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Chemical oxygen demand reduction of Aqueous Active Pharmaceutical Ingredient - Furosemide waste water streams using Advanced Oxidation-Fenton process based on H_2O_2/Fe^{+2} salt

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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 and low BOD_3 and hence difficult to treat biologically. In this study, advanced oxidation processes (AOPs) utilizing the H_2O_2/Fe^{+2} , Fenton, reactions were investigated in lab-scale experiments for the degradation of Furosemide containing waste water streams. The experimental results showed that the Fenton process using H_2O_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 Furosemide 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 Furosemide by advanced oxidation Fenton process under optimum conditions. The Fenton process with H_2O_2/Fe^{+2} is considered a suitable pretreatment method to degrade the Active pharmaceutical molecules and improve the biodegradability of the waste water.

Key words: COD reduction, Fenton Process, Advanced Oxidation Process.

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 Contaminants¹⁻⁵. 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 contaminants⁶⁻⁹. 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/Fe⁺² ratio, reaction time) of the advanced oxidation processes using H₂O₂/Fe⁺² for the different waste water streams containing Furosemide and Furosemide spiked water. The H₂O₂/Fe⁺² is used as the oxidant. The optimum conditions of the Fenton process were tried for different furosemide containing waste water streams.

MATERIALS AND METHODS

2.1. Wastewater Characterization: The characteristics of waste water of different streams from furosemide has been given in table 1.

Table 1: Properties of waste water streams from the Furosemide Manufacturing Unit

Waste Stream	pH	COD(mg/lit)	TDS (mg/lit)	Furosemide %
Acidic Main ML	Acidic	10780 - 12000	25000-40000	0.035
Acidic washing ML Washing	Acidic	10000-12000	8000-10000	0.055
Second crop ML	Neutral	67000 - 78000	67000-60000	0.5

Reagents: Waste water streams of Furosemide Manufacturing unit, spiked water with Furosemide. 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.

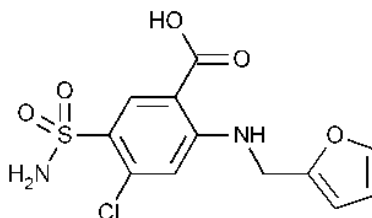
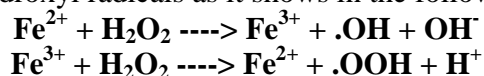


Fig 1: Molecular structure of Furosemide

The chemical name of furosemide is 4-Chloro-N-furfuryl-5-sulfamoylanthranilic acid.

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:



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

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 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 Furosemide containing water stream are as below:

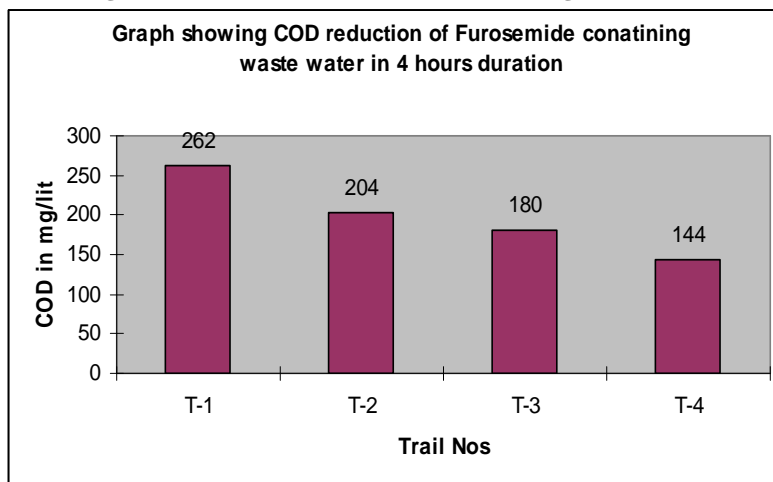
Table 2: COD reduction after four hours

Effluent qty-Furosemide spiked water(500mg/lit)	pH	Initial COD (mg/lit)	H ₂ O ₂ (ml)	FeSO ₄ (g)	COD after 4 Hrs (mg/lit)	Percentage Reduction of COD
500 ml	2.0	469	10	1.0	262	45
500 ml	2.0	469	15	1.5	204	57
500 ml	2.0	469	20	2.0	180	62
500 ml	2.0	469	25	2.5	144	70

From the table 2, it is observed that the Furosemide Spiked water is degraded with the advanced oxidation process. The max COD reduction was found to be 70 % with the peak condition of H₂O₂ 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 Furosemide is about 70 % by the Fenton process and the trials were highly encouraging.

Fig 2 COD reduction of furosemide containing waste water



From fig 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 70.0 percentage.

Table 3:Variation of COD reduction FeSO₄

Sr. No	Qty of H ₂ O ₂ -ml	Qty of FeSO ₄ g	COD Initial-mg/l	COD After 4 hrs-mg/l
1	10	0.25	469	440
2	10	0.5		400
3	10	1		268
4	10	1.5		294

