Distillery Waste Water Treatment by Advanced Oxidation Process

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ABSTRACT

Waste water produced from distillery containing highly color, COD, BOD, TDS and other organic matter. The hydroxyl radicals can be generated by different advanced oxidation processes Hydrogen peroxide combined with ultraviolet radiation (H₂O₂/UV), Fenton reagent (Fe²⁺/H₂O₂) be used for water and wastewater treatment for pollution removal. The effect of pH on % COD and Color Reduction from distillery waste comparing the various AOPs such as Fe²⁺/ H₂O₂ and UV/H₂O₂. The optimum value for pH 4 having very high efficiency of COD and decolorization of distillery waste water for all process which analyses by experimental observations. The optimum value of reaction time between 90-120 min for having very high efficiency of COD and decolorization of distillery waste water. For Fe²⁺/ H₂O₂ process % reduction of COD at 90 min is 85-90 %. For the UV/H₂O₂ process % COD and % Color reduction for the UV/H₂O₂ is 80-85% and 70-80% resp. The optimum value for both H₂O₂ and Fe²⁺ are 900 mg/l for all experimental processes. As the intensity of UV light increase the rate of photolysis of H₂O₂ increase. Optimum value of UV 400-450 nm after that rate of degradation reduced. Value of UV intensity should be λ< 450 nm.

Keywords – AOPs, Distillery Waste Water, Fe²⁺/ H₂O₂ and UV/H₂O₂, COD and Decolorization.

1. INTRODUCTION

Distillery waste water have very high Chemical Oxygen Demand (COD) and these effluents are environmental hazards when released in water bodies they cause oxygen depletion and associated problems. Spent wash produce from the distillery poses a serious threat to water quality in several regions of the country.

Various Conventional Methods

1. Biological flocculation
2. Nano filtration
3. Activated carbons
4. Bio electrochemical process
5. Ozonation-based process electro oxidation
6. Membrane-based Nano filtration
7. Reverse osmosis.
8. Aerobic and Anaerobic process
9. Electro Coagulation
10. Chemical Coagulation

Application of Advanced Oxidation Process

1. Chemical Industry
2. Pharmaceutical Industry
3. Pulp and Paper Industry
4. Textile Industry
5. Food Industry
6. Landfill Leachates
7. Biomedical Application
8. Dye-Process Industrial Waste
9. Pre-treatment to wastewater
10. Organic pollutant destruction
11. Toxicity reduction
12. Biodegradability improvement
13. BOD / COD removal

2. LITERATURE REVIEWS

The best operating conditions for the treatment of the distillery wastewater containing 43.85 mg/L BOD concentration and 274.28 mg/L COD concentration in the raw material was 2% H₂O₂ dosage at constant loadings of Fe²⁺ (1.5 g), 80 oC pretreatment temperature, and 1 h reaction time. At this optimized condition, the BOD content reduced to about 35 mg/L (about 21% removal) and COD content reduced to about 53 mg/L (about 81% removal). [8]. As per experimental analysis the influence of hydrogen peroxide concentration and pH on percentage color and COD removal of the distillery effluent has been studied. The concentration of H₂O₂ increases from 35 to 100 mM, the decolorization and COD removal are increased from 46.9 to 90 % and 34.8 to 83.3 % respectively. It is observed that pH increases from 1 to 7 the percentage color and COD removal increased from 48.78 to 96.43 % and 42.3 to 91.59 %, respectively. Further increasing the pH from 7 to 11, color and COD removal percentage decreased from 96.43 to 90.5% and 91.59 to 80.76%, respectively. As per observation Color and COD removal H₂O₂/Fe²⁺ 55-53%, UV/H₂O₂ 73-66% resp. [11]. As per experimental analysis by H₂O₂-FeSO₄ maximum removal efficiency is COD was observed at 120 ml H₂O₂ dosage 3.45 pH and 4 hour reaction time significant reduction in the COD value and removal efficiency to be 83.70%. The maximum removal efficiency was found to be occurring at 60 min that is 76.63%. FeSO₄ showed effective COD removal efficiency. [15].

3.1 Characteristics of Distillery Waste Water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4 - 4.5</td>
</tr>
<tr>
<td>TDS</td>
<td>65000-100000 mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>80000 -125000 mg/l</td>
</tr>
<tr>
<td>BOD</td>
<td>40000- 50000 mg/l</td>
</tr>
</tbody>
</table>

Table 3.1 Characteristics of DWW

3.2 Materials

1. Hydrogen Peroxide (H₂O₂)
   This is the strong oxidant and its application in the treatment of various inorganic and organic pollutants. H₂O₂ consist of two hydrogen molecules and two oxygen molecules.

2. Fenton’s Reagents (Fe salt/ FeSO₄ Solution).
   Metal salts (e.g. iron salts) which are strong oxidants that is the Fenton’s process. Fe³⁺ and Fe²⁺ is used to oxidation of H₂O₂ which decompose or cause of degradation of waste water. The amount of this Fenton reagent is based on amount of H₂O₂.

