Pretreatment of coffee pulping wastewater by Fenton’s reagent

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The present study deals with treatment of coffee pulping wastewater using Fenton’s oxidation process. The coffee pulping wastewater used for the present study is characterized by low pH with high concentration of COD, ammonia nitrogen, nitrate nitrogen and phosphorous with BOD/COD ratio varying from 0.037 to 0.050. The effect of different operating conditions, namely Fenton dosage, mixing speed, pH and reaction time, is evaluated. Working with the wastewater pH of 6.42, mixing speed of 25 RPM, molar ratio of 12.43 and mass ratio of 0.60 for reaction time of 60 min makes possible the COD conversion of 84.39%. The percentage removal of other pollutant parameters, such as ammonia nitrogen, nitrate nitrogen and phosphorous, is found to be 90.75, 57.5 and 80% respectively.

Keywords: Chemical oxygen demand, Coffee, Fenton reagent, Pulping, Wastewater

Coffee is a major commercial crop in India with its cultivation being undertaken in hilly regions of Karnataka, Kerala, Tamil Nadu, Andhra Pradesh, Orissa, West Bengal and North Eastern states. The total area under coffee cultivation is about 0.305 mha with arabica and robusta being cultivated in about the same extent of land. India grows about 3 lakh tones of coffee annually and has ranked sixth in the world in coffee production. Coffee grown in many regions is processed using wet method and the wastewater generated can be divided into two parts. Firstly, the pulping water with high content of quickly fermenting sugars using enzymes from the bacteria on the coffee cherries. Secondly depending on the processing method applied the water from fermentation/washing or the thick effluents from the mechanical mucilage removers. One kilogram of dried coffee produces around 2.5 kg of wet pulp and 12.4 kg of effluent. The disposal of coffee pulping wastewater is an environmental issue in countries like India, since a large number of coffee pulping units are located near streams and rivers.

At present coffee pulping wastewater is let into small lagoons and these lagoons are operated only during the coffee pulping season. These lagoons often fail since they are operated in winter at low temperatures and sometimes they get overloaded with accumulation of volatile fatty acids and become malodorous, causing potential hazards to ground and surface water resources. When these lagoons get filled up, the wastewater overflows into nearby streams and rivers. In Karnataka state the coffee pulping wastewater is disposed into unlined Kutcha pits and major disadvantages associated with it are odour problems, mosquito breeding (public health issues), low loading rates, unsatisfactory treatment and loss of cultivable area.

Attempts made by the previous researchers to treat coffee processing wastewater using biological methods include mesophilic and thermophilic digestion of instant coffee wastewater, use of UASB reactor at mesophilic and thermophilic conditions, using anaerobic hybrid reactor (UASB/Filter), anaerobic digestion in multi feed bioreactor, etc. The review of the literature suggests that anaerobic digestion of coffee pulping wastewater is possible but long term stability is an operational problem. Application of advanced oxidation processes on treatment of coffee processing wastewater is very meager. Review of the earlier studies revealed treatment of coffee processing wastewater by chemical coagulation-flocculation and advanced oxidation processes, decolorization of synthetic coffee effluent, using solar Photo-Fenton reaction and decolorization of UV assisted Photo-Fenton for model coffee effluent. Advanced oxidation processes (AOP’s) is found to be very effective in the treatment of pharmaceutical wastewater, pigment wastewater, cork cooking

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wastewater\textsuperscript{14}, olive mill wastewater\textsuperscript{15}, wastewater with high detergent content\textsuperscript{16}, degradation of synthetically prepared malachite green found in textile wastewaters\textsuperscript{17} and in post treatment of mature municipal landfill leachate\textsuperscript{18}.

