

Fenton's Reagent for the Treatment of Pharmaceutical Industry Wastewater

Ronak Shetty¹, Shweta Verma²

¹Savitribai Phule Pune University, D.Y. Patil College of Engineering, Akurdi,
Department of Civil Engineering, Pune, Maharashtra, India

²Savitribai Phule Pune University, D.Y. Patil College of Engineering, Akurdi,
Department of Civil Engineering, Pune, Maharashtra, India

Abstract: *Pharmaceutical industry often generates highly toxic wastewater and sludge depending upon the used manufacturing process and season. The high BOD to COD ratio of this particular wastewater makes biological treatment difficult. Hence chemical treatment proves to be a useful option. Fenton's reagent is used in the treatment of pharmaceutical industry wastewater in this study. The ferrous and hydrogen peroxide were used in the molar ratio of 1:1, 1:2 and 1:3. Ferrous was added in the form of ferrous sulphate. A reaction time of one hour was provided. A magnetic stirrer was used for mixing the Fenton's reagent and the wastewater sample. Different doses of hydrogen peroxide and ferrous sulphate was added as per the ratio decided. 82% reduction of COD was observed at 3267 mg/L of ferrous sulphate and 800 mg/L of hydrogen peroxide for 1:1 ratio. For a ratio of 1:2 an efficiency of 85% COD reduction was observed at doses of 3675 mg/L of ferrous sulphate and 900 mg/L of hydrogen peroxide. For ratio of 1:3 the maximum reduction of COD was observed in doses of 2450 mg/L of ferrous sulphate and 900 mg/L of hydrogen peroxide. Based on these dosages the removal of other parameters of wastewater like phenol, heavy metals, total phosphates, total dissolved solids and ammonia nitrogen were analyzed. The ferrous sludge generated has good settling characteristics and has potential for recovery of iron.*

Keywords: Fenton's Reagent, Advance oxidation process, hydrogen peroxide, Fenton's chemistry.

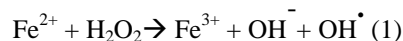
1. Introduction

The oxidation of organic substrates by ferrous and hydrogen peroxide is Fenton's reaction. This reaction was first observed by H.J.H. Fenton who first observed the oxidation of tartaric acid by hydrogen peroxide in the presence of ferrous ions. The application of Fenton's reagent came to existence 110 years after its discovery. Since then Fenton's reagent is used in treating different wastewaters. Some of these include aromatic amines, textile dyes, pesticides, surfactants and explosives [1].

Generation of wastewaters in industrial processes is unavoidable and a process to reduce the organic load and other contaminants must be employed before water is discharged. To remove part of the organic load, biological processes are usually used. In some cases, however, due to the high organic load, toxicity or presence of bio-recalcitrant compounds, biological processes cannot be used, since no chemical oxygen demand (COD) removal is achieved biologically. For these wastewaters, the biochemical oxygen demand (BOD) is much lower than the COD. Thus, a biological treatment is not feasible. In these cases, chemical pre-treatment can adequately reduce the COD prior to biological treatment [2].

Among the chemical processes, advance oxidation process can efficiently reduce organic loading. Advance oxidation processes are based on the generation of hydroxyl radical. The hydroxyl radical is second strongest oxidizing agent next to fluorine [3]. This radical can be generated by a number of processes. One such process is the Fenton's process. The Fenton's reaction consists of ferrous salts combined with hydrogen peroxide under acidic conditions.

The reaction is as follows:



The efficiency of Fenton's reaction depends on pH, temperature, ferrous to hydrogen peroxide ratio and iron concentration. Fenton's reaction works in a pH range that is in between 2 and 6 [1-5]. The aim of the present study is to reduce the chemical oxygen demand from pharmaceutical wastewater and to decide the suitable dose of hydrogen peroxide and ferrous for maximum reduction of COD and to check the suitability of Fenton's reagent to treat other wastewater parameters.

2. Materials and Methods

2.1 Chemicals

1% Ferrous sulphate, 30% Hydrogen peroxide (as commercially available), 10% sulfuric acid, 1N sodium hydroxide.

