# Application of a hybrid Electrocoagulation-Fenton process in yarn dye wastewater: Kinetic study



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# Application of a hybrid Electrocoagulation-Fenton process in yarn dye wastewater : Kinetic study

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**Abstract**. Reactive dyes contain a significant portion of colorants used in yarn dying process and also in textile industry. Since the COD content is usually high in such wastewater,we conducted a hybrid electrocoagulation-fenton method to treat the wastewater. This work describes the application of the hybrid system to the removal of chemical oxygen demand and color from the wastewater in a batch reactor. Having worked with initial pH of 3,0; temperature at 30$^o$C, molar ratio of $Fe^{2+}/H_2O_2$ =1/10 and the mol ratio $H_2O_2$/COD = 4, we got 88.3% COD conversion and 88.5% color removal. The COD degradation process can be explained in two phases, the first phase is instantaneous reaction and the second phase is first order reaction. The kinetic constant was 0.0053 minute$^{-1}$ and the rate of COD degradation was 0.0053[COD] mg/L minute.

## 1. Introduction

The disposal of yarn dye wastewater is a problematic issue in the area of high density population in Surabaya city. The wastewater is dark black to red colored, since it contains a lot of dye substances. Since the wastewater can not be treated biologically, we proposed a hybrid method to remove color, Chemical Oxygen Demand (COD) and Total Suspended Solid (TSS) from the wastewater. Advanced Oxidation Processes (AOPs) has been known for its capacity in reducing COD from recalcitrant wastewaters [1-5] . A hybrid system consists of electrocoagulation-fenton process will give a good combination to solve the wastewater. Electrocoagulation will help fenton oxidation process since high TSS will impair the oxidation. Hydrogen peroxide has been widely used for oxidizing agent, it is not effective to oxidize the organic compounds if it is used alone. The presence of metal salts especially ferrous ions can enhance hydrogen peroxide to form hydroxyl radicals. The standard redox potential of hydroxyl radical is 2.80 V and hydrogen peroxide is 1.77 V [6], so the radicals are more powerful oxidizing agent. Ferrous ions and hydrogen peroxide are known as Fenton's reagent and used in ambient temperature..The Fenton used in this study is a homogenous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions. The hydroxyl radicals are generated from this reaction :

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

In the presence of organic contaminants (RH), the contaminants will be oxidized by the radicals as following

$$RH + HO\bullet \rightarrow R\bullet + H_2O \quad (2)$$

The hydrogen peroxide also can regenerate $Fe^{3+}$ to form $Fe^{2+}$ ,

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

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

The new radical ( R●) and also the hydroxyl radical (HO●) can degrade organic compound to carbon dioxide and water. Result from our previous study showed that the best performance of COD removal was at molar ratio of $Fe^{2+}/H_2O_2$ =1/10 and the mol ratio of $H_2O_2$/COD = 4. The aim of this work is to investigate the application of hybrid method Electrocoagulation-Fenton in the removal of color and COD from yarn dye wastewater at various pH. The kinetic of the Fenton process in degrading the COD was also studied.

## 2. Materials and Methods

### *2.1. Yarn dye wastewater*

The wastewater in this study was collected from a yarn dye industry utilizing variety of textile color with the COD content of 872 ppm, BOD ( Biological Oxygen Demand) = 108 ppm, TSS 6220 ppm, color ( Optical Density) =1.65 and pH 4.8.

### *2.2. Methods*

#### *2.2.1. Experiments*

A flexi glass reactor with 1500 $cm^3$ volume was used. Anode and Cathode Al/Al was used with a distance between two electrodes was 2 cm. The size of Alumunium plate was 8cm x 8 cm, with a thickness of 2 mm.The electrocoagulation process used a method as described by Riadi *et.al* [7]. The effluent from electrocoagulation process was then used as influent for Fenton oxidation process. A 1.5 L reactor equipped with stirrer and cooling jacket was used for the experiment. The cooling jacket was used to maintain the experiment at room temperature. The molar ratio of $Fe^{2+}/H_2O_2$ =1/10 and molar ratio of $H_2O_2$ to COD = 4. The initial pH in these experiments were varied. Samples were withdrawn periodically up to 90 minutes of experiment.

