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Treatment of Tannery Waste Water using Advanced Oxidation Process

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ABSTRACT

This paper evaluates the efficiency of Fenton process for the treatment of tannery waste water. Advanced oxidation processes is based on the chemistry of hydroxyl radicals (•OH) production and are used for destroying organic pollutants. Fenton's reaction is a system based on the generation of very reactive free radicals, especially hydroxyl radicals, which have a stronger oxidation potential. Fenton reagent is the result of reaction between hydrogen peroxide and ferrous iron producing hydroxyl radical. Studies were made to investigate the maximum removal of COD from tannery waste water varying Fe^{2+}, H_2O_2 dosage and initial pH. The initial characteristics of the wastewater were checked. Experiments were carried out at a laboratory scale at different dosage to find out the optimum dosage of ferrous sulphate and H_2O_2 and also optimum pH value for maximum COD removal.

Keywords: Advanced oxidation process, COD, Fenton Reaction, Tannery Waste Water.

I. INTRODUCTION

The economic sustainability of India chiefly dependent on the constant and continuous growth of industries. India has several major and minor or small-scale industries; which are either process-based or manufacturing-based; functioning throughout the year or seasonally; and are integrated or non-integrated, universal or non- universal, and combinations of these. Tannery industry is one of the leading economic sectors in many countries. There has been an increase in the environmental concern regarding the release of various recalcitrant pollutants in tannery waste water. From past several decades, classical physico-chemical techniques like screening, grease and fat skimming, coagulation-cum-flocculation followed by settling are being used either individually and in combinations to make the effluent amenable for biological treatment. The emerging technologies such as advanced oxidation process have been attempted as extensive research technologies to destroy toxic and biologically refractory organic contaminants. The leather industry is associated with the generation of huge amounts of liquid effluents. The wastewater may be characterized by several key parameters such as sulphide, chromium, oil and grease, BOD and COD [1]. Tannery wastewater is difficult to treat biologically because of complex characteristics like high salinity high content of xenobiotic compounds. After conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as BOD, COD, salinity, ammonia and surfactants[2].

Advanced oxidation process (AOP) is a promising method for generation of hydroxyl radical which is a powerful and non - selective oxidant for mineralization or degradation of these recalcitrant organic pollutants present in tannery effluent. One of these processes is Fenton's oxidation process in which organic pollutants react with hydrogen peroxide in the presence of ferrous sulphate to reduce toxicity and organic load (COD). It is based on the generation of very reactive free radicals, especially hydroxyl radicals, which have a stronger oxidation potential. This oxidation may occur via one of three general pathways: hydrogen abstraction, electron transfer and radical addition.

In Fenton reaction, hydroxyl radicals $^{\bullet}OH$ are produced by interaction of H_2O_2 with ferrous salts according to Equation 1.

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

Fe^{3+} can react with H_2O_2 in the Fenton-like reaction (Eqs. 2 to 4), regenerating Fe^{2+} and thus supporting the Fenton process.

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \quad (2)$$
$$Fe\text{-}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (3)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (4)$$

Table 1 : Characterization of the tannery wastewater

Parameters	Values
pH	7.35
Total dissolved solids, mg/l	6310
Acidity, mg/l as $caco_3$	485
Alkalinity, mg/l as $caco_3$	2100
BOD, mg/l	2470
COD, mg/l	5200
Sulphates, as so_4^{2-}, mg/l	9400
Chlorides, as cl^-, mg/l	4590

II. MATERIALS AND METHODS

Ferrous sulphate $FeSO_4.7H_2O$, sulphuric acid and hydrogen peroxide (30% wt.) of analytical grade were used. The wastewater sample used in this study was taken from the outlet of primary treatment tank of a commercial tannery industry in erode.