Coffee pulping activity is seasonal in nature and the wastewater is generated only for four months in a year which is characterized by low $p$H and low BOD to COD ratio. In addition, the presence of tannins, alkaloids and flavanoid components of the pulp makes the environment for biological degradation more difficult. Thus, present study is undertaken with the aim of determining efficiency of Fenton’s reagent in the pre-treatment of coffee pulping wastewater. Different Fenton dosages, $p$H, mixing speed as well as contact time are the subject of experiments.

**Experimental Procedure**

**Characterization of coffee pulping wastewater**

The coffee pulping wastewater used in this study was collected from coffee pulping units of different coffee estates located in Kodagu district of Karnataka state, India. The raw wastewater was analyzed for various parameters and the characteristics are shown in the Table 1. It can be seen that the chemical oxygen demand (COD) concentration is very high with low biological oxygen demand (BOD) and $p$H. The initial BOD to COD ratio was found to be very low in the range 0.037 - 0.05, which suggests that there is a presence of recalcitrant nature of organics in the wastewater and this type of wastewater is very difficult to treat in biological reactors.

**Fenton oxidation experiments**

The chemical oxidation experiments of coffee pulping wastewater were undertaken in Jar apparatus with speed regulator. ORP, $p$H and temperature were online monitored. Adjustment of $p$H was carried out using 1 N NaOH solution. Experiments were carried out with 500 mL of diluted coffee pulping wastewater to which weighed amount of FeSO$_4$.7 H$_2$O was added and dissolved under stirring. The Fenton oxidation began with the addition of hydrogen peroxide. Initial studies were done for molar ratio of 15 at 15%, 25% and 50% of hydrogen peroxide demand calculated theoretically followed by another set of study carried out for molar ratio of 12.3 at 6.5%, 10%, 13.5%, 17% and 20% of theoretical hydrogen peroxide demand. Control experiments were also performed in the absence of either Fe$^{2+}$ or H$_2$O$_2$ to know the effect of individual species on the COD removal. Samples were withdrawn from the reactor at predetermined time intervals. For all the experiments the raw coffee pulping wastewater was diluted in the ratio of 1:1 using distilled water.

**Analytical methods**

The raw wastewater sample and samples collected from the reactor were filtered before analysis. The COD analyses were performed by dichromate closed reflux method using Hach-389, USA apparatus followed by titrimetric method. Biological oxygen demand (BOD$_{3}$ at 27°C) was done by modified Winklers method. Ammonia-nitrogen, nitrate-nitrogen and phosphorus were analyzed as per the standard methods\textsuperscript{19} using Hach spectrophotometer, USA instrument. ORP and $p$H were measured using Adwa instruments, (Hungary). Research grade reagents such as hydrogen peroxide (30% w/v) supplied by Qualigens, ferrous sulfate hepta hydrate (FeSO$_4$.7 H$_2$O) from Merck, potassium permanganate AR grade from Sd Fine Chemicals were used without purification.

**Results and Discussion**

Chemical oxidation of coffee pulping wastewater with Fenton’s reagent was studied in order to minimize the impact of coffee pulping wastewater discharge on lagoons and natural water courses. Ferrous sulfate hepta-hydrate (FeSO$_4$.7H$_2$O) was used as source of iron, based on the earlier studies\textsuperscript{15,17,20}.

Initial studies were performed at Fenton dosage of 15, 25 and 50% of hydrogen peroxide demand calculated theoretically using the following equation:

\[
H_2O_2 \rightarrow H_2O + {1/2} O_2
\]

\[
34/16 * \text{COD mg/L} = A \text{ mg of H}_2O_2
\]

The concentration of Fe$^{2+}$ was fixed assuming the molar ratio to be 15. Molar ratio of 15 was applied based on the earlier study\textsuperscript{15}, for olive mill wastewater treatment achieving 70% COD conversion.