#### *2.2.2 Analytical methods*

Chemical Oxygen Demand was measured using closed reflux, colorimetric method [8]. Total Suspended solid was measured using dried method based on a method from APHA, color measurement was conducted using UV-Vis spectrophotometer from APHA [8]. The BOD (Biological Oxygen Demand) was measured by respirometer using BOD system BD600,Lovibond.

## 3.Results and Discussion

Effluent from electrocoagulation process has characteristic as presented in Table 1. Electrocoagulation will help fenton oxidation process since high TSS will hinder fenton oxidation. Suspended solid in the wastewater will interfere fenton process, hence electrocoagulation was introduced prior fenton process. Hence, we proposed hybrid system electrocoagulation-fenton processes in this study. Before performing a batch process for Fenton oxidation, the effluent from electrocoagulation process was examined.

Table 1. Characteristic of yarn dye wastewater after electrocoagulation

| Parameters | Value | % removal |
|---|---|---|
| pH | 4.8 | n/a |
| COD | 515 ppm | 41 |
| TSS | 5810 ppm | 6.6 |
| Color (Optical Density) | 0.192 | 88.4 |

### *3.1.Effect of intial pH*

An important variable process in Fenton oxidation is pH, the best operation pH in the experiment was pH=3.0 (Table 2) which gave the best of COD removal. Result from the experiment is in line with a review reported by Wang.*et.al* [9]. The process is called homogenous Fenton process. The production of hydroxyl radicals is influenced by pH [10]. Since it is a homogenous Fenton process, the optimum of initial pH range is 2.5-3.0 for degradation of the most organic compounds. In higher pH (pH>3.0) the hydrolysis and precipitation of $Fe^{3+}$ in the liquid phase can reduce the capacity of the the catalyst itself [11]. However, if the pH is too low ( < 2.50) , there will be a strong scavenging effect of hydroxyl radical by $H^+$ as reaction below :

$$HO\bullet + H^+ + e^- \rightarrow H_2O \tag{5}$$

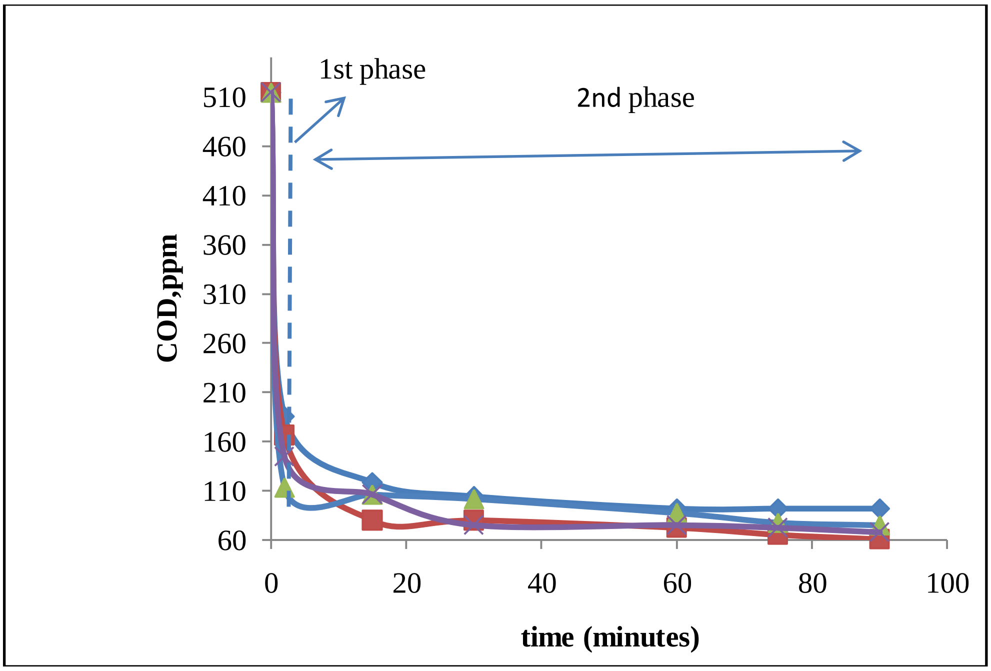


**Figure 1.** COD profile in a fenton oxidation batch system at molar ratio of $Fe^{2+}/H_2O_2$ =1/10; molar ratio of $H_2O_2$ to COD =4.0, x= pH 5.0, ▲=pH4.0,■ =pH=3.0, ♦ pH=2.0