Fenton experiment was carried in jar test apparatus at a constant rate of 100 rpm. Different concentrations of ferrous sulphate and hydrogen peroxide were mixed with tannery wastewater. The reaction was assumed to start with the addition of H_2O_2. All experiments were carried out for a period of 4 hours reaction time at an initial pH of 3. The pH value was adjusted to acidic pH using 5N sulphuric acid. Residual COD and pH were measured after settling of the supernatant.

III. RESULTS AND DISCUSSION

3. Fenton process

The effects of different parameters such as H_2O_2 concentration, $FeSO_4.7H_2O$ concentration, pH value and reaction time on the COD removal percentage were studied.

3.1 Effect of H_2O_2 concentration on COD removal by Fenton process.

Optimization of H_2O_2 was performed by varying H_2O_2 doses (i.e., 20g/l, 30g/l, 40g/l, &50g/l) at a fixed dose of Fe^{2+} i.e. 800mg/l as Fe^{2+}. Figure 1 shows the effect of H_2O_2 concentration on COD removal of tannery waste water at pH 3. The maximum COD removal % of 90% was obtained for a concentration of 30g/l of H_2O_2. Therefore the optimum concentration of H_2O_2 dosage is 30g/l. It can be observed from the results that the COD removal increases with increase in H_2O_2 concentration up to the optimum concentration (30g/l) beyond which it decreases again. It increases with increase of H_2O_2 concentration due to the degradation of organic pollutants present in tannery wastewater. Beyond the optimum concentration, generation of less reactive hydroxyl radical and scavenging of hydroxyl radical inhibits the degradation rates of organic pollutants. Thus the percentage of COD removal decreased [4].

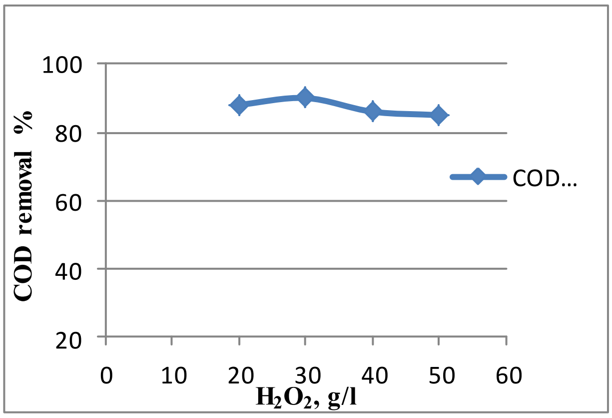

Figure 1. Effect of H_2O_2 concentration on COD removal

3.2 Effect of Fe^{2+} concentration on COD removal by Fenton process

Optimization of Fe^{2+} dose was performed by varying Fe^{2+} concentration (i.e. 200mg/l, 500mg/l, 800mg/l &1200mg/l as Fe^{2+}) at a fixed dose of H_2O_2 dosage as 40g/l. The optimum Fe^{2+} concentration obtained was 500mg/l as Fe^{2+} for a maximum COD removal of 91%. Figure 2 shows the effect of Fe^{2+} concentration on COD removal of tannery waste water at pH 3. The optimum dose range for iron catalyst is the characteristic of Fenton's reagent and its range varies with the type of contaminants in waste water. At higher pH values, iron precipitate as ferric hydroxide therefore degradation strongly decreases.

