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Feasibility Study of Fenton Method for the Treatment of Dyeing and Printing Mill Wastewater

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Abstract:

Textile industry is one of the most important and rapidly developing industrial sectors. It has a high importance in terms of its environmental impact, as it consumed high amount of processed water and produce highly polluted discharge water in large amount. Dying and printing mills comprises various operations include desizing, scouring, washing, finishing etc so they produces large amount of polluted effluent having high chemical Oxygen Demand. Advanced oxidation processes have emerged as a technology to accelerate the oxidation by generating hydroxyl radicals. Fenton treatment is one of the most attractive methods for the treatment of textile effluent. The use of Fenton's reagent for the degradation of organic matter present in dying and printing mill's effluent has been studied. The characteristics of the wastewater were checked. Experiments were carried out at a laboratory scale at different dosage to find out the optimum dosage of $FeSO_4$ and H_2O_2.The optimum condition and efficiency were determined. Effect of the process parameter (dosage of $FeSO_4$ and H_2O_2) has been checked. Highest efficiency of COD (74.24%) & BOD (72.41%) were achieved.

Key Words: Dyeing and Printing Mill's Wastewater, Fenton's Method, $FeSO_4$, H_2O_2, COD and BOD, Removal efficiency

1. Introduction

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment. Cotton provides an ecologically friendly textile, but more than 50% of its production volume is dyed with reactive dyes. Unfortunately, dyes are unfavorable from an ecological point of view, because the effluents generated are heavily colored; contain high concentrations of salts, and exhibits high chemical oxygen demand/ biological oxygen demand values.

Textile dyeing wastewater risk

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor in the human future. If a textile mill discharges the wastewater into the local environment without any treatment, it will have a serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, and oil and grease in the effluent causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. Effluent from textile mills also contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body.

Textile wastewater is difficult to treat with the use of classical physicochemical and biological methods, which is mainly due to their intensive color, high content of surfactants and other organic and inorganic compounds, a significant toxicity and poor biological recovery. The development of novel treatment methods encompasses investigations of advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical ($OH^{\bullet}$) as a primary oxidant. Among various AOPs, the Fenton reagent (H_2O_2/Fe^{2+}) is one of the most effective methods of organic pollutant oxidation. The Fenton reagent has been found to be effective in treating various industrial wastewater components including aromatic amines and a wide variety of dyes as well as many other substances, e.g. pesticides and surfactants. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

2. Fenton's Oxidation

The Fenton reagent, a mixture of hydrogen peroxide and iron (II) salt, is discovered by Henry J.H. Fenton. He described the oxidation power of hydrogen peroxide on certain organic molecules in which OH^- radicals are produced from hydrogen peroxide under the addition of Fe(II) as a catalyst. This system is considered as the most promising treatment among AOPs for remediation of highly contaminated water.
The oxidation of organic compounds is much faster in the solutions which contain hydrogen peroxide and iron (II) salts that form hydroxyl radicals during the reaction:

$$H_2O_2+Fe^{2+} \rightarrow Fe_3^{+}+OH^{-}+HO^{\bullet} \quad (1)$$

This system is known as the Fenton reagent, and is used for wastewater treatment. The oxidising efficiency of the Fenton reagent is the highest for pH ranging from 2 to 5, and for molar H_2O_2 to Fe^{2+} ratio, about 1:1.
The mechanism of this reagent was tested in detail for many reactions of organic compounds and enzymatic reactions; however it has not been fully explained because of the variety of iron (II) and iron (III) complexes, numerous radical intermediate products and their consecutive reactions.
A significant role is played here by the formation of Fe^{3+} ions, which decompose H_2O_2 and produce $HO_2^{\bullet}$ radicals:

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^{+}+HO_2^{\bullet} \quad (2)$$

In the solutions of H_2O_2 and iron (II) salts, organics (RH) are oxidised during radical chain reactions. The main agents oxidising and propagating the reactions are $HO^{\bullet}$ radicals:

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad (3)$$
$$R^{\bullet} + H_2O_2 \rightarrow ROH + HO^{\bullet} \quad (4)$$

$HO^{\bullet}$ radicals also decompose H_2O_2, producing $HO_2^{\bullet}$ radicals.

