Chemical oxygen demand(COD) reduction of Aqueous Active Pharmaceutical Ingredient of Isorobide 5-mononitrate waste water streams by Advanced Oxidation-Fenton process based on H_2O_2/Fe^{+2} salt

Sayyed Hussain[a*], Shahid Shaikh[a] and Mazahar Farooqui[b]

[a]*Sir Sayyed College, Aurangabad*
[b]*Post Graduate and Research Centre, Maulana Azad College, Aurnagabad*

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ABSTRACT

Active Pharmaceutical Intermediates from waste water streams of API companies are emerging contaminants in the aquatic environment, because of their adverse effect on aquatic life and humans. These contaminants are high in COD and difficult to treat biologically. In this study, advanced oxidation processes (AOPs) utilizing H_2O_2/Fe^{+2}, Fenton reactions were investigated in lab-scale experiments for the COD degradation of different waste water streams of Active Pharmaceutical Intermediates -ISMN (Isosorbide 5- Mononitrate) . The experimental results showed that the Fenton process using H_2O_2/Fe^{+2} was the most effective Pre treatment process for waste water streams before Activated sludge 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 Active Pharmaceutical Intermediates- ISMN (Isosorbide 5- Mononitrate) 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.
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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[1-8] Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical

169

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($\cdot$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,H_2O_2/Fe^{+2} ratio, reaction time) of the advanced oxidation processes using H_2O_2/Fe^{+2} for the different waste water streams containing Isosorbide 5- Mononitrate and Isosorbide 5- Mononitrate spiked water. The H_2O_2/Fe^{+2} is used as the oxidant. The optimum conditions of the Fenton process were tried for different Isosorbide 5- Mononitrate containing waste water streams.

MATERIALS AND METHODS

**Wastewater Characterization:** The characteristics of waste water streams are given in the table1.

Table 1:Characterstic of different waste water streams from the ISMN Manufacturing Unit:

Waste Stream	PH	COD(mg/lit)	TDS (mg/lit)	Chlorides(mg/lit)	Atenolol (%)
Sorbitol distillate distillate	4.05	26697	2230	1278	
Acetate wash	5.13	456276	2620	1207	
Acidic layer	1.18	291240	25860	16330	< 0.30
Caustic layer	6.50	81702	2330	1420	< 0.35
Salt layer	4.33	46598	295070	20179	< 0.40

Reagents: Waste water streams of Active Pharmaceutical Intermediates ISMN (Isosorbide 5- Mononitrate) Manufacturing unit. Hydrogen peroxide solution (33%, v/v) Heptahydrated ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were all commercial grade. All reagents employed were not subjected to any further treatment. Water used throughout was form distillation. 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 H_2O_2 and ferrous sulphate was done manually at room temp.The reaction was carried in batch mode for each of the above stream separately and in combination with the proportion ratio equal to the actual generation

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:

$$Fe^{2+} + H_2O_2 ----> Fe^{3+} + \cdot OH + OH^-$$
$$Fe^{3+} + H_2O_2 ----> Fe^{2+} + \cdot OOH + H^+$$

170

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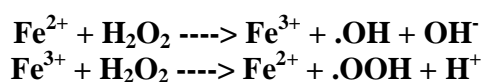
After that the hydroxyl radicals are going to react with the pollutants to oxidize its. Actually the hydroxyl radicals can react according 4 kinds of reactions with the pollutants:

- Addition: $^{\cdot}OH + C_6H_6 ----> (OH)C_6H_6$
- Hydrogen Abstraction: $OH + CH_3OH ----> CH_2OH + H_2O$
- Electron Transfer: $^{\cdot}OH + [Fe(CN)_6]^{4-} ----> [Fe(CN)_6]^{3-} + OH^{-}$
- Radical Interaction: $^{\cdot}OH + {}^{\cdot}OH ----> H_2O_2$

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.

