A CONTINUOUS FENTON'S PROCESS FOR TREATMENT OF TEXTILE WASTEWATER

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ABSTRACT

Treatment of textile wastewaters from a large dyeing and finishing mill by a continuous process of combined chemical coagulation, Fenton's reagent and activated sludge process is investigated. The experimental results are assessed in terms of COD and colour (turbidity) reductions to determine the overall treatment efficiency of the continuous process. Operating variables, such as pH, polyaluminium chloride (PAC) and polymer addition and treatment time are explored to determine their respective effects on the treatment efficiency. Optimum range for the above operating variables is experimentally obtained. Economic evaluation of the continuous Fenton's treatment method indicates that it is a method which is highly competitive with conventional treatments practised in the textile industry.

Keywords: Fenton's reagent, textile wastewater, chemical coagulation, activated sludge treatment, economic evaluation.

INTRODUCTION

Textile wastewaters have been known to have a wide variability in wastewater quality, organic content and temperature (1). Treatment of wastewaters has not been easy. When the COD content of the textile wastewater exceeds 1200 mg/L, the conventional activated sludge process becomes seriously inadequate (1, 2). In these instances, chemical treatment in conjunction with the biological treatment has been considered as a good alternative for overcoming the difficulty.

Chemical treatment processes previously proposed include adsorption by activated carbon (3, 4), electrochemical treatment (5) and ozonation (2, 6, 7). In recent work, Kuo (8) utilised Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulphate, to decolourise dye wastewaters. The author found that Fenton's reagent is effective in decolourising and reducing the COD content of the wastewaters that contain reactive, direct, basic, acid or disperse dye. Fenton's reagent has also been found effective in treating various industrial wastewaters (9-14). The paper by Kuo (8) represents the first attempt to utilise Fenton's reagent in dealing with the dye wastewater. In his investigation, Kuo (8) primarily considered the dye wastewater prepared in the laboratory with one dye component. In actual textile wastewaters contain a wide variety of dyes and additional chemicals (such as polyvinyl alcohol, surfactants, etc.). Therefore its colour, pH, COD and SS concentrations vary widely over time.

This work investigates the treatment efficiency of Fenton's reagent from a systematic standpoint. The process considered here consists of chemical coagulation, Fenton's reagent and the activated sludge process. The treatment efficiency of this process obtained in a laboratory-scale, continuous system could offer much practical value to the textile industries.

METHOD AND MATERIALS

The continuous experimental apparatus is shown in Figure 1. The continuous process
consists primarily of a wastewater reservoir, chemical coagulation tank, pH controller, Fenton’s reactor and activated sludge treatment reactor. The reservoir holds about 300 litres of screened raw textile wastewater. The screened textile wastewater was adjusted to pH 7 and was pumped to the chemical coagulation tank. In the front section of the chemical coagulation tank, polyalumnum chloride (PAC) was added at 100 mg/l dosage with the mixer operating at 150 rpm. Polymer was added in the back section of the tank at a fixed concentration of 0.5 mg/l and the mixer speed was maintained at 50 rpm for slow mixing. The retention time in the chemical coagulation tank was 2 minutes in each section. The sedimentation tank following chemical coagulation had a retention time of approximately 60 minutes. The top clear textile wastewater was then adjusted to a proper pH using a pH control unit (Model CP-2100, Yang Shi Instrument, Taiwan). It went to the Fenton’s reactor for further treatment. The Fenton’s reactor had a size of 25x25x88 cm. Appropriate amounts of hydrogen peroxide and ferrous sulphate were added to the reactor by two metering pumps and rapid mixing was provided in the reactor.

The treated textile wastewater from the Fenton’s reactor went to a second sedimentation tank with a 60 min retention time. The retention time was sufficient to settle out suspended solids. The top textile wastewater was finally passed to the activated sludge tank where it was mixed with equal volume of activated sludge seeded from a biological treatment plant of the dyeing and finishing mill. The mixed liquor suspended solids (MLSS) were measured to be slightly less than 2915 mg/l, about the average operating value for an activated sludge process. Aeration was provided in the activated sludge treatment tank. COD concentrations of the effluents from the first and second sedimentation tanks and from the aerobic digester of the system were measured by the standard method (15). The colour and turbidity of the treated textile wastewater was determined in terms of transparency using an apparatus similar in basic structure to the candle turbidimeter (15) which is used for measuring the Jackson unit. The iron concentration (Fe3+) at the exit of the aerobic digester was measured using an atomic absorption spectrophotometer (Varian Spectra-AA-20, Varian, Inc., California, USA). According to the Taiwan EPA stipulations, the acceptable transparency and COD concentration of all treated industrial wastewaters needs to exceed 15 cm and below 200 mg/l, respectively.