3. Acid or Alkali
   H₂SO₄ acid or NaOH alkali to be used for Ph maintain of waste water. The optimum Value of pH necessary for the Fenton process.

4. UV Light
   UV light is the oxidizing agent used for the process. 400-450 nm after that rate of degradation reduced.
   Value of UV intensity should be λ< 450 nm.

   Fenton Process (Fe²⁺ + H₂O₂)

Reaction Mechanism
The reaction of Fenton reagent and oxidizing agent H$_2$O$_2$. The generation of hydroxyl radicals following the chain reaction.

Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + OH$^-$ + OH$^-$

OH$^-$ + Fe$^{2+}$ $\rightarrow$ H + Fe$^{3+}$

As per reaction (1) and (2) the ferrous iron (Fe$^{2+}$) starts the reaction and catalyses the decomposition of H$_2$O$_2$ in hydroxyl radicals and newly formed ferric ions (Fe$^{3+}$) may decompose hydrogen peroxide in water and oxygen (forming ferrous ions and radicals)

Fe$^{3+}$ + H$_2$O$_2$ $\rightarrow$ FeOOH$^{2+}$ + H$^+$

Fe OOH$^{2+}$ $\rightarrow$ HO$^{2-}$ + Fe$^{2+}$

All of above reactions are the Fenton process which carried out step by step.

HO$^-$ + RH $\rightarrow$ H$_2$O + R$^-$

R$^-$ + Fe$^{3+}$ $\rightarrow$ R+ + Fe$^{2+}$

The organics (RH) are oxidized by hydroxyl radicals proton abstraction ending with the production of organics radicals (R$^+$).

**Fenton Treatment Procedures**

Fenton treatment procedure of waste water was carried out at ambient temperature in the following sequential steps.

1. 5-10 L of distillery waste water was put in a beaker and stirred for mixing.
2. Add known amount 35 Wt. % H$_2$O$_2$.
3. Add oxidizing agent 35 Wt. % H$_2$O$_2$ 0.5:1 or 1:1 proportion with Fenton reagent.
4. Amount of both agents between 200-900 mg/l volume was added in a single step.
5. After fixed reaction time before carrying out COD tests, pH was adjusted 3 to 4.
6. Settlement was achieved for 30 minutes and then examination of COD should be done.
7. After settlement check COD of sample per 15 min interval of time.
8. In between continuous stirring process will require.

**Photocatalytic Oxidation with UV/H$_2$O$_2$**

**Reaction Mechanism**

This process includes H$_2$O$_2$ injection and mixing followed by a reactor that is equipped with UV light (200 to 280 nm). During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. The reactions describing UV/H$_2$O$_2$ process are presented below.

H$_2$O$_2$+ uv→ 2 HO$^-$

H$_2$O$_2$ + HO$^-$→ HO$_2^-$ + H$_2$O

H$_2$O$_2$ + HO$_2^-$→ HO$^-$ + H$_2$O + O$_2$

2HO$^-$→ H$_2$O$_2$

2 HO$_2^-$→ H$_2$O + O$_2$

HO$^-$ + HO$_2^-$→ H$_2$O + O$_2$

**UV/H$_2$O$_2$ Treatment Procedures**

Treatment procedure of waste water was carried out at ambient temperature in the following steps.

1. 5-10 L of distillery waste water was put in a beaker and stirred for mixing.
2. Add known amount 35 Wt. % H$_2$O$_2$.
4. Amount of H$_2$O$_2$ between 200-900 mg/l volume was added in a single step.
5. Start the UV light by supply Ac current.
6. After fixed time of measure the take samples and calculate COD.
7. Also calculate reduction in Color from waste water with the help of spectrophotometer.
8. Settlement was achieved for 30 minutes.
9. Sample should take after settlement for COD and Color measurement.
10. In between continuous stirring process will require.

RESULTS AND DISCUSSION

Effect of Reaction Time on COD Reduction

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>% Reduction COD with 0.5:1</th>
<th>% Reduction COD with 1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>42</td>
<td>52</td>
</tr>
<tr>
<td>45</td>
<td>56</td>
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<td>68</td>
<td>90</td>
</tr>
<tr>
<td>90</td>
<td>68</td>
<td>90</td>
</tr>
</tbody>
</table>

Table Effect of pH for Fenton Process

<table>
<thead>
<tr>
<th>pH</th>
<th>% Reduction COD with 0.5:1</th>
<th>% Reduction COD with 1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td>2.5</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>3.5</td>
<td>65</td>
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<td>4</td>
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<td>72</td>
<td>80</td>
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<td>6.5</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>7.5</td>
<td>60</td>
<td>65</td>
</tr>
</tbody>
</table>

Effect of pH on % COD Reduction DWW for Fenton Process

Table shows the effect reaction time at different proportions of $\text{H}_2\text{O}_2$:$\text{Fe}^{2+}$ for $\text{Fe}^2$/ $\text{H}_2\text{O}_2$ Process on % COD Reduction of distillery waste. As per observation table comparing as proportions of $\text{H}_2\text{O}_2$:$\text{Fe}^{2+}$ for $\text{Fe}^2$/ $\text{H}_2\text{O}_2$ process % COD Reduction is more with 1:1 is increase with reaction time. As per table comparing as proportions of $\text{H}_2\text{O}_2$:$\text{Fe}^{2+}$ for $\text{Fe}^2$/ $\text{H}_2\text{O}_2$ process % COD Reduction is more with 1:1. optimum Reaction time is 90 – 120 Min.