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O+ HO_2^{\bullet} \quad (5)$$

In the reactions of $R^{\bullet}$ radicals with Fe^{3+} ions, carbo-cations R^+ may be formed, while in these involving Fe^{2+} ions, carbo-anions R^- may occur. The kinetic chain is terminated in the reactions between radicals:

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (6)$$

$$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (7)$$
$$HO_2^{\bullet}+ HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

Radicals $R^{\bullet}$ and $RO_2^{\bullet}$ also recombine, contributing in this way to the termination of the chain reaction:

$$R^{\bullet} + RO_2^{\bullet} \rightarrow ROOR \quad (9)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2 \quad (10)$$

These short characteristics of reactions (1) to (10) show the complex mechanism of the Fenton reagent's oxidation. The most significant are $HO^{\bullet}$ radicals, because they propagate the chain reaction of oxidation, and in parallel, in reaction (5), they produce HO_2 radicals which also take part in the propagation. Among various AOPs, the Fenton reagent is one of the most effective methods of organic pollutant oxidation. Fenton technology with sufficient aeration is very effective treatment for COD-BOD removal due to proper & vigorous mixing of Fenton chemicals.

However, it is necessary to exhaustively control the pH of the medium similar to dark Fenton. Generally, the pH range should be between 2.6 and 3 for the best performance of the system. The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. However, disadvantages in using the Fenton reagent include the production of a substantial amount of $Fe(OH)_3$ precipitate and additional water pollution caused by the homogeneous catalyst that added as an iron salt, cannot be retained in the process. To solve these problems, the application of alternative iron sources as cata-lysts in oxidizing organic contaminants has been studied extensively

3. Material and Methodology

3.1 Apparatus - Beakers, Burette, Funnel, Measuring Cylinder, Pipette, Weighing Machine, COD Test tubes, COD Digester, BOD incubator, Magnetic Stirrer are required.

3.2 Chemicals and Reagents- Wastewater from dying and printing mill situated at outskirt of surat city, 30% Hydrogen Peroxide (H_2O_2), Hydrated Ferrous Sulphate ($FeSO_4$. $7H_2O$), Mercuric Sulphate ($HgSO_4$), 0.25N Potassium Dichromate Solution ($K_2Cr_2O_7$), Concentrated Sulphuric acid (H_2SO_4), 0.25N Ferrous Ammonium Sulphate solution

$(Fe(NH_4)_2(SO_4).6H_2O)$, Sulphuric acid concentrated with silver sulphate, Ferroin Indicator.

3.3 Characteristics of raw wastewater of industry A

Parameters	Values
pH	7-8
Chemical Oxygen Demand (mg/l)	6200±400
Biological Oxygen Demand (mg/l)	2066±200
TDS (mg/l)	2100
Color	Brown

3.4 Fenton Process

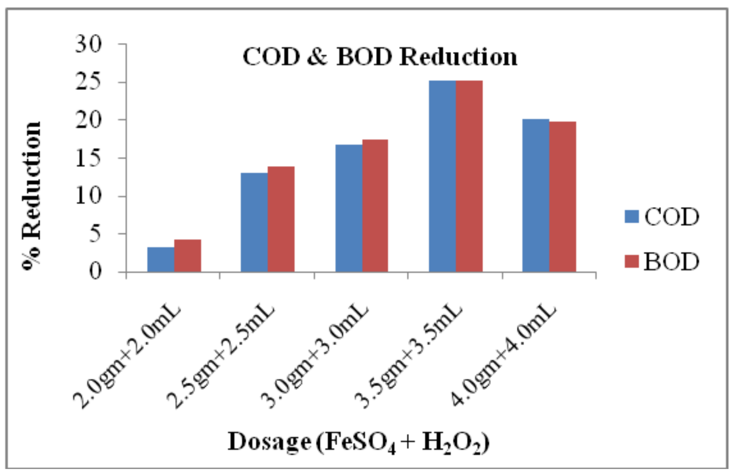
- 300 ml wastewater sample was added into the beaker.
- pH was measured, and it was adjusted to acidic pH by using sulphuric acid.
- The dosage of Ferrous Sulphate was added to find optimum dosage.
- A required amount of 35% Hydrogen Peroxide was added to start up the Fenton's reaction.
- Magnetic Stirrer was used to achieve the vigorous mixing for different reaction time.
- Treated wastewater was allowed to settle for 1 hr, after settling the supernatant was taken for COD-BOD analysis.
- Whole experiment was carried out by batch type process.