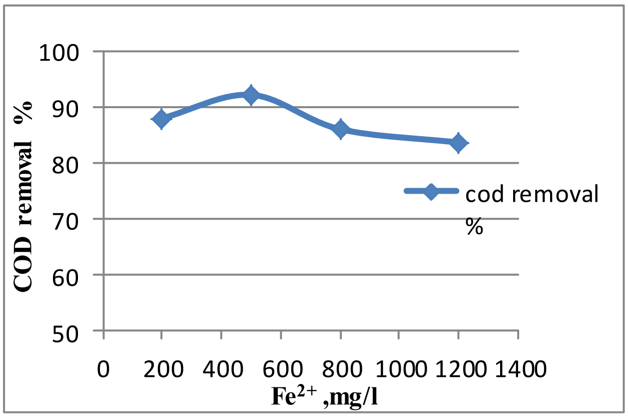

Figure 2. Effect of Fe^{2+} concentration on COD removal

3.3 Effect of pH on COD removal by Fenton process

Optimum pH value for maximum COD removal was investigated by varying initial pH value of waste water. The initial pH value was adjusted to pH 2, 3&4 by addition of 5N H_2SO_4. At pH 3 maximum COD removal was obtained. Figure 3 shows the effect of pH on COD removal percentage of tannery waste water. If the pH is too high, the iron precipitate as $Fe(OH)_3$ and if the pH is too low iron catalytically decomposes H_2O_2 in to oxygen and water without forming hydroxyl radical.

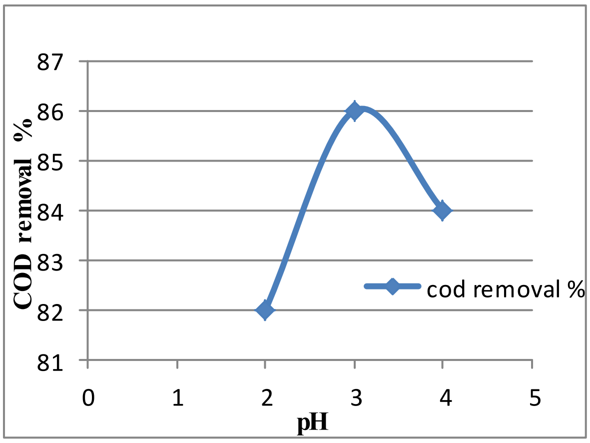

Figure 3. Effect of pH on COD removal

3.4 Effect of reaction time on COD removal by Fenton process

To study the effect of reaction time on COD removal a set of experiments under optimum condition of 800mg/l as Fe^{2+} and 40g/l of H_2O_2 at pH 3 was carried out. The result shown in figure 4 indicates that optimum time for maximum COD removal is 4 hrs. The reaction time needed for Fenton reaction to reach completion depends on many factors mainly catalyst dose and waste water strength. Therefore for more concentrated waste water the reaction may take several hours.

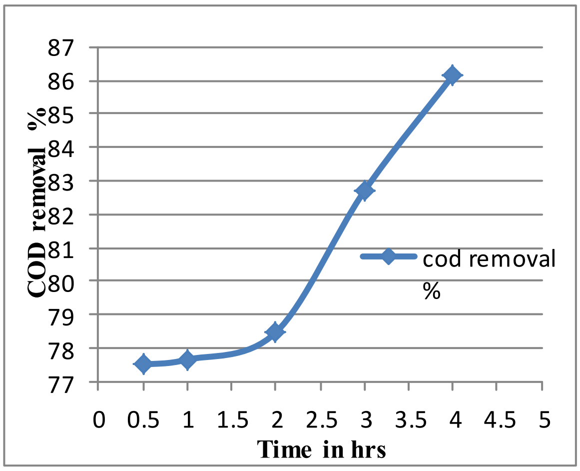

Figure 4. Effect of reaction time on COD removal

IV. CONCLUSION

The application of Fenton's reagent in treatment of tannery waste water is an efficient method for the degradation of organic matter since a satisfactory decrease in COD value was obtained.

From the experiments conducted it has been concluded that,

1) Maximum COD removal of 91% was obtained by varying Fe^{2+} and H_2O_2 dosage.
2) The Optimum concentration of H_2O_2 dosage was 30g/l for a COD removal of 90%.
3) The optimum Fe^{2+} concentration obtained was 500mg/l as Fe^{2+} for a COD removal of 91%.
4) The initial pH value was adjusted to pH 2, 3&4 by addition of 5N H_2SO_4. At pH 3 maximum COD removal was obtained.
5) The optimum time for maximum COD removal is 4 hours because for more concentrated waste water the reaction may take several hours.

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