COD REDUCTION OF WASTE WATER STREAMS OF ACTIVE PHARMACEUTICAL INGREDIENT - IBUPROFEN BY ADVANCED OXIDATION-FENTON PROCESS BASED ON H$_2$O$_2$/Fe$^{+2}$ SALT

Shiaikh Shahid and *Sayyed Hussain

Sir sayyed college of Arts Commerce and Science, Roshangate, Aurangabad. (M.S.) 431001.

ABSTRACT

Active Pharmaceutical Intermediates in waste waters is emerging contaminants in the aquatic environment because of their adverse effect on aquatic life and Environment. The API have high COD value Ibuprofen and low BOD$_3$ and hence difficult to treat biologically. In this study, advanced oxidation processes (AOPs) utilizing the H$_2$O$_2$/Fe$^{+2}$, Fenton, reactions were investigated in lab-scale experiments for the degradation of Ibuprofen containing waste water streams. The experimental results showed that the Fenton process using H$_2$O$_2$/Fe$^{+2}$ was the most effective treatment process. With Fenton processes, COD Reduction of wastewater can be achieved successfully. It is suggested that Fenton processes are viable techniques for the degradation of from the Waste water stream with relatively low toxicity of the by-products in the effluent which can be easily biodegradable in the activated sludge process, and other less degraded streams with high total dissolved solids can be taken to multiple effect evaporator or Reverse osmosis. In addition, study the degradation of Ibuprofen by advanced oxidation Fenton process under optimum conditions. The Fenton process with H$_2$O$_2$/Fe$^{+2}$ is considered a suitable pretreatment method to degrade the Active pharmaceutical molecules and improve the biodegradability of the waste water.

Keywords: Oxidation, Fenton, Biodegradability.

INTRODUCTION

Due to high consumptions of the API by the human being lot of API are passing from the manufacturing units to the environment through the waste water discharged from the factories. This is due to the low biodegradability of the API molecules. In the past two
decades, advanced oxidation processes (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic Contaminants. Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical (OH) generation as the primary oxidant (second highest Powerful oxidant after the fluorine) Hydroxyl radicals are non-selective in Nature and they can react without any other additives with a wide range of contaminants. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization.

This paper aims at studying the effect of the operating conditions (pH, H₂O₂/Fe²⁺ ratio, reaction time) of the advanced oxidation processes using H₂O₂/Fe²⁺ for the different waste water streams containing Ibuprofen and Ibuprofen spiked water. The H₂O₂/Fe²⁺ is used as the oxidant. The optimum conditions of the Fenton process were tried for different Ibuprofen containing waste water streams.

MATERIALS AND METHODS

Reagents: Spiked waste water streams of Ibuprofen, Hydrogen peroxide solution (33%, w/w), Heptahydrated Ferrous sulfate (FeSO₄·7H₂O) were all commercial grade. All reagents employed were not subjected to any further treatment. Distilled water used throughout as diluents. Compressed air was used from small compressor

Experimental set-up: All experiments were performed in a Round bottom flask in laboratory. Compressed air was used for purging to keep the reaction mass mixing. The addition of the H₂O₂ and ferrous sulphate was done manually at Room temp. The reaction was carried in batch mode for each of the above stream separately.