2.2 Wastewater

Wastewater was obtained from a pharmaceutical industry located at Ranjangaon having COD between 4000 and 10000. The characteristics of the wastewater are shown in table 1.

Table 1: Inlet Wastewater parameters of pharmaceutical wastewater

Sr. No.	Parameter	Range
1.	pH	6-7.8
2.	COD	4000-10000 mg/L
3.	TDS	8486 mg/L
4.	BOD ₅ at 20 ⁰ C	660 mg/L
5.	Phenols	4.65 mg/L
6.	Total Phosphates	53.47 mg/L
7.	Ammonia Nitrogen	64.40 mg/L

2.3 Procedure

Wastewater samples were filtered and pH was adjusted between 2 and 5. 125 ml sample was taken in a beaker. Different doses of hydrogen peroxide and ferrous salt were added. These doses were decided on basis of the molar ratio of ferrous to hydrogen peroxide. 1:1, 1:2 and 1:3 molar ratios was adopted for the purpose of reducing the COD. The sample was stirred in a magnetic stirrer for 1 hour. After one hour, residual hydrogen peroxide was removed by heating the sample at a temperature of 40°C for 10 minutes [1]. The sample was neutralized by addition of 1N sodium hydroxide and filtered to remove the ferrous hydroxide and tested for COD [5]. Based on these dosages the reduction of various other parameters such as phenols, total dissolved solids, heavy metals, total phosphates and ammonia nitrogen were studied. COD was measured by standard method. Phenols, total dissolved solids, heavy metals, total phosphates and ammonia nitrogen were tested by a NABL accredited laboratory.

pH was measured with help of a pH meter. The ratios were calculated analytically.

3. Results and Discussion

Concentrations of hydrogen peroxide and ferrous are important parameters for determining the ratio to achieve the maximum COD removal efficiency. A constant range of hydrogen peroxide dosage was maintained for each ratio and accordingly the ferrous dosage was determined. Hydrogen Peroxide dosage for all ratios were 400 mg/L, 500 mg/L, 600 mg/L, 700 mg/L, 800 mg/L, 900 mg/L and 1000 mg/L respectively. A molar ratio of 1:1 was maintained initially and the subsequent dosage for maximum COD removal was calculated. The results are shown in figure 1. It was observed that a maximum removal efficiency was observed at ferrous sulphate concentration of 7350 mg/L and hydrogen peroxide concentration of 900 mg/L. Further increase in the dosage of hydrogen peroxide and ferrous sulphate showed a decrease in the efficiency of COD removal. This is probably due to both the auto-decomposition of hydrogen peroxide into oxygen and water, and scavenging of hydroxyl radicals by hydrogen peroxide [6].

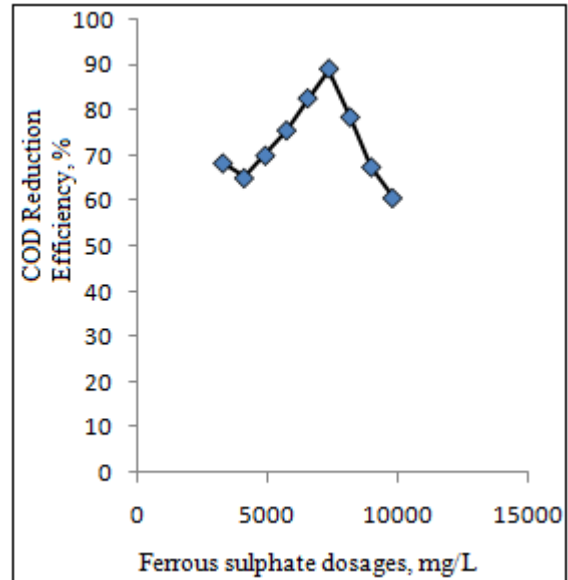


Figure 1: Efficiency of COD reduction based on dosage of ferrous sulphate for 1:1 molar ratios

A molar ratio of 1:2 results are shown in figure 2. A maximum COD removal efficiency was observed at hydrogen peroxide dose of 800mg/L and ferrous sulphate dose of 3267 mg/L.

