

Treatment Of Textile Finishing Wastewater Using Fenton's Reagent

Azmi Aris, M. Eng.

Razman Salim, Ph.D

Department of Environmental Engineering

Faculty of Civil Engineering, UTM

Marsin Sanagi, Ph.D

Department of Chemistry

Faculty of Science, UTM

ABSTRACT

In this study, textile finishing wastewater was treated with Fenton's reagent (hydrogen peroxide-ferrous iron system). Under unstable and complex wastewater condition, Fenton's reagent was unable to comply with the standard set by the authority with respect to COD. However, removal of SS complies with the standard while visibility of the wastewater improves by more than 50 %. Removal was mainly by OH radical oxidation as compared to hydroxide precipitation. Mineralisation of more than 50 % organics was observed after 5 minutes reaction while 77 % mineralisation was observed after 30 minutes reaction. The amount of hydrogen peroxide and ferrous iron substantially affects the quality of the treated wastewater.

Key words: *textile finishing wastewater, Fenton's reagent, COD, TOC, decolourisation*

INTRODUCTION

The textile industry is one of the largest industries in Malaysia (after electronics) in terms of export amount [1]. Yet, it is one of the major polluters to the environment in terms of organics and colour. Although most textile factories are equipped with treatment facilities, many of them are far from satisfying the standard set by the regulation [2].

There are various methods available to treat textile finishing wastewater. Among these techniques, biological systems are the most commonly used by the industry as in general, they are economically effective in removing contaminants from wastewater. However, with the use of non-biodegradable chemicals particularly dyes in the industry, the microorganisms that are normally being depended upon in the biological system seem to be helpless. Furthermore, as the regulations become more stringent, the need for better technologies arise.

Despite the capability of the chemical oxidation method in destroying organics in the wastewater, it is rarely used in the industry due to its cost. Nevertheless, if an efficient and economical oxidant is found, chemical oxidation could be the favoured method as it does not produce any solid residue and could render the wastewater into its simplest and harmless form.

Hydroxyl (OH) radicals, a relatively new oxidising agent, offers a viable alternative in the wastewater industry, particularly in removing non-biodegradable and toxic contaminants from the waste stream. As shown in Table 1, it is one of the most reactive oxidising agents known to mankind and is 10^6 to 10^9 times stronger than chlorine or ozone [3]. Typical rates of reaction between OH radical and organic materials are 10^9 to $10^{10} \text{ M}^{-1}\text{s}^{-1}$ [4]. In contrast, typical reaction rates for its closest competitor, ozone, is in the order of 10^{-4} to $10^2 \text{ M}^{-1}\text{s}^{-1}$ [5]. Several methods have been used in producing the OH radicals and these include the use of hydrogen peroxide (H_2O_2) catalysed by ferrous sulphate (FeSO_4), known as Fenton's reagent (FR).

Table 1 Comparative oxidation potential of several oxidising agents.

Species	Volts
Fluorine	3.0
OH radical	2.8
Ozone	2.1
Hydrogen Peroxide	1.8
Potassium permanganate	1.7
Hypochlorous acid	1.5
Chlorine dioxide	1.5
Chlorine	1.4
Oxygen	1.2

Previous extensive studies on FR systems treating simulated dye wastewater showed promising results [6]. An extension of the study was carried out at UTM focusing on actual textile finishing wastewater. Since the characteristics of textile finishing wastewater are highly dependent on the type of chemicals (e.g. dyes, bleaching solution) used in the finishing processes, which normally changes from time to time in terms of amount and concentration, it is therefore important to evaluate the performance of FR under such unstable condition. This paper discussed the results of the study.

THEORY OF FENTON'S REAGENT

Fenton's Reagent can be considered as the earliest technique to generate OH radical that have been studied. In 1894, a scientist named Fenton discovered a strong promotion by FeSO_4 when he tried to oxidise polycarboxylic acids with H_2O_2 . However, the idea of OH radical was first suggested by Haber and Weiss in 1952 and further developed by other researchers [7].