For initial COD concentration of 7360 mg/L (after dilution 1:1), the theoretical hydrogen peroxide

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$H</td>
<td>4.27 - 4.40</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>9270-14800</td>
</tr>
<tr>
<td>BOD$_{3}$ @ 27°C, mg/L</td>
<td>472- 551</td>
</tr>
<tr>
<td>Ammonia nitrogen, mg/L</td>
<td>42-57</td>
</tr>
<tr>
<td>Nitrate nitrogen, mg/L</td>
<td>32-48</td>
</tr>
<tr>
<td>Phosphorous, mg/L</td>
<td>60-90</td>
</tr>
</tbody>
</table>
required was found to be 15.64 g and the studies were carried out for existing wastewater \(pH\) of 4.27 at 50 RPM and for reaction time of 60 min. For 15, 25 and 50% of theoretical hydrogen peroxide demand, the COD removal varied between 27.17% and 32.60%. The COD removal was not considerable even at 50% of theoretical hydrogen demand, which may be attributed to the self scavenging effect of \(\text{OH}\) radicals by \(\text{Fe}^{2+}\), thus inducing decrease in the degradation rate of pollutants at higher calculated dosages. Thus, based on these results an attempt was made to treat the coffee pulping wastewater at lower Fenton dosages (less than 25% of the theoretical hydrogen peroxide demand).

For COD concentration of 4860 mg/L (after 1:1 dilution), theoretical hydrogen peroxide required was found to be 8.84 g. The Fenton dosage was varied using different hydrogen peroxide dosages 6.5, 10, 13.5, 17 and 20% of the theoretical hydrogen peroxide demand and iron concentration was increased to 0.04 g at every successive dosages monitored. The molar ratio for all the Fenton dosages was varied between 12.27 and 12.39. Table 2 shows the results of the experiments carried out for various Fenton dosages at existing wastewater \(pH\) of 4.27, stirring rate of 50 RPM and reaction time of 60 min.

From Table 2 it is observed that highest percentage of COD removal was obtained for Fenton dosage of 0.20 g \(\text{Fe}^{2+} + 1.5 \text{ g H}_2\text{O}_2\) which accounts for 17% of the theoretical \(\text{H}_2\text{O}_2\) demand and further increase in the Fenton dosage \((0.24 \text{ g \text{Fe}^{2+} + 1.8 \text{ g H}_2\text{O}_2})\) led to decrease in COD removal. It is also observed that too low concentration of 0.008 g \(\text{Fe}^{2+} + 0.6 \text{ g H}_2\text{O}_2\) resulted in lower percentage removal of COD from coffee pulping wastewater which may attributed to the fact that lower concentrations of Fenton dosage do not ensure proper chain reaction of hydroxyl radicals formation and oxidation of compounds in the solution.\(^{16}\)

### Table 2—Experimental conditions, COD conversion (%) obtained after chemical oxidation of coffee pulping wastewater with Fenton’s reagent

<table>
<thead>
<tr>
<th>Fenton dosage</th>
<th>Molar ratio</th>
<th>COD, mg/L</th>
<th>COD removal, %</th>
<th>Mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.08 g (\text{Fe}^{2+} + 0.6 \text{ g H}_2\text{O}_2)</td>
<td>12.29</td>
<td>4860</td>
<td>1682</td>
<td>34.61</td>
</tr>
<tr>
<td>0.12 g (\text{Fe}^{2+} + 0.9 \text{ g H}_2\text{O}_2)</td>
<td>12.32</td>
<td>4860</td>
<td>2430</td>
<td>50.00</td>
</tr>
<tr>
<td>0.16 g (\text{Fe}^{2+} + 1.2 \text{ g H}_2\text{O}_2)</td>
<td>12.29</td>
<td>4860</td>
<td>2336</td>
<td>52.00</td>
</tr>
<tr>
<td>0.20 g (\text{Fe}^{2+} + 1.5 \text{ g H}_2\text{O}_2)</td>
<td>12.27</td>
<td>4860</td>
<td>1944</td>
<td>60.00</td>
</tr>
<tr>
<td>0.24 g (\text{Fe}^{2+} + 1.8 \text{ g H}_2\text{O}_2)</td>
<td>12.29</td>
<td>4860</td>
<td>2235.6</td>
<td>54.00</td>
</tr>
</tbody>
</table>