DISCUSSION OF RESULTS

According to Walling and Kato (16), the basic mechanism of the Fenton’s treatment consists of oxidation and chemical coagulation of dye molecules. In an acidic environment, Walling and Kato (16) proposed that the hydrogen peroxide in the presence of excess ferrous ions incurs the following redox reactions

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO} \quad [1] \]

\[ \text{HO} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R} \quad [2] \]

\[ \text{R} + \text{Fe}^{3+} \rightarrow \text{R}^+ + \text{Fe}^{2+} \quad [3] \]

\[ \text{R}^+ + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{H}^+ \quad [4] \]

The hydroxyl radical HO attacks the organic compounds RH (the unsaturated dye molecules) and thus render the dye colourless.

The ferric ions generated in the above redox reactions reacts with hydroxide ions to form ferric hydroxo complexes, capable of capturing
the decolourised dye or other organic molecules and precipitating out. Such a coagulation/precipitation action perhaps accounts for the major COD reduction of the Fenton's process.

A run was performed to determine the start-up time of the Fenton's reactor which was sized to have a retention time of 60 minutes. The reactor was first filled with screened textile wastewater. The feed pump was turned on to feed the reactor with a textile wastewater flow rate at 1 l/min and simultaneously the Fenton's reagent was added to the reactor. The COD concentration was monitored at the exit of the reactor. The COD change with time was shown in Figure 2. The COD curve tends to flatten out after 120 minutes, implying that the steady state operation can be achieved after two times the reactor's volume of the textile wastewater has been fed in.

The pH was reported to be a highly important factor for effective Fenton's treatment (8-14). Figure 3 demonstrated the pH effect on the COD removal of the present continuous Fenton's process and the COD removal represents the COD decrease up to that point. Note that the COD concentration represent these measured at the exit from the second sedimentation tank. The optimum pH is seen to be around pH 4 in line with previous observations (8). Hence the feed textile wastewater to the Fenton's reactor was adjusted to pH 4 for all test runs in the present study.

The effects of the amounts of Fenton's reagent on the COD removal are shown in Figures 4 and 5. Regardless of significant COD change with increasing \( \text{H}_2\text{O}_2 \), the total COD removal

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**Figure 2.** The COD change vs the Fenton's treatment time with 200 mg/l each of H\(_2\)O\(_2\) and FeSO\(_4\) and at pH 4.

**Figure 3.** Effect of pH on the COD removal with 100 mg/l each of H\(_2\)O\(_2\) and FeSO\(_4\)
appears to increase only slowly beyond 100 mg/l \( \text{H}_2\text{O}_2 \). Hence 100 mg/l \( \text{H}_2\text{O}_2 \) was adopted for the present study due to the consideration that an increase in the total COD removal by 12% w/w with a fourfold increase in \( \text{H}_2\text{O}_2 \) is not justified. Selection of 100 mg/l FeSO\(_4\) for the present study was repeated in Figure 5 for the same reason.

The flow rate of textile wastewater in the previous figures was set at 1 l/min. It is of interest to examine how the flow rate affects COD removal. Since the volume of the Fenton’s reactor was fixed, a change in the wastewater flow rate will affect the retention time and thus treatment efficiency. Such an effect is displayed in Figure 6. There is a drastic decrease in COD removal for wastewater flow rates larger than 1 l/min, due apparently to the short retention time of the textile wastewater in the Fenton’s reactor and thus the short treatment time. As the flow rate is reduced to 0.5 l/min, there is surprisingly little improvement in COD removal. The reason is not established. It could be due to that at the flow rate of 1 l/min, the treated textile wastewater exiting the Fenton’s reactor only had a residual oxidisable organic substance left. Hence, further oxidation, as reflected by the longer retention time, did not much improve the further COD removal.

In the last step of the treatment process, activated sludge treatment was adopted. A 1:1 volume ratio of the textile wastewater and the activated sludge was adopted. Within the first hour of aerobic digestion, the COD concentration of the effluent textile wastewater from the
Fenton’s reactor was reduced by nearly 50% w/w. After three hours of aeration, there appears to be little further COD reduction. Hence three hours of activated sludge treatment was recommended as the last step of the present Fenton’s process. The COD change along with the transparency after each treatment unit is shown in Table 1. The COD concentration of the original wastewater sample was reduced by 72% w/w to slightly less than 200 mg/l after chemical coagulation and the Fenton’s treatment. The transparency of the wastewater was elevated from 3.7 to 30 cm. After three hours of aerobic digestion, the COD concentration was further reduced to 83 mg/l with a transparency about 28 cm. At that point, only very faint colour remained in the treated wastewater.