3.5 Setup after giving chemical dosage

4. Results and Discussion

SET 1: Varying dosage of $FeSO_4$ and H_2O_2 (pH= 3, Reaction time= 2hrs)

Dosage ($FeSO_4$ + H_2O_2)	Parameter	Initial Concentration (mg/L)	Final Concentration (mg/L)	% Reduction
2.0gm + 2.0mL	COD	6200	6000	3.22
	BOD	2066	1980	4.16
2.5gm + 2.5mL	COD	6200	5391.3	13.04
	BOD	2066	1779	13.89
3.0gm + 3.0mL	COD	6200	5166.6	16.66
	BOD	2066	1708.9	17.28
3.5gm + 3.5mL	**COD**	**6200**	**4640**	**25.16**
	BOD	**2066**	**1548**	**25.07**
4.0gm + 4.0mL	COD	6200	4956.5	20.05
	BOD	2066	1660	19.65

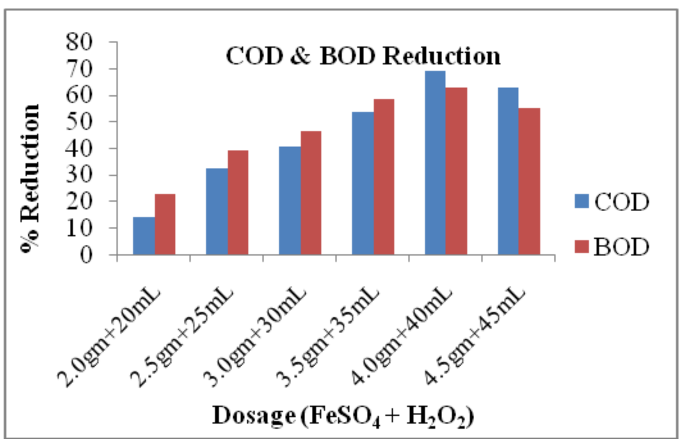


Graph 1: Removal efficiency of COD & BOD

SET 2: Varying dosage of $FeSO_4$ and H_2O_2 (pH= 3, Reaction time= 2hrs)

Dosage ($FeSO_4$ +	Parameter	Initial Concentration (mg/L)	Final Concentration (mg/L)	% Reduction

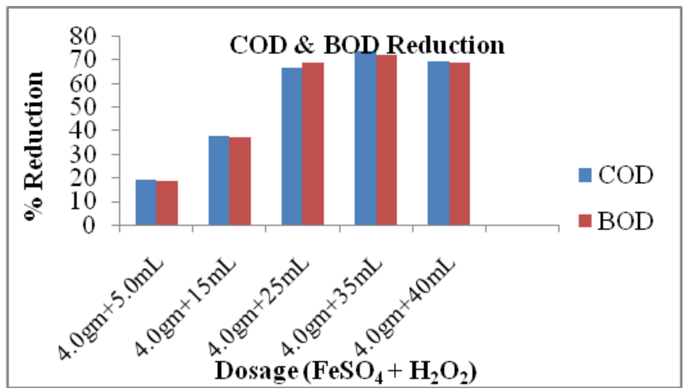
H_2O_2)				
2.0gm + 20mL	COD	6200	5333.3	13.97
	BOD	2066	1599	22.60
2.5gm + 25mL	COD	6200	4200	32.25
	BOD	2066	1260	39.01
3.0gm + 30mL	COD	6200	3700	40.32
	BOD	2066	1110	46.27
3.5gm + 35mL	COD	6200	2869	53.72
	BOD	2066	860.7	58.34
4.0gm + 40mL	**COD**	**6200**	**1920**	**69.03**
	BOD	**2066**	**768**	**62.82**
4.5gm + 45mL	COD	6200	2320	62.58
	BOD	2066	928	55.08



Graph 2: Removal efficiency of COD & BOD

SET 3: Varying dosage of H_2O_2 (pH= 3, Reaction time= 2hrs, $FeSO_4$ = 4gm)

Dosage ($FeSO_4$ + H_2O_2)	Parameter	Initial Concentration (mg/L)	Final Concentration (mg/L)	% Reduction
4.0gm + 5.0mL	COD	6200	5000	19.35
	BOD	2066	1680	18.68
4.0gm + 15mL	COD	6200	3846.1	37.96
	BOD	2066	1294	37.36
4.0gm + 25mL	COD	6200	2000	67.08
	BOD	2066	680	68.85
4.0gm + 35mL	**COD**	**6200**	**1545.45**	**74.24**
	BOD	**2066**	**570**	**72.41**
4.0gm + 40mL	COD	6200	1900	69.35
	BOD	2066	637	69.16