Molecular structure of Isosorbide -5-Mononitrate:
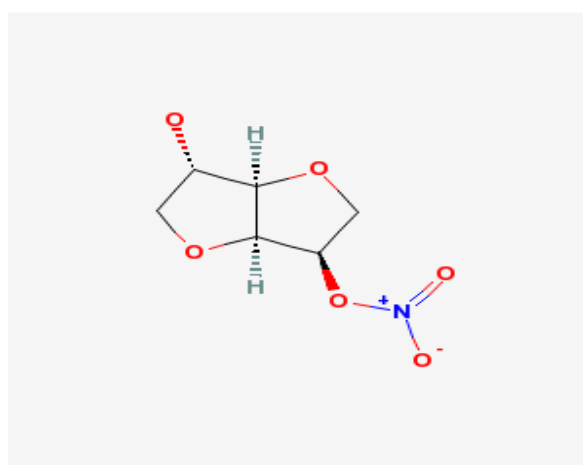
Analytical method: After the completion of the reaction time, the samples were removed from RBF and the samples were made alkaline (pH-10-12) using sodium hydroxide. These removed samples were digested for 1 hrs on hot water bath and kept overnight and then filtered to remove the insoluble ferric hydroxide. The filtrate collected was used for estimation of COD by Open Reflux Method as given below.APHA 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

Table: 2 COD reduction with variation of H₂O2 and FeSO4

T.NO	Initial COD (mg/l)	H$_2$O$_2$ (ml)	pH	FeSO4(gm)	COD after 4 hrs (mg/lit)	Percentage Reduction of COD
T-1	571	10	2.0	1.0	222	61
T-2	571	15	2.0	1.5	122	78.6
T-3	571	20	2.0	2.0	100	82.4
T-4	571	25	2.0	2.5	72	87.3

171

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It is observed that(table 1) the ISMN spiked water is degraded with the advanced oxidation process. The maximum COD reduction was found to be 87.3% with the peak condition of H_2O_2 at 25 ml and ferrous sulphate at 2.5gm in four hour duration. Therefore it is concluded that the ISMN molecule can be successfully degraded from the water with the application of the advanced oxidation Fenton Process.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 87.3 percentage.

Table 3:Effect of variation of $FeSO_4$ on COD reduction

Sr.No	Qty of H_2O_2-ml	Qty of $FeSO_4$-gm	COD Initial-mg/Lit	COD After 4 hrs-mg/lit
1	10	0.25	571	340
2	10	0.5		275
3	10	1		100
4	10	1.5		135

COD reduction at 10 ml of hydrogen peroxide and varying concentration of ferrous sulphate is shown in table 3. It is clear that the maximum COD reduction is achieved at 10 ml of H_2O_2 and 1.0 gm FeSO4.

Table 4: COD reduction with time

Sr.No	Qty of H_2O_2-ml	Qty of $FeSO_4$-gm	Volume of spiked sample	Spiked Impurity-mgl	COD Initial-mg/l	Time in hrs	COD mgl	% Reduction
1	25	2.5	500	ISMN		1	120	79
2	25	2.5	500	ISMN	571	2	110	80
3	25	2.5	500	ISMN		3	100	81
4	25	2.5	500	ISMN		4	60	89

The hourly COD reduction, with COD reduction completes maximum at 4 hours and COD reduction in 4 hours is 60 mg/lt i.e. reduction of 89 percentage(table 4).

Table 5: Effect of pH on COD reduction

T. NO	Initial COD (mg/l)	H_2O_2 (ml)	pH	$FeSO_4$ (gm)	COD after 4 hrs (mg/lit)	Percentage Reduction of COD
T-1	571	25	1.0	2.5	120	79
T-2	571	25	2.0	2.5	100	82.5
T-3	571	25	3.0	2.5	280	51

From the table5 it is evident that the rate of the degradation of the ISMN molecule is maximum at pH 2.0.The COD reduction for the above waste water stream is about 81 % by the Fenton process and the trials were highly encouraging. Fenton process is to be explored on waste water streams containing ISMN are required to establish for the final outcome.

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CONCLUSION

1. The said method is very efficient, economical, robust and can be reproduced at large scale level for the reduction of COD from the ISMN waste water stream.

2. With the above trial on the spiked water with ISMN and advanced oxidation Fenton process on it shows about 87 % COD reduction.

3. The said method is very efficient, economical, and robust and can be reproduced at large scale level for the reduction of COD from the ISMN waste water stream.

4. This process can be used as a pretreatment to activated sludge process, thereby making the biodegradability easy in aeration tank of the activated sludge process.

5. The pre Fenton treatment for ISMN waste water stream can help in reducing the ETP construction cost as the COD load to ETP will be reduced with the application of Fenton process.

6. Fenton process can be successfully implemented to many API manufacturing factories which will help in curbing the land and water pollution.

7. The Ferric oxide waste generated can be isolated and disposed to hazardous waste facility as landfill

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