Iron ion concentrations after activated sludge treatment measured for all experimental samples using a Varian atomic absorption spectrophotometer were less than 0.5 mg/l which was very low. Such a low iron ion concentration amply satisfies the government discharge requirement.

**ECONOMIC EVALUATION OF THE CONTINUOUS FENTON’S PROCESS**

The results of the continuous Fenton’s process assessed in terms of COD removal and transparency reductions discussed above are very satisfactory. From the practical standpoint, it is interest to the textile industries to establish the approximate cost associated with the continuous treatment method. Cost estimations need to include the following major items: Fenton’s reagent (H₂O₂ and FeSO₄), PAC, polymer and chemicals (H₂SO₄ and NaOH) required for pH adjustment. The cost for each item was estimated as follows:

1. Using 100 mg/l of PAC for all runs and based on the price of PAC solution (11% w/w) of $0.135/kg (unit cost in USD supplied by the dyeing and finishing mill), the cost of PAC was estimated to be $0.123/ton of

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**Table 1. The COD and Transparency Changes of the Fenton’s Process.**

<table>
<thead>
<tr>
<th>Original Sample</th>
<th>After Coagulation</th>
<th>After Fenton’s Treatment 1</th>
<th>A.S. 2</th>
<th>A.S. 3</th>
<th>A.S. 4</th>
<th>A.S. 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>697</td>
<td>316</td>
<td>196</td>
<td>98</td>
<td>87</td>
<td>83</td>
</tr>
<tr>
<td>Transparency</td>
<td>3.7</td>
<td>10.3</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: 1. COD in mg/L and transparency in cm.
2. A.S. means “after activated sludge treatment”.

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**Figure 6.** Effect of wastewater flow rate on the COD removal with 100 mg/l each of H₂O₂ and FeSO₄ at pH 4.
wastewater. The cost for polymer was less than 5% of PAC's and assumed to be negligible.

(2). Based on 100 mg/l H₂O₂ and a unit price of $0.32/kg of 35% w/w H₂O₂, the cost of H₂O₂ amounts to $0.095/ton.

(3). The amount of FeSO₄ used was 100 mg/l. With a unit of $0.247/kg, the cost of was estimated to be $0.061/ton.

(4). The cost for pH adjustment includes those of H₂SO₄ and NaOH. Based on the amounts of 0.92 g/l H₂SO₄ at $0.052/kg and 0.25 g/l NaOH at $0.081/kg, the pH adjustment cost comes to $0.068/ton.

(5). Cost of aerobic digestion was difficult to estimate. According to the ball-park figure supplied by the operating personnel of the waste treatment plant, it would cost approximately $0.056/ton which was accepted in the present estimation.

Note that other power costs were not included here because there were deemed as negligible one in comparison with other cost items. Based on the above estimations, the total treatment cost of the continuous Fenton's process would come to about $0.403/ton of wastewater. The current cost figure of the conventional treatment process, as supplied by the operating personnel, was $0.45/ton. Hence the continuous Fenton's process had an estimated cost advantage of about 10%. Besides this, the water quality of the present continuous Fenton's process in terms of COD concentration and transparency was significantly better than those of the conventional treatment.

CONCLUSIONS

A continuous process of combined chemical coagulation, Fenton's reagent and aerobic digestion has been employed in the present study to treat the textile wastewater. The operating variables, such as pH, wastewater flow rate, amounts of Fenton's reagent and PAC, are explored to determine their effects on the treatment efficiency. It has been observed that the Fenton's process a maximum efficiency at a pH around 4. The amount of Fenton's reagent required for efficient treatment of the textile wastewater consists 100 mg/l each of H₂O₂ and FeSO₄. A PAC amount of 100 mg/l has been seen to significantly enhance the overall treatment efficiency of the process. The water quality of the treated textile wastewater in terms of COD concentration and transparency amply exceed the government safe discharge standard. An economic evaluation of the operating cost of the continuous Fenton's process has indicated that the process enjoys a 10% cost advantage over the conventional method currently practised by the textile company. Besides the cost advantage, the water quality of the treated textile wastewater is significantly improved when compared to that treated by the conventional method.

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REFERENCES