Figure 1 shows the COD profile at different initial pH of wastewater. The first two minutes was a instantaneous reaction which showed a sharply decrease of COD which we mentioned as first phase. After 2 minutes of reaction the reduction of COD was continue up to 90 minutes of experiment,but the degradation was not as fast as that at the first two minutes. The poor performance for COD removal was at initial pH of 2.0, since at lower pH the reaction of hydrogen peroxide with $Fe^{2+}$ is affected because of complex species formation ( $Fe(H_2O)_6)^{2+}$ [3].

Table 2. Percentage removal of COD at different initial pH of wastewater

| Initial pH | % removal of COD for the first two minutes | % total removal of COD |
|---|---|---|
| 2.0 | 63.9 | 82.1 |
| 3.0 | 67.8 | 88.3 |
| 4.0 | 78.1 | 85.4 |
| 5.0 | 71.8 | 86.0 |

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Fenton process can improve the treatment of COD removal for additional 47.3 % removal since the hydroxyl radicals which is produced from Fenton process is a strong oxidation agent. The color removal almost didn't occur in the Fenton process since all color has been removed in electrocoagulation process.

*3.2..Kinetic study*

The kinetic removal of COD during Fenton oxidation process was studied based on the assumption that hydrogen peroxide was in excess as the molar ratio of $H_2O_2$ to COD was 4.0.Hence, the kinetic removal of COD in batch system will follow the pseudo first order and can be written as follows :

$$\frac{-dCOD}{dt} = k\,[COD] \tag{6}$$

The equation can be integrated between time of experiment, t=0 and $t = t_{final}$, which giving equation 7:

$$ln\frac{COD_0}{COD} = k\,t \tag{7}$$

The first two minutes of the reaction is an instantaneous reaction, which is predicted as written in equation (1) and (2). The reaction after two minutes was slower, which is predicted that the hydrogen peroxide reacted with $Fe^{3+}$ to form $Fe^{2+}$ and hydroperoxy radical $HO_2\bullet$ . The standard redox potential of hydroperoxy radical is lower than that of hydroxyl radical. Hence, the oxidation of organic compound is slower compare to that in the first two minutes. The values of k( kinetic constant) and $R^2$( R-squared) are presented in Table 3.

Table 3. The parameter kinetic constant obtained from Fenton oxidation at various intial pH.

| Initial pH | k ( kinetic constant, $min^{-1}$) | R-squared value |
|---|---|---|
| 2.0 | 0.0033 | 0.8348 |
| 3.0 | 0.0053 | 0.9718 |
| 4.0 | 0.004 | 0.983 |
| 5.0 | 0.0046 | 0.6716 |

The value of k decreases with the pH decrease below 3.0.The best performance of the Fenton oxidation is for pH=3.0. The degradation of COD can be written as $\frac{-d\ COD}{dt} = 0.0053\ (COD)$ mg/L min. The R-squared value is lower in Initial pH 5.0 since the precipitation of $Fe^{3+}$ in higher pH can hinder the oxidation process and impair the COD analysis which gave a poor data of COD and lead to the unfit model of pseudo first order.

## 4.Conclusion

The overall results of this study show that the application of hybrid Electrocoagulation-Fenton oxidation is a promising method to treat yarn dye wastewater. The treatment achieved a significant decrease of COD which has been shown as 88.3 % removal. The color was also removed by 88.5 %. The best performance for the Fenton oxidation in batch system was at initial pH 3.0 and molar ratio of $Fe^{2+}/H_2O_2$ =1/10 ; molar ratio of $H_2O_2$ to COD = 4. The kinetic study based on COD degradation showed that the reaction is first order with kinetic constant (k) 0.0053 $min^{-1}$.

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