Molecular structure of Ibuprofen

```
[Chemical structure of Ibuprofen]
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<table>
<thead>
<tr>
<th><strong>Formula</strong></th>
<th>C₁₃H₁₈O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mol. mass</strong></td>
<td>206.29 g/mol</td>
</tr>
</tbody>
</table>
C13H18O2.

**Fenton Reaction:** After addition of the iron and the hydrogen peroxide, they are going to react together to generate some hydroxyl radicals as it shows in the following equations:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + .\text{OH} + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + .\text{OOH} + \text{H}^+
\end{align*}
\]

After that the hydroxyl radicals are going to react with the pollutants to oxidize its. Actually the hydroxyl radicals can react according 4 kinds of reactions with the pollutants:

- Addition: \(\cdot\text{OH} + \text{C}_6\text{H}_6 \rightarrow (\text{OH})\text{C}_6\text{H}_6\)
- Hydrogen Abstraction: \(\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}\)
- Electron Transfer: \(\cdot\text{OH} + [\text{Fe(CN)}_6]^{4-} \rightarrow [\text{Fe(CN)}_6]^{3-} + \text{OH}^-\)
- Radical Interaction: \(\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2\)

During the Fenton's reaction all the parameters are adjusted to promote the two first kind of reaction between the pollutant and the hydroxyl radicals.

**Analytical method:** After the completion of the reaction time, the samples were removed from RBF and the samples were made alkaline (pH-10-12) using Sodium Hydroxide. These removed samples were digested for 1 hrs on hot water bath and kept overnight and then filtered to remove the insoluble ferric hydroxide. The filtrate collected was used for estimation of COD by Open Reflux Method as given below. APHA methods were used for COD analysis; The COD was determined by an open reflux method (Eaton, 1995). The sample was refluxed with a known excess of potassium dichromate for two hours. After digestion, the excess dichromate was titrated against standard ferrous ammonium sulfate.

**RESULTS AND DISCUSSION**

The results of Fenton process for Pure-spiked Ibuprofen containing water stream are as below Table No 1:

<table>
<thead>
<tr>
<th>Effluent qty-Furosemide spiked water(500mg/lit)</th>
<th>pH</th>
<th>Initial COD(mg/lit)</th>
<th>H2O2 (ml)</th>
<th>FeSO4 (gms)</th>
<th>COD after 4 Hrs (mg/lit)</th>
<th>Percentage Reduction of COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ml</td>
<td>2.0</td>
<td>1080</td>
<td>10</td>
<td>1.0</td>
<td>600</td>
<td>44.45</td>
</tr>
<tr>
<td>500 ml</td>
<td>2.0</td>
<td></td>
<td>15</td>
<td>1.5</td>
<td>480</td>
<td>55.56</td>
</tr>
<tr>
<td>500 ml</td>
<td>2.0</td>
<td></td>
<td>20</td>
<td>2.0</td>
<td>440</td>
<td>59.26</td>
</tr>
<tr>
<td>500 ml</td>
<td>2.0</td>
<td></td>
<td>25</td>
<td>2.5</td>
<td>360</td>
<td>66.67</td>
</tr>
</tbody>
</table>
From the table No 1, it is observed that the Ibuprofen Spiked water is degraded with the advanced oxidation process. The max COD reduction was found to be 66.67% with the peak condition of H$_2$O$_2$ at 25 ml and Ferrous sulphate at 2.5gms in four hour duration. From the above it is concluded that the Furosemide molecule can be successfully degraded from the water with the application of the advanced oxidation Fenton Process.

The COD reduction for the above water spiked with Ibuprofen is about 66.67% by the Fenton process and the trials were highly encouraging.

**Table No 1.1**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>T.No</th>
<th>Qty of H$_2$O$_2$-ML</th>
<th>Qty of FeSO$_4$-Gms</th>
<th>COD Initial- Mg/Lit</th>
<th>COD After 4 hrs-Mg/Lit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10</td>
<td>0.25</td>
<td>720</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>10</td>
<td>0.5</td>
<td>540</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>10</td>
<td>1</td>
<td>380</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>10</td>
<td>1.5</td>
<td>475</td>
<td>56</td>
</tr>
</tbody>
</table>
From the table No 2.it is evident that the COD reduces with respect to time. The COD reduction with T-4 conditions is maximum with COD reduction upto 66.67 percentage.

**Table No 2.0**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Trial No</th>
<th>Qty of H2O2-ML</th>
<th>Qty of FeSO4-Gms</th>
<th>Volume of spiked sample</th>
<th>Spiked Impurity-mg/Lit</th>
<th>COD Initial-Mg/Lit</th>
<th>Time in Hrs</th>
<th>COD After Mg/Lit</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>25</td>
<td>2.5</td>
<td>500</td>
<td>1080</td>
<td>1</td>
<td>900</td>
<td>16.67</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>25</td>
<td>2.5</td>
<td>500</td>
<td>2</td>
<td>680</td>
<td>37.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>25</td>
<td>2.5</td>
<td>500</td>
<td>3</td>
<td>560</td>
<td>48.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>25</td>
<td>2.5</td>
<td>500</td>
<td>4</td>
<td>360</td>
<td>66.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table No 2.1 shows the hourly COD reduction, with COD reduction completes maximum at 4 hours and COD reduction in 4 hours is 140 mg/lit i.e. reduction of 66.67 percentage

Further trials are required to establish the final outcome for the COD reduction of actual waste water streams containing Ibuprofen as an Active Pharmaceutical Ingredient.

Table No 3.

<table>
<thead>
<tr>
<th>T.N O</th>
<th>Initial COD(mg/l)</th>
<th>H2O 2(ml)</th>
<th>pH</th>
<th>FeSO 4(gms)</th>
<th>COD after 4 Hrs (mg/lit)</th>
<th>Percentage Reduction of COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1</td>
<td>1080</td>
<td>25</td>
<td>1.0</td>
<td>2.5</td>
<td>680</td>
<td>37</td>
</tr>
<tr>
<td>T-2</td>
<td>1080</td>
<td>25</td>
<td>2.0</td>
<td>2.5</td>
<td>340</td>
<td>69</td>
</tr>
<tr>
<td>T-3</td>
<td>1080</td>
<td>25</td>
<td>3.0</td>
<td>2.5</td>
<td>560</td>
<td>48</td>
</tr>
</tbody>
</table>

From the above table it is evident that the rate of the degradation of the Ibuprofen molecule is maximum at pH 2.0. At pH-2 the maximum COD reduction is upto 69 Percentage

Graph No 3.1.

1) **Effect of Reaction Time:** Seventy percentage of the COD reduction is completed in about four hours. The rate of COD reduction with different ratios of Hydrogen Peroxide and Ferrous sulphate at acidic Ph is as shown in the table No .1. The correct rate of reaction will require further trials beginning from 1 hrs to 12 hrs. Also the rate of reaction for actual effluent samples is to be explored.
2) **Effect of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) Ratio:** The COD reduction is maximum with the Hydrogen peroxide at 25 ml and Ferrous sulphate at 2.5 gms

3) **Effect of PH:** The rate of the reaction is maximum at pH-2, which is evident from the Table No 3.0 and Graph 3.1. Aslo it shows that as the pH is raised the COD reduction decreases.

**CONCLUSION**
1. With the above trial on the spiked water with Ibuprofen and advanced oxidation Fenton process on it shows about 66.67 % COD reduction.
2. The said method is very efficient, economical, and robust and can be reproduced at large scale level for the reduction of COD from the Ibuprofen waste water stream.
3. This process can be used as an pretreatment to activated sludge process, thereby making the biodegradability easy in aeration tank of the activated sludge process.
4. The pre Fenton treatment for Ibuprofen waste water stream can help in reducing the ETP construction const as the COD load to ETP will be reduced with the application of fenton process.

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**REFERENCES**