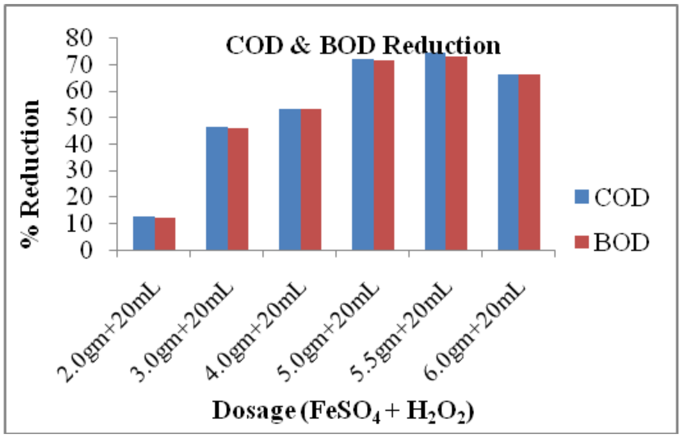


Graph 3: Removal Efficiency of COD & BOD

SET 4: Varying dosage of $FeSO_4$ (pH= 3, Reaction time= 2hrs, H_2O_2 = 20ml)

Dosage ($FeSO_4$ + H_2O_2)	Parameter	Initial Concentration (mg/L)	Final Concentration (mg/L)	% Reduction
2.0gm + 20mL	COD	6200	5428.57	12.44
	BOD	2066	1821.4	11.83
3.0gm + 20mL	COD	6200	3333.3	46.23
	BOD	2066	1123.9	45.60
4.0gm + 20mL	COD	6200	2900	53.22
	BOD	2066	974	52.85
5.0gm	COD	6200	1739.13	71.94

+20mL	BOD	2066	587.8	71.54
5.5gm + 20mL	**COD**	**6200**	**1600**	**74.19**
	BOD	**2066**	**567.1**	**72.55**
6.0gm + 20mL	COD	6200	2100	66.12
	BOD	2066	697	66.26



Graph 4: Removal efficiency of COD & BOD

Effect of $FeSO_4$ & H_2O_2 on COD & BOD

From the above set of experiment significant reduction was observed with:

1) COD (25.16%) & BOD (25.07%) with dosage 3.5gm $FeSO_4$ + 3.5ml H_2O_2

2) COD (69.03%) & BOD (62.82%) with dosage 4.0gm $FeSO_4$ + 40ml H_2O_2.

3) COD (74.24%) & BOD (72.41%) with dosage 4.0gm $FeSO_4$ + 35ml H_2O_2

4) COD (74.19%) & BOD (72.55%) with dosage 5.5gm $FeSO_4$ + 20ml H_2O_2

The result indicates that very less reduction observed with 1:1 ratio of reagents, the good reduction observed in COD and BOD values up to certain extent with increase in dosage of Fenton's reagent with 1:10 ratio. Further increase in dosage shows the reduction in removal efficiency. By performing the experiment with keeping the dosage of $FeSO_4$ constant of 4 gm, the highest efficiency observed at the dosage of 4gm $FeSO_4$ + 35ml H_2O_2 & with keeping the dosage of H_2O_2 constant of 20 ml, the highest efficiency observed at the dosage of 5.5gm $FeSO_4$ + 20ml H_2O_2.

5. Conclusion

It is evident from result & discussion that good reduction is achieved with Fe^{+2}:H_2O_2 – 1:10 ratio. Optimum Dosage found by experiments is 4.0gm $FeSO_4$ + 35ml H_2O_2 with the reduction in COD (74.24%) & BOD (72.41%). The application of Fenton's reagent in Dyeing and Printing Mill's wastewater treatment technology is an efficient method for the decomposition of pollutants present in it and can be used successfully as a preliminary stage preceding its biological treatment. For higher removal efficiency one of the solution is to use two stage process- Fenton's reaction and Biological methods. It is necessary to check the reaction with respect to the large amount of various type of wastewater and find proper relation which enables the quick optimization of the process with respect to the changing input parameters of the wastewater subjected to treatment.

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