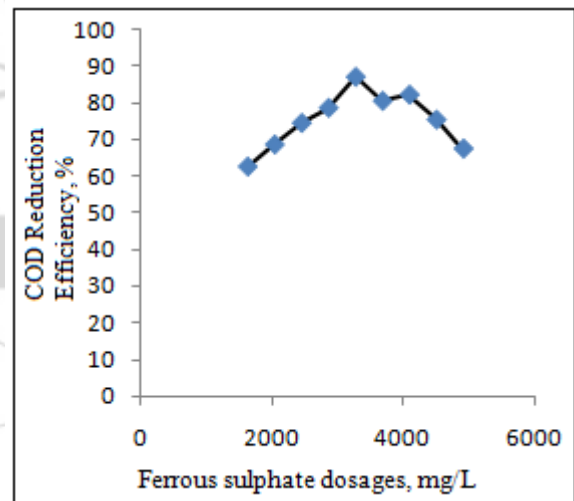


Figure 2: Efficiency of COD reduction based on dosage of ferrous sulphate for 1:2 molar ratios

A molar ratio 1:3 results are shown in figure 3. A dosage of 900 mg/L of hydrogen peroxide and 2450 mg/L of ferrous sulphate gave an efficiency of 92%.

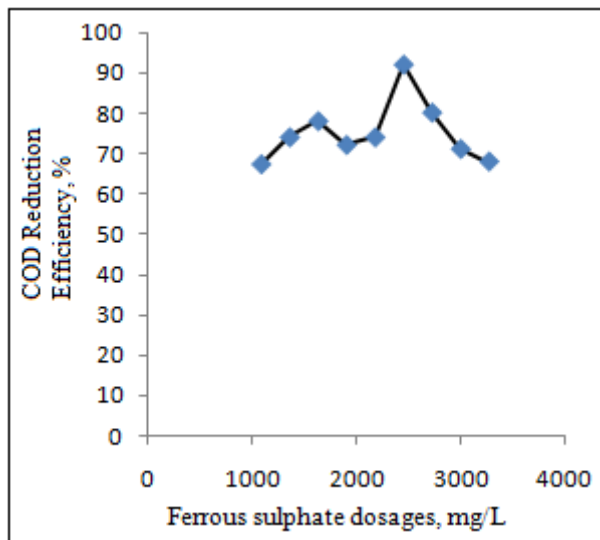


Figure 3: Efficiency of COD reduction based on dosage of ferrous sulphate for 1:3 molar ratios

An overall concentration of 900 mg/L of hydrogen peroxide gave best efficiency for all subsequent molar ratios. Concentration of 800mg/L, 900 mg/L and 1000mg/L of hydrogen peroxide for subsequent concentration of ferrous sulphate gave best efficiency for 1:2 and 1:3 molar ratios.

These dosages were used for the removal of other parameters from wastewater as tabulated in table 2 and 3.

Table 2: Dosages for reduction of phenol and TDS

Ratio	Ferrous sulphate (mg/L)	Hydrogen Peroxide (mg/L)	Phenol Removal (%)	TDS Removal (%)
1:2	3267	800	86	51
1:2	3675	900	91	64
1:2	4083	1000	77	70
1:3	2178	800	96	32
1:3	2450	900	86	60
1:3	2722	1000	85	25

Table 3: Dosage for reduction of total phosphates and ammonia nitrogen

Ratio	Ferrous sulphate (mg/L)	Hydrogen Peroxide (mg/L)	Total Phosphate Removal (%)	Ammonia Nitrogen Removal (%)
1:2	3267	800	96	40
1:2	3675	900	99	37
1:2	4083	1000	99	35
1:3	2178	800	72	38
1:3	2450	900	85	65
1:3	2722	1000	94	60

Total phosphates were effectively removed for all higher dosages of ferrous sulphate and hydrogen peroxide. However, ammonia nitrogen reduction efficiency was less.

