluation of COD removal from wastewater of dyes

Fenton's oxidation process has the advantage of both oxidation and coagulation processes. During the process, the organic substances are reacted with hydrogen peroxide ( $H_2O_2$ ) in the presence of inexpensive ferrous sulfate ( $FeSO_4$ ) to reduce COD content and color of wastewater.

In current study the application of Fenton's oxidation not only leads to color removal of the dyes from wastewater but also leads to a significant COD reduction and in turn, might enhance the biodegradability of this oxidized wastewater. This adapts the resultant water to be subjected to biological

treatment. To evaluate the effect of Fenton's oxidation process on COD removal, COD was measured before and after the oxidation process. Fig. 16 shows COD reduction after different times at optimum conditions for each dye. Results indicate that COD reduction was in the range of 64-83%. This achieves good removal which in accordance of the degradation of these dyes by Fenton oxidation process and; this step must be followed by raising pH again to neutral conditions to help in the coagulation process; this will adapt wastewater to biological oxidation especially in the presence of remaining hydrogen peroxide which increases the amount of dissolved oxygen [3, 6, 28-30].

Results indicated that percent of color removal is always higher than percent of COD removal. It is well known that the removal of color is due to the cleavage of chromophore bond in the dye molecule. But the oxidation of aromatic ring compound such as dye molecule takes long time and hence the removal of COD is lower, because of the formation of lower molecular weight aliphatic compounds [10, 31].

#### 4. Conclusions

The following conclusions can be withdrawn from this research:

1. The optimum conditions for the best color removal from aqueous dyes solutions and wastewater were determined by studying different parameters which affect the process of chemical oxidation, these optimum conditions were: pH = 3,  $H_2O_2$  dose = 1 g/l,  $FeSO_4$  = 90 mg/l, and retention time = 60-80 minutes
2. Fenton's oxidation process successfully achieved very good removal efficiency of dyes (over 95%) in most cases. This behavior was accompanied with a reduction in chemical oxygen demand (COD) in the range of 64-83%.
3. As a final conclusion from this study, it is highly recommended to apply Fenton oxidation as a preliminary treatment prior to biological oxidation of wastewater resulting from dyeing baths.

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