### Effect of initial \(pH\)

Based on the results of above study, Fenton dosage of 0.2 g \(\text{Fe}^{2+} + 1.5 \text{ g H}_2\text{O}_2\) was found to be optimum and the effect of \(pH\) was studied at two selected \(pH\) values i.e for the existing wastewater \(pH\) of 4.27 and at higher wastewater \(pH\) value of 6.4. For the experiments, the wastewater was diluted in the ratio 1:1, resulting in initial COD value of 4160 mg/L. For wastewater \(pH\) of 6.4, mixing speed of 50 RPM, reaction time of 60 min and optimum Fenton dosage of 0.2 g \(\text{Fe}^{2+} + 1.5 \text{ g H}_2\text{O}_2\), the findings show 83.9% COD removal. The changes in \(pH\) during the Fenton reaction time were also observed. Initially there was a gradual drop in \(pH\) due to the addition of FeSO\(_4\) catalyst which typically contains residual H\(_2\)SO\(_4\). A second, more pronounced drop in \(pH\) was observed as the H\(_2\)O\(_2\) is added. This \(pH\) change is often monitored to ensure that the reaction is progressing as planned and the absence of such a \(pH\) decrease indicates that the reaction is inhibited and that a potentially hazardous build-up of H\(_2\)O\(_2\) is occurring within the reaction mixture. This drop in \(pH\) is attributed to the fragmenting of organic material into organic acids\(^{21}\). The COD removal efficiency at existing wastewater \(pH\) (4.27) achieved was only 60% whereas at \(pH\) value of 6.4 for the same optimum Fenton dosage 0.2 g \(\text{Fe}^{2+} + 1.5 \text{ g H}_2\text{O}_2\) it shows more removal efficiency of 83.9%. For the study made at 4.27 \(pH\), the \(pH\) values dropped below 2. This drop in wastewater \(pH\) from 4.27 to below 2 after the addition of Fenton reagent resulted in lower COD removal efficiency, as low \(pH\) disfavors (below 3) Fenton reaction because of predominant side reactions like hydrogen abstraction, radical interaction (rather than desired Fenton reaction).

### Effect of mixing speed

The apparent advantage of Fenton reaction is that oxidation and coagulation processes take place simultaneously\(^{22}\). Fenton studies were carried out at
Effect of reaction time

The time needed to complete a Fenton reaction will depend on many variables such as wastewater pH, mixing speed, wastewater strength and most notably catalyst dose. From the previous experiments the Fenton dosage as well wastewater pH was optimized. Based on the results of these studies for finding the optimum reaction time, the wastewater pH was maintained at 6.4 with initial COD concentration of 4160 mg/L (1:1 dilution) and Fenton dosage applied was 0.2 g Fe$^{2+} + 1.5$ g H$_2$O$_2$ at a mixing speed of 25 RPM. It was observed that nearly 62% COD removal occurs during the first fifteen minutes of reaction time and further 22% additional COD removal takes place in the remaining 45 min of reaction time, resulting in 84.61% overall COD removal. This experiment showed that there was an initial rapid COD removal in first 15 min and then onwards it was gradual.

Effect of weight ratio

In Fenton’s reagent the H$_2$O$_2$ dosage used could be referred to as the stoichiometric weight ratio (R) between the hydrogen peroxide concentration used and the COD removed (R = H$_2$O$_2$/COD = 2.125), which are calculated assuming the complete oxidation of COD. For the present study R value was varied between 0.41 and 2.32. COD removal of 84.39% was obtained at Fenton dosage of 0.2 g Fe$^{2+} + 1.5$ g H$_2$O$_2$ over a time of 60 min at pH 6.4 for the weight ratio of 0.60, which is below the theoretical value of 2.125. This demonstrates the Fenton’s reagent ability to degrade a great amount of oxidizable organic matter present in coffee pulping wastewater.

