Advance Fenton's Oxidation Treatment for COD Reduction on CETP Waste Water

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Abstract— Several small scale industries have formed cooperatives and established Common Effluent Treatment Plants (CETP) to treat wastewater in India. The wastewaters are subjected to primary treatment in the industry and thereafter discharged to be further treated at the CETPs. The management and treatment costs are shared by the member industries. Wastewater treatment is always highly concerned in the sake of environmental protection. A considerable effort has been made into exploring and implementing new methods of wastewater treatment. The principle way to remove the pollutants from wastewater is by combining different treatment methods in one wastewater treatment system. Fenton's oxidation was one of the best known metal