In the absence of organic substrate, OH radicals are produced as H_2O_2 oxidises Fe(II) to Fe(III) under acidic condition yielding,



The ferric ion produced during the above reaction (or those originally present) will also react with H_2O_2 , as shown below:



Although reaction 2 is slower than reaction 1, both produce radicals (hydroxyl, OH and peroxy, HO_2^\cdot) that can participate in the oxidation of the organics in the waste stream. In the presence of organic substrate containing hydrogen (RH), a series of chain reactions may occur as shown below [8]:



An organic radical (R^\cdot) is formed in the above reaction which can be further oxidised by hydroxy or peroxy radicals or can react with oxygen to form an organic peroxy radical (ROO^\cdot):



The organic peroxy radical can then react with an organic substrate (RH) to form an organic hydro-peroxide (ROOH) and another radical (R^\cdot):



In the presence of ferrous or ferric ion, the following reactions occur, involving the iron-catalysed decomposition of hydroperoxide:



Reactions 3 through 7 represent a chain of reactions which contribute to the oxidation of the organics. In addition, some degree of non-chain oxidation involving the radicals as well as H_2O_2 may occur.

Redox reactions explained above is one of the mechanisms that are involved in removal of organics in FR system. Another mechanism, namely coagulation also takes place in the system with the formation of ferric hydroxo complexes with hydroxide ions which then polymerises at pH greater than 3.5 [6].

With both mechanisms taking place in the FR system, the remaining organics that are not oxidised by the radicals can be coagulated and precipitated out from the wastewater. Furthermore, the production of sludge from the coagulation process is minimised by the preceding redox reactions.

MATERIALS AND METHODS

An experimental study was carried out using jar test apparatus. Equal volumes of sample (500 mL) was filled in each beaker. The samples were stirred and the initial pH of the samples was adjusted to 3.5. Then, suitable amounts of H_2O_2 and FeSO_4 were added into the samples accordingly. H_2O_2 doses tested were 300, 600, and 900 mg/L while FeSO_4 doses were 250, 350, and 500 mg/L. These values are in the range of optimum doses determined by Kuo [6] for types of dyes used by the mill i.e. reactive and dispersive.

The samples were allowed to react with the chemicals for 30 minutes. After the reaction period elapsed, pH of the samples was readjusted to 7.0 and after one minute, the stirrer was stopped and the samples were left to stand for four hours. The samples were then analysed for COD and SS. Transparency of the wastewater was also evaluated to determine the visible effect of FR. Similar procedures as described earlier (except for chemical doses) were used.

In another series of study, samples were pipetted out during the reaction process at 5-minute intervals and were analysed for TOC. Samples following the 4-hour sedimentation were also analysed for TOC.

Wastewaters were taken from a nearby textile mill. To be representative, the samples were collected at different times of the day and different days of the week throughout the study period.

All chemicals used as standard and in the experimentation were of reagent grade. COD determination was conducted using HACH DR2000 closed reflux colorimetric method. TOC was measured using DOHRMANN TOC analyser while SS was analysed using gravimetric method. Transparency was measured using a transparency meter which consists of a vertical transparent glass column held by a column shelf and a coloured marker at the bottom of the column. Visibility of the marker from top of the column when filled with sample determined the transparency of the sample.

RESULTS AND ANALYSIS

Characteristics of the raw wastewater during the study period is given in Table 2. The wastewater was alkaline with pH ranging from 8 to 12. The organics were of mid strength with COD ranging from 400 to 1000 mg/L. The solids content was quite low with SS concentrations ranging from 40 to 200 mg/L. Visibility through the wastewater was also low with transparency ranging from 2 cm to 12.5 cm.

Table 2 Characteristics of raw wastewater during the study period.

Parameter	Range
Chemical oxygen demand (COD)	400 – 1000 mg/L
pH	8-12
Suspended solids (SS)	40 – 200 mg/L
Transparency	2 – 12.5 cm

As expected, the characteristics of the wastewater was unstable. This is due to the types of dyes and chemicals used in the manufacturing processes. The differences in molecular structures of dyes, the concentration and amount that were used, and the different amount and types of other chemicals, contribute to the unpredictable wastewater condition.

Chemical Oxygen Demand (COD)

Removal percentage of COD ranges from 70 % to about 80 %. The treated COD ranges from 120 mg/L to 231 mg/L which do not meet the Standard B of Malaysia Environmental Quality Act (EQA), 1974 (Tables 3 and 4).

Table 3 Percentage of COD removal with respect to H_2O_2 and $FeSO_4$ doses*

	H_2O_2 (mg/L)		
	300	600	900
$FeSO_4$	% COD Removal, Treated COD (mg/L)		
250	72, 170	70, 213	71, 212
350	74, 163	75, 158	72, 178
500	81, 120	80, 132	78, 231

*Average of five runs.

