Treatment of Industrial Waste Water by Fenton Process

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ABSTRACT: - *In the present study, reduction of chemical oxygen demand (COD) and biological oxygen demand of industrial waste water has been carried out using Fenton process. The process parameters such as solution pH, loading of* H_2O_2*, loading of* $FeSO_4 .7H_2O$ *and settling of suspended solids were investigated in detail to evaluate their effects on the reduction of COD and BOD of industrial waste water. Effective optimum conditions were found to be pH of 4, loading of* H_2O_2*, 800 mg/L, loading of* $FeSO_4.7 H_2O$*, 250 mg/L and 60 min settling suspended solids.*

KEYWORDS:- *Fenton Process, Chemical Oxygen Demand (COD), Biological Oxygen Demand, Total suspended solids (TSS).*

1. INTRODUCTION

Due to increasing awareness about the environment and more stringent environmental rule and regulations, treatment of industrial wastewater has always been a key aspect of research. Much work has been done in developing and testing newer techniques and their combinations for wastewater treatment either individually or as a supplementary role to the conventional methods.

Advanced oxidation processes are defined as oxidation processes in which hydroxyl radicals are the main oxidants involved. This radical is a very powerful oxidant which leads to a very effective oxidation process *(Canizares, P., et al., 2007).*

The Fenton process employs ferrous ions and hydrogen peroxide (H_2O_2) under acidic pH conditions. As shown in reactions (1)–(5), strong oxidative hydroxyl radical ($HO^\bullet$) is produced and the ferrous ions are oxidized to ferric ions and ferric hydroxo complexes which accounts for the coagulation capability of Fenton reagents. Then suspended solids are captured and precipitated out. The $HO^\bullet$ attacks organic compounds and thus causes chemical decomposition of these compounds. The Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process *(Xiang-Juan Ma, et al., 2009).*

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad \text{----------------- (1)}$$

$$HO^\bullet + RH \rightarrow R\bullet + H_2O \quad \text{-------------------------- (2)}$$

$$[Fe(H2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+ \quad \text{-------------------- (3)}$$

$$[Fe(H_2O)_5OH]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4(OH)_2]^+ + H_3O^+ \quad \text{---------------- (4)}$$

$$2[Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe_2(H_2O)_8(OH)_2]^{4+} + 2H_2O \quad \text{--------------------- (5)}$$

In the past few years, many experiments have been carried out to remove COD and BOD from industrial wastewater by Fenton's reactions. The efficiency of Fenton process depends on the properties of the wastewater, the pH value, the Fe^{2+} concentration, the H_2O_2 dosage and the settling time *(Kurt, U., et al., 2006)*. Fenton process for high concentration of COD and BOD of industrial wastewater has not yet been reported in the literature. This study attempts to explore the possibility of treating concentration high COD and BOD in industrial wastewater by Fenton process. Experiments were conducted to examine the effects of various operating conditions on the performance of the Fenton treatment system.

2. MATERIALS AND METHODS

Materials

Raw industrial wastewater was obtained from chemical manufacturing company, Bharuch, India at an interval of 15 days and stored in the refrigerator, in order to maintain their physical and chemical characteristics throughout the research.

Chemicals and reagents

Hydrogen peroxide (30 % W/V H_2O_2), Ferrous sulfate heptahydrate ($FeSO_4 .7H_2O$), Sulfuric acid (98 % H_2SO_4) and Sodium hydroxide (NaOH) etc. of Fisher Scientific Inc. were purchased from the local supplier, India. All reagents and chemical were used as received from venders without any purification or further treatment.

Methods

2.1. Characterization of industrial waste water

The waste water parameters like pH, COD, BOD and TSS of industrial waste were analyzed using APHA, Standard Methods for the Examination of Water and Wastewater, 2012 ***(****Baird, R. B., et al., 2012****)***. The main characteristics of the industrial waste water used in this work were presented in **Table 1**.

Table 1. Characteristics of the industrial waste water

Sr. No.	Parameters	Raw effluent
1.	pH	10.5 ± 1
2.	Chemical Oxygen Demand	14560 ± 100
3.	Biological Oxygen Demand	5151 ± 50
4.	Total suspended solids	820 ± 50

The ratio of BOD/COD is equal to or less than 0.3, then industrial waste water treated by only chemical treatment. The ratio of BOD/ COD is equal to or greater than 0.5, industrial waste water treated by biological treatment *(Bhaskar, G., et al., 2014).*

2.2. Fenton Process

The Fenton process experiments were conducted by using 1000 ml glass beaker. The operating parameters included dosages of H_2O_2 and $FeSO_4.7\ H_2O$, pH value and settling time. One glass beakers of 1000 ml were first filled with 600 ml of wastewater sample, and the pH was adjusted to the designed value with 0.5 N H_2SO_4 solutions. Then H_2O_2 and $FeSO_4.7H_2O$ were added and the process was preceded with rapid mixing of wastewater sample at 50 rpm with help of magnetic stirrer for 30 min, and then maintaining standstill for 60 min. The supernatant was withdrawn for pH, COD, BOD and TSS analyses.