4. Conclusion

The Fenton's reaction was found to be efficient in reduction of chemical oxygen demand from pharmaceutical wastewater. A hydrogen peroxide dosage of 900 mg/L was found to be efficient in reducing COD for subsequent dosage of ferrous sulphate. 1:3 molar ratio gave maximum COD

reduction efficiency. Further increase in the reaction time had little effect on the reduction of COD. Phenol and total phosphates were considerably reduced. However, TDS and ammonia nitrogen did not show much reduction. The sludge generated from this process has potential for recovery of iron. Fenton's reaction proves to be an efficient treatment technology when biological treatment is not feasible.

5. Acknowledgement

The authors wish to thank Aavanira laboratories for their analytical assistance.

References

- [1] Krzysztof Barbusinski, "Fenton Reaction-Controversy concerning the chemistry", Journal of society of ecological chemistry and engineering, Vol. 16, No. 3, 2009.
- [2] Nora San Sebastián Martínez, Josep Fíguls Fernández, Xavier Font Segura, Antoni Sánchez Ferrer, "Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent", Journal of Hazardous Material B101, 2003 pp 315-322.
- [3] K. Barbusinski, K. Filipek, "Use of Fenton's reagent for removal of pesticides from industrial wastewater", Polish Journal of Environmental Studies, Vol. 10, 2001, No 4, pp 207-212.
- [4] Mohammedine El Haddad, Abdelmajid Regti, My Rachid Laamari, Rachid Mamouni, Nabil Saffaj, "Use of Fenton reagent as advance oxidative process for removing textile dyes from aqueous solutions", Journal of Material and environmental science 5 (3), 2014, pp 667-674.
- [5] K. Barbusinski, "Toxicity of industrial wastewater treated by Fenton's reagent", Polish Journal of Environmental Studies, Vol. 14, 2005, No. 1, pp 11-16.
- [6] M.I. Badawy, M.E.M. Ali "Fenton's preoxidation and coagulation processes for the treatment of combined industrial and domestic wastewater", Journal of material and science, 2006.
- [7] A.R. Dincer, N. Karakaya, E. Gunes, Y. Gunes, "Removal of COD from oil recovery industry wastewater by the advance oxidation processes (AOP) based on hydrogen peroxide", Global Nest Journal, Vol. 10, No 1, 2008, pp 31-38.
- [8] Rajesh Nithyanandam, Raman Saravanane, "Treatment of Pharmaceutical Sludge by Fenton Oxidation Process", International Journal of Chemical Engineering and Applications, Vol. 4, No. 6, December 2013.
- [9] Scott J.P., Ollis D.F., "Integration of chemical and biological processes for water treatment: review and recommendations",
- [10] Plant L., Jeff M., "Hydrogen peroxide: A potent force to destroy organics in wastewater", chemical engineering, 101, ee 16 [SUPT.-September], 1994.
- [11] C. Höfl, S. Sigl, O. Specht, I. Wurdack, D. Wabner, "Oxidative degradation of AOX and COD by different advanced oxidation processes: a comparative study with two samples of a pharmaceutical wastewater, Water", Sci. Technol. 35, 1997, pp 257-264.
- [12] H.J.H. Fenton, "Oxidation of tartaric acid in the presence of iron", J. Chem. Soc. 65, 1894, pp 899-910.

- [13] Z. Wanpeng, Y. Zhihua, W. Li, "Application of ferrous-hydrogen peroxide for the treatment of H-acid manufacturing process wastewater", *Water Res.* 30, 1996, pp 2949–2954.
- [14] M. Pérez, F. Torrades, X. Doménech, J. Peral, "Fenton and photo-Fenton oxidation of textile effluents", *Water Res.* 36, 2002, pp 2703–2710.
- [15] M. Pérez, F. Torrades, J.A. Garc'ia-Hortal, X. Doménech, J. Peral, "Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions", *Appl. Catal. B: Environ.* 36, 2002, pp 63–74.

Author Profile



Ronak Shetty has done bachelors in environmental engineering at Shivaji University. He has pursued internal auditors coarse in EMS and carbon footprints.



Dr. Shweta Verma did Ph. D from university of Delhi and did further research training from Columbia university, New York, USA.