Effect of pH on % COD Reduction DWW for Fenton Process

Table shows effect of pH at different proportions of $\text{H}_2\text{O}_2$ : $\text{Fe}^{2+}$ for $\text{Fe}^2$/ $\text{H}_2\text{O}_2$ Process on % COD Reduction of distillery waste. As per observation table comparing as proportions of $\text{H}_2\text{O}_2$ : $\text{Fe}^{2+}$ % COD Reduction is more with 1:1.
COD and color decrease. The optimum pH for maximum COD and color reduction is 4.

**Effect of Reaction Time on COD and Color DWW UV/H\(_2\)O\(_2\) Process**

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>% Reduction COD with UV/H(_2)O(_2)</th>
<th>% Reduction Color with UV/H(_2)O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>30</td>
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<td>90</td>
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<td>80</td>
</tr>
<tr>
<td>120</td>
<td>86</td>
<td>82</td>
</tr>
</tbody>
</table>

**Table Effect of Reaction Time on % COD and Color Reduction with UV/H\(_2\)O\(_2\)**

Table shows the Effect of Reaction Time on % COD Reduction and Color on distillery waste water with UV/H\(_2\)O\(_2\) . As Reaction Time increase % Reduction COD and Color increase up to 120 min. The optimum reaction time is 90 min for UV/H\(_2\)O\(_2\).

**CONCLUSION**

The effect of pH, UV light, Reaction Time, Fe\(^{2+}\) and H\(_2\)O\(_2\) on % COD and Color Reduction from distillery waste water for processes Fe\(^{2+}/\) H\(_2\)O\(_2\) and UV/H\(_2\)O\(_2\) Oxidation by using UV/H\(_2\)O\(_2\) have high removal efficiency COD and Color Reduction from distillery waste. The effect of pH on % COD and Color Reduction from distillery waste comparing the various AOPs such as Fe\(^{2+}/\) H\(_2\)O\(_2\) and UV/H\(_2\)O\(_2\) The optimum value for pH 4 having very high efficiency of COD and decolorization of distillery waste water for all process which analyses by experimental observations. As per observation effect of Reaction Time on % COD and Color Reduction from distillery waste for processes Fe\(^{2+}/\) H\(_2\)O\(_2\) and UV/H\(_2\)O\(_2\). The optimum value of time between 90-120 min for having very high efficiency of COD and decolorization of distillery waste water. As per observation study optimum amount of H\(_2\)O\(_2\) obtained is 600-900 mg/l of waste water treated. As intensity of UV light increase the rate of photolysis of H\(_2\)O\(_2\) increase. Optimum value of UV 400-450 nm after that rate of degradation reduced. Value of UV intensity should be \(\lambda< 450\) nm.

**REFERENCES**

2. A. H. Mahvi, Application of Ultrasonic Technology for Water and Wastewater Treatment, School of Public Health and Center for Environmental Research, Tehran University of Medical Sciences, Iran.
3. Anna Goi, Advanced Oxidation Processes for Water Purification and Soil Remediation, Faculty of Chemical and Materials Technology Department of Chemical Engineering Tallinn University.

7. A.S. Stasinakis, Use of Selected Advanced Oxidation Processes (AOPs) For Wastewater Treatment – A Mini Review, Water and Air Quality Laboratory, Department of Environment University of the Aegean, University Hill, 81100, Greece.

8. Augustine O. Ayeni1, Termitary E. Oladimeji, Distillery Wastewater Decontamination by the Fenton Advanced Oxidation Method Department of Chemical Engineering, College of Engineering, Covenant University, Canaan land Ota, Nigeria, IJRES, ISSN (Online): 2320-9364.


14. Mie Mie Han Htun and Ei Thiri Khaing, Distillery Waste Water Treatment using Photo-catalytic UV-TiO2 System, Professor and Research Scholor, Department of Chemical Engineering, Mandalay 05072, Mandalay Technological University Mandalay City, Mandalay State Myanmar, IJASRE, Volume 5, November – 2019.

15. Vinutha N and Dr. D P Nagarajappa, Fenton’s Oxidation of Distillery Spent Wash, P G Student and Professor, Department of Studies in Civil Engineering, U B D T College of Engineering, Davanagere, IJTSE Vol. 6, 2019, ISSN 2349-0780.