2.3. Chemical Analyses

Prior to and after treatment, samples were withdrawn from the glass beaker regular interval of time and analyzed of pH, COD, BOD and TSS. It was determined by APHA, Standard Methods for the Examination of Water and Wastewater *(Baird, R. B., et al., 2012).*

3. RESULTS AND DISCUSSION

3.1. Calculation of Percentage of Reduction of COD and BOD:-

The percentage of reduction of COD and BOD of industrial wastewater was calculated according to equation.

$$\%\ \boldsymbol{of\ COD\ Reduction} = \left[\frac{(\boldsymbol{COD0 - CODt})}{\boldsymbol{COD0}}\right] \times \mathbf{100}$$

COD0: initial COD of the industrial wastewater (mg/l)

CODt : COD of the industrial wastewater after time ‘t’ (mg/l)

$$\%\ \boldsymbol{of\ BOD\ Reduction} = \left[\frac{(\boldsymbol{BOD0 - BODt})}{\boldsymbol{BOD0}}\right] \times \mathbf{100}$$

BOD0: initial BOD of the industrial wastewater (mg/l)

BODt : COD of the textile industrial wastewater after time ‘t’ (mg/l)

3.2. Factors Affecting the Performance of Fenton Process

3.2.1 Effect of pH

The pH has been observed to be a highly important factor for the effective Fenton treatment *(Lin, S. H. et al., 1997)*. These experiments were conducted at 600 ml industrial wastewater in 1000 ml glass beaker, fixed amount of 100 mg/l H_2O_2 and 50 mg/l $FeSO_4.7\ H_2O$ and 30 min total treated time with continuous stirring at 50 rpm with help of magnetic stirrer. **Table 2** demonstrates the pH effect on the % of COD reduction and % of BOD reduction of the wastewater treated by Fenton process with a fixed amount of 100 mg/l H_2O_2 and 50 mg/l $FeSO_4.7\ H_2O$. As the pH increased from 2 to 10, the % of COD reduction and % of BOD reduction remained in the range of 10–16% and 5-10 %, and the maximum value of % of COD reduction and % of BOD reduction was 16 % and 10 % at pH 4. The % of COD reduction and % of BOD reduction started to decrease slightly 4 pH to 10 pH, due to the increasing rate of auto decomposition of H_2O_2, deactivation of iron ion into iron oxy hydroxides and the increased scavenging effect of $HO^\bullet$ resulting in the decreased oxidation potential of $HO^\bullet$ *(Deng, Y. et al., 2007).*

Table 2. Shows effect of pH on % of COD reduction and % of BOD reduction

pH	% of COD Reduction	% of BOD Reduction
2	10	05
4	16	10
6	15	09
8	13	08
10	11	07

3.2.2. Effect of H_2O_2 dosage

These experiments were conducted at 600 ml industrial wastewater in 1000 ml glass beaker, optimized 4 pH and 30 min total treated time with continuous stirring at 50 rpm with help of magnetic stirrer. **Table 3** shows the % of COD reduction and % of BOD reduction at different H_2O_2 dosages. The pH was controlled at 4 and the dosage of H_2O_2 increased from 200 mg/L to 800 mg/L, the % of COD reduction increased from 23 % to 58 % and % of BOD reduction increased from 15 % to 41 %. However, the dosage of H_2O_2 varied from 800 mg/L to 1000 mg/L, the % of COD reduction and % of BOD reduction decreased from 58 % to 52 % and 41 % to 38 %. The increase in the % of COD reduction and % of BOD reduction is due to the increase in hydroxyl radical concentration by the addition of H_2O_2. This adverse effect after optimum concentration is due to scavenging effect. On increasing concentration of H_2O_2 rate of hydroxyl radical also increases but beyond certain concentration some of H_2O_2 remains in excess. This excess H_2O_2 recombines with $OH^\bullet$ radicals and form H_2O and $O_2H^\bullet$ radical that have low oxidation potential compared to that of $OH^\bullet$ radical, which results into decrease in rate of degradation *(Gogate, P. R. et al., 2004, Thakare, Y. D. et al., 2016).*

Table 3. Shows effect of H_2O_2 dosage on % of COD reduction and % of BOD reduction

Dosage H2O2 (mg/L)	% of COD Reduction	% of BOD Reduction
200	23	15
400	38	22
600	49	32
800	**58**	**41**
1000	52	38