Controlled experiments

Controlled experiments with addition of 0.2 g of iron (FeSO$_4$. 7H$_2$O) were conducted and the mixture was agitated for mixing period of 60 min at 25 rpm. Analysis of sample revealed the COD removal efficiency of 4.3% only. Controlled experiment only with hydrogen peroxide of 1.5 g (0.0440 M) resulted in COD removal efficiency of 16.3%. Thus, from these controlled experiments it was evident that removal efficiency of 84.61% achieved for Fenton dosage of 0.20 g of Fe$^{2+} + 1.5$ g H$_2$O$_2$ was due to the established Fenton reaction alone and not due to these individual chemical species.

Evolution of oxidation reduction potential (ORP) during Fenton reaction

ORP is reported to be a surrogate parameter for monitoring the Fenton reaction in a real time system. ORP values measured with respect to time own a characteristic performance at an early stage after the addition of the oxidizing agent H$_2$O$_2$, where a high increment of ORP occurs. Initial ORP value of the coffee pulping wastewater was 22 mV and after the addition of Iron sulfate hepta hydrate, the value increased to 32 mV. Further addition of H$_2$O$_2$ oxidizing agent increased the ORP value to 154 mV and accordingly decreased concentration of COD was observed which is in accordance with previous research work$^{13}$. This is due to the presence of species with a high oxidation potential such as hydroxyl radicals OH$^-$ in the reaction media. Further ORP value remained elevated for some time, while the oxidation process took place$^{15}$, absence of further change in ORP is the indication of the completion of the reaction. In addition during the Fenton experiments it was observed that wastewater becomes dark after H$_2$O$_2$ addition and clear up as the reaction progressed and reaches the completion$^{11}$.

Based on the results of various experiments a final study was made for wastewater with COD of 4100 mg/L at optimized conditions of 0.2 g Fe$^{2+} + 1.5$ g Fenton dosage, wastewater pH of 6.4, and 50 RPM mixing speed. Table 3 shows the results of Fenton experiment at optimized conditions. It can be

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before Fenton treatment</th>
<th>After Fenton treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg/L</td>
<td>4100</td>
<td>640</td>
</tr>
<tr>
<td>BOD, mg/L</td>
<td>475</td>
<td>184</td>
</tr>
<tr>
<td>BOD / COD</td>
<td>0.051</td>
<td>0.288</td>
</tr>
<tr>
<td>Ammonia nitrogen, mg/L</td>
<td>28</td>
<td>2.59</td>
</tr>
<tr>
<td>Nitrate nitrogen, mg/L</td>
<td>18</td>
<td>7.65</td>
</tr>
<tr>
<td>Phosphorous, mg/L</td>
<td>72</td>
<td>14</td>
</tr>
<tr>
<td>pH</td>
<td>6.75</td>
<td>3.3</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 3—Experimental results for optimized conditions
observed from the Table 3 that there was an increase in BOD to COD ratio and also considerable reduction in nitrogen and phosphorus concentration was observed. During this experiment 104 mL of sludge was produced for a settling time of 15 min.

Conclusion
Several experiments were done for optimizing the conditions for treatment of coffee pulping wastewater. From the experiments it is found that the Fenton dosage of 0.2 g Fe²⁺ + 1.5 g H₂O₂ with a molar ratio of 12.43 and at wastewater pH of 6.4 results in effective treatment of coffee pulping wastewater with COD conversion of 84.39%. The other pollution parameters such as ammonia nitrogen, nitrate nitrogen and phosphorus concentrations were less than 15 mg/L. From this study it is found that Fenton’s oxidation is a promising treatment process for coffee pulping wastewater which is generated during coffee pulping season. However, post treatment of Fenton’s treated wastewater is necessary and for that anaerobic biological treatment can be adopted.

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References