Table 4 Standards A and B of Malaysia EQA, 1974.

Parameter	Standard A	Standard B
BOD_5 (mg/L)	20	50
COD (mg/L)	50	100
SS (mg/L)	50	100

The removal percentage in the study is much lower than those obtained by Kuo [6] studies. However, the presence of similar removal mechanisms were observed. As shown in Figure 1, better organics removal were obtained with increasing $FeSO_4$ dosage. At low doses, formation of OH radical was incomplete and organics removal via coagulation was minimal. Increasing the $FeSO_4$ completes the OH radical formation and also improves the coagulation process.

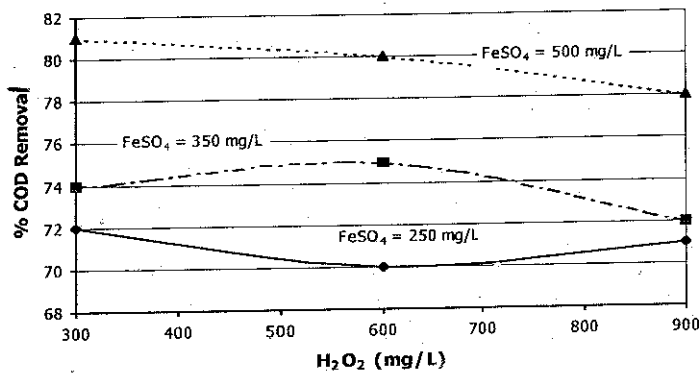


Figure 1 Percentage of COD removal with respect to $FeSO_4$ and H_2O_2 doses.

Nevertheless, as more H₂O₂ was added, the removal percentage tends to decline. Such phenomenon could be due to the presence of excessive H₂O₂ that did not react with either the contaminants or the ferrous ions and thus contributes to the final COD value.

Suspended Solids (SS)

With low initial SS concentration, removal of SS from the wastewater was not a problem. On average, removal was greater than 80 %. As shown in Table 5, the SS of the treated wastewater ranges from 8 mg/L to 30 mg/L, which complies with the Standard A of the EQA.

Table 5 Percentage of SS removal with respect to H₂O₂ and FeSO₄ doses *

	H ₂ O ₂ (mg/L)		
	300	600	900
FeSO ₄	% SS Removal, Treated SS (mg/L)		
250	80, 28	90, 9	88, 14
350	80, 30	90, 8	82, 21
500	87, 18	87, 17	90, 9

*Average of five runs.

Transparency

Transparency of the treated wastewater is given in Table 6. It ranges from 10 cm to 30 cm, showing improvement of more than 50 %.

Table 6 Transparency of treated wastewater with respect to H₂O₂ and FeSO₄ doses .

	H ₂ O ₂ (mg/L)		
	300	600	1200
FeSO ₄	Transparency (cm)		
200	17	14	10
500	19	23	27
700	24	24	30

*Average of three runs

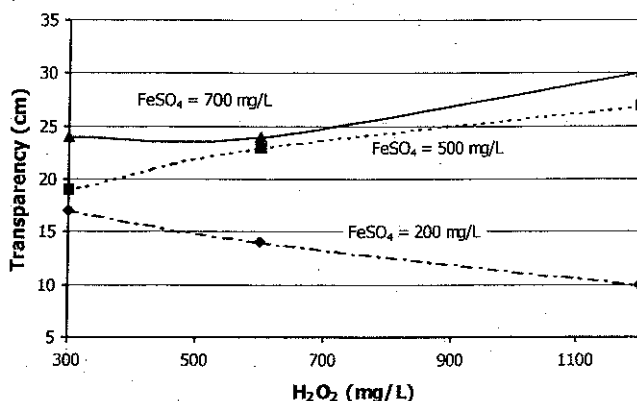


Figure 2 Transparency with respect to FeSO₄ and H₂O₂ doses.

As shown in Figure 2, effect of increasing FeSO₄ was also observed with transparency. As with COD, transparency was better with higher FeSO₄ doses. Except at the FeSO₄ dose of 200 mg/L, increasing H₂O₂ doses also improve transparency. This confirmed the earlier finding by Kuo [6] that increasing H₂O₂ improves decolourisation but at the same time, increases the COD value due to its residual effect mentioned earlier.