Fig 3: Effect of varying concentration of ferrous sulphate on COD reduction

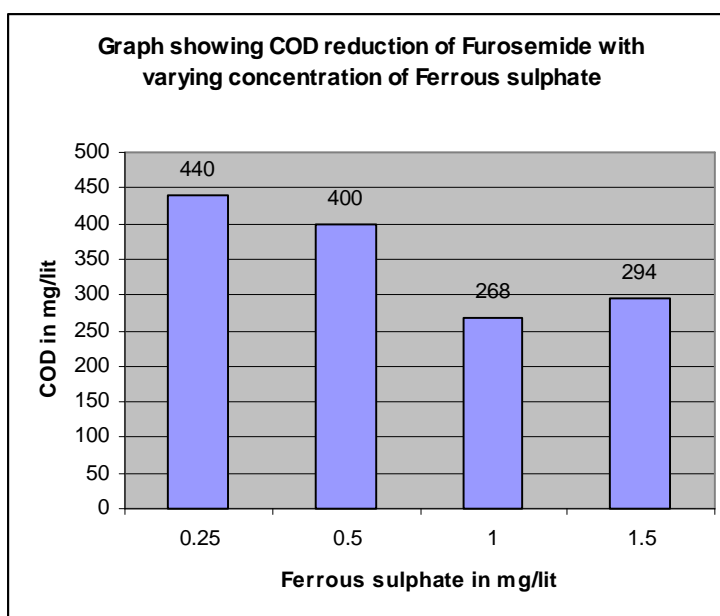


Table 3 showing COD reduction at 10 ml of Hydrogen peroxide and varying concentration of Ferrous Sulphate.

Table 4: Effect of variation of time on COD reduction

Sr. No	Qty of H ₂ O ₂ -ml	Qty of FeSO ₄ g	Volume of spiked sample	Spiked Impurity-mg/l	COD Initial-Mg/l	Time in hrs	COD After 4 Hrs mg/l	% Reduction
1	25	2.5	500	Furosemide	469	1	230	51
2	25	2.5	500	Furosemide		2	200	57
3	25	2.5	500	Furosemide		3	180	62
4	25	2.5	500	Furosemide		4	140	70

From the table 4.it is evident that the COD reduces with respect to time. The COD reduction is maximum upto 70 percentage.

Fig 4: Variation of COD with time

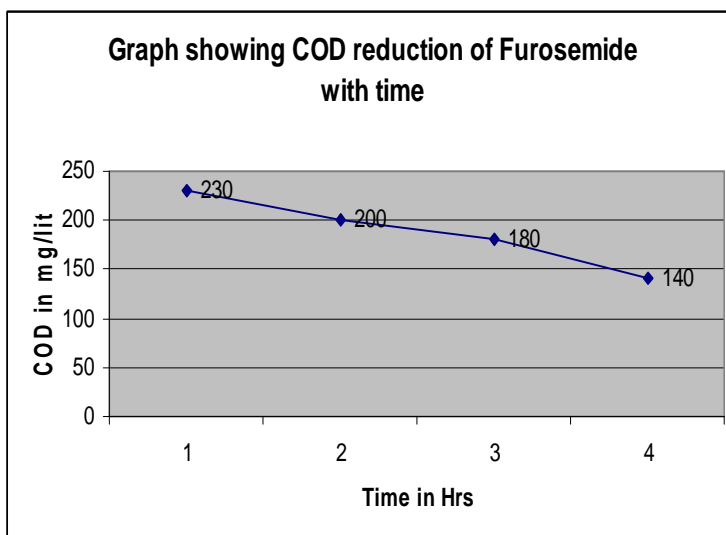


Fig4 shows the hourly COD reduction, with COD reduction completes maximum at 4 hours and COD reduction in 4 hours is 140 mg/lit i.e. reduction of 70 percentage

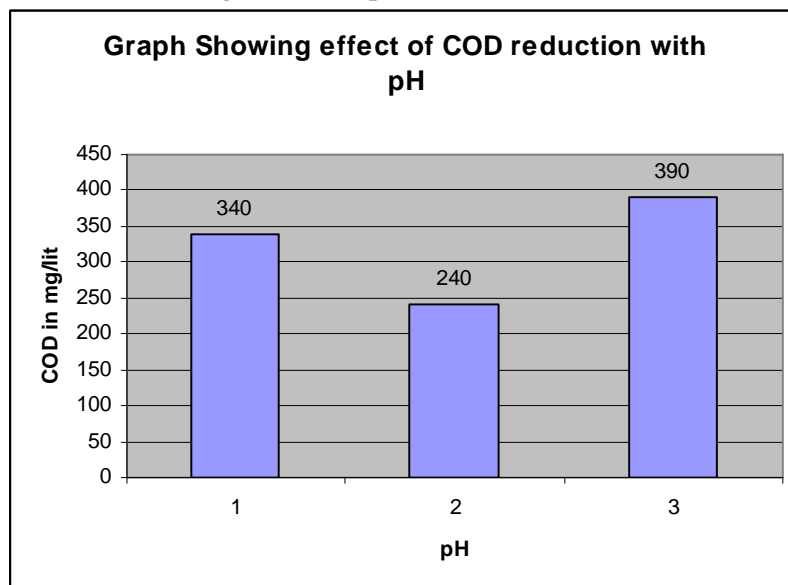
Further trials are required to establish the final outcome for the COD reduction of actual waste water streams containing Furosemide as an Active Pharmaceutical Ingredient.

Table 5: COD reduction with pH of the waste water streams

Sr No	Initial COD (mg/l)	H ₂ O ₂ (ml)	pH	FeSO ₄ (g)	COD after 4 Hrs (mg/lit)	Percentage Reduction of COD
1	571	25	1.0	2.5	340	41
2	571	25	2.0	2.5	240	58
2	571	25	3.0	2.5	390	32

From the above table it is evident that the rate of the degradation of the Furosemide molecule is maximum at PH 2.0. At pH-2 the maximum COD reduction is upto 58 Percentage

Fig 5: Effect of pH on COD reduction



CONCLUSION

1. With the above trial on the spiked water with Furosemide and advanced oxidation Fenton process on it shows about 70 % 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 Furosemide waste water stream.
3. 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.
4. The pre Fenton treatment for Furosemide 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.

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