3.2.3. Effect of ferrous dosage

These experiments were conducted at 600 ml industrial wastewater in 1000 ml glass beaker, optimized 4 pH, optimized 800 mg/L H_2O_2 dose and 30 min total treated time with continuous stirring at 50 rpm with help of magnetic stirrer. **Table 4** shows the effect of ferrous dosage on the % of COD reduction and % of BOD reduction with an optimized dose of 800 mg/l H_2O_2 for the industrial wastewater. When the ferrous dosage increased from 50 mg/l to 250 mg/l then % of COD reduction and % of BOD reduction increased from 55 % to 80 % and 33 % to 70 %. This was due to the increasing amount of ferric hydroxo complexes and HO• generated by the redox reaction with the increasing dosage of ferrous sulfate *(Vlyssides, A.G., et al., 2004).*

Table 4. Shows effect of FeSO4. 7 H2O dosages on % of COD reduction and % of BOD reduction

Dosage FeSO4.7H2O (mg/L)	% of COD Reduction	% of BOD Reduction
50	55	33
100	62	49
150	67	55
200	76	63
250	**80**	**70**

Meanwhile, it had been observed that large amounts of small flocs were suspended in the treated industrial waste water after adding ferrous dosage and difficult to settle down. The TSS of the treated effluent increased from 820 mg/L to 1470 mg/L due to adding ferrous sulphate.

Table 5 shows the % of COD reduction and % of BOD reduction at settling time (60 min) after Fenton process. The dosages of H_2O_2 and $FeSO_4$ $7H_2O$ used were 800 mg/l and 250 mg/l. The pH was controlled at 4. After the mixing, large amounts of small flocs were consistently observed and would take a very long time to settle down. Furthermore, these small flocs frequently interfered with COD and BOD measurement. After settling treated sample for 60 min, the % of COD reduction and % of BOD reduction increased from 80 % to 90 % and 70 % to 76 %. The TSS of treated water was reduced from 1470 mg/l to 822 mg/l after settling sample for 60 min.

Table 5. Shows effect of settling time on % of COD reduction and % of BOD reduction

	Before Settling		**After Settling**	
Dosage FeSO4.7H2O (mg/L)	% of COD Reduction	% of BOD Reduction	% of COD Reduction	% of BOD Reduction
50	55	33	60	45
100	62	49	64	51
150	67	55	71	60
200	76	63	82	68
250	**80**	**70**	**90**	**76**

3.2.4 Total Analysis of Treated Water after Fenton Treatment (Chemical Treatment)

Table 6. shows the analysis of industrial waste water after Fenton treatment (chemical treatment)

Sr. No.	**Parameters**	**Raw effluent**	**After Fenton treatment**
1.	pH	10.5 ± 1	4.5
2.	Chemical Oxygen Demand	14560 ± 100	1476
3.	Biological Oxygen Demand	5151 ± 50	1260
4.	Total suspended solids	820 ± 50	822

4. CONCLUSIONS

The overall results of this study indicate that the application of Fenton’s reagent is a feasible method to partially treat high concentration of COD and BOD of industrial wastewaters. Fenton’s treatment gave maximum reduction COD and BOD at initial pH 4, 800 ppm H_2O_2 dose, 250 ppm $FeSO_4$. 7 H_2O dose and 60 min settling, leads to a COD reduction of 90% and BOD reduction of 76%. The BOD and COD ratio after Fenton treatment of treated effluent is greater than 0.5, hence Fenton process treated industrial waste water will be treated by biological process, it will be reduce COD and BOD Fenton treated waste water up to 85 % and 95 %.

5. REFERENCES

Baird, R.B., Eaton, A.D., Rice, E.W., Standard Methods for the Examination of Water and waste-Water, 2012, 23th edition, American Public Health Association, Washington, DC.

Bhaskar, G., Naidu G.R.K., Madan Iyengar, Laboratory Experiment of Advanced Oxidation Process Coupled Coagulation, Flocculation, and Biological Treatment, Bioremed. Biodeg. 5 (2014), 5-7.

Canizares, P., Lobato, J., Paz, R., Rodrigo, M.A., Saez, C., Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere 67 (2007), 832–838.

Deng, Y., Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate, Journal of Hazardous Material 146 (2007), 334–340.

Gogate, P.R., Pandit, A.B., A review of imperative technologies for wastewater treatment II: hybrid methods, Advance in Environmental Research, 8 (2004), 553–597.

Kurt, U., Avsar, Y., Talha Gonullu, M., Treatability of water-based paint wastewater with Fenton process in different reactor types, Chemosphere 64 (2006), 1536–1540.

Lin, S.H., Lo, C.C., Fenton process for treatment of desizing wastewater, Water Research 31 (1997), 2050–2056.

Vlyssides, A.G., Loukakis, H.N., Karlis, P.K., Olive mill wastewater detoxification by applying pH related Fenton oxidation process. Fresenius Environ. Bull. 13 (2004), 501–504.

Xiang-Juan Ma, Hui-Long Xia, Treatment of water-based printing ink wastewater by Fenton process combined with coagulation, Journal of Hazardous Materials 162 (2009), 386–390.