Total Organic Carbon (TOC)

As discussed in the methodology section, application of FR requires the adjustment of pH, initially to 3.5 and then to 7.0. At pH 3.5, chemical oxidation occurs when FeSO₄ is added to the wastewater along with the H₂O₂, forming OH radicals. When pH is raised to 7.0, the ferrous ions (soluble Fe⁺²) precipitates out from the solution in the form of ferric hydroxo complexes and thus helps to remove the organics through coagulation.

The purpose of analysing TOC was to identify the main mechanism that contributes to the removal of organics from wastewater i.e. chemical oxidation vs. precipitation. Furthermore, it determines the mineralisation level that could be achieved via OH radicals oxidation.

As depicted in Table 7 and Figure 3, 53 % of the organics were destroyed during the first five minutes of the reaction, 77 % were destroyed after 30-minute reaction while an additional 3 % were removed following precipitation of Fe(OH)₃. From these results, it could be concluded that OH radicals oxidation is the main mechanism in removing contaminants in FR process. It also suggests

that only small amounts of organics are trapped in the hydroxides and thus may not pose any significant problems in the recovery of Fe²⁺.

Table 7 Removal of TOC from the wastewater *

Time (min)	TOC (mg/L)	% Removal
0	137	0
5	64	53
10	53	61
15	39	71
20	35	75
25	33	76
30	32	77
After 4 hours sedimentation	28	80

*Average of three runs.

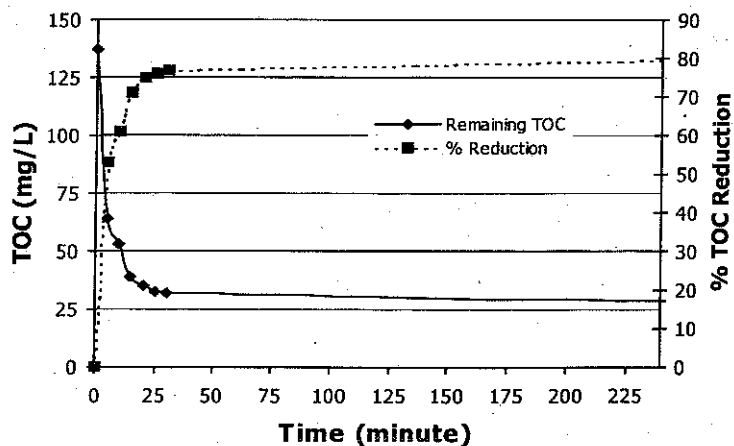


Figure 3 Overall removal of TOC from wastewater.

The results also showed that significant mineralisation took place during the first, five minutes of the reaction. Removal was much lesser beyond the five minutes. This may be due to the lesser amount of OH radical available and may also be due to the stability of the oxidation byproducts.

CONCLUSIONS

Performance of FR in treating actual textile finishing wastewater was evaluated in this study. Under unstable and complex wastewater characteristics, FR was not able to produce wastewater that complies with the standard requirement with respect to COD. Nevertheless, removal of SS was not a problem.

Using the optimum oxidant doses determined in earlier studies, removal of COD was between 70 % to 81 % with treated COD ranging from 120 mg/L to 231 mg/L. Removal of SS was greater than 80 % with treated SS ranging from 8 mg/L to 30 mg/L. Visibility through the wastewater, measured by the transparency column, improved by more than 50 %.

As with earlier studies, increasing FeSO_4 doses improves COD removal and decolorisation. However, increasing H_2O_2 beyond its optimum dose, improves decolourisation but increases treated COD value.

Based on TOC removal, OH radical oxidation was found to play a significant role in organics removal as compared to the hydroxide precipitation mechanism. About 50 % of the organics was mineralised within 5 minutes of the reaction. Organics mineralisation of 77 % was achieved after 30 minutes reaction while only 3 % of the organics was removed via hydroxide precipitation. It indicates that the sludge generated in FR process, mainly consists of recoverable iron in the form of hydroxides.

In conclusion, this study shows that

1. The FR system alone is not sufficient to treat textile finishing wastewater to the quality required by the Malaysian EQA.
2. More studies are needed to determine the effect of other chemicals used in textile finishing industry in order to further optimise the system,
3. Conjunctive use of FR with other processes might provide a more economical and efficient system.
4. FR can still be considered an attractive treatment alternative as it mineralises more than 75 % of the organics within 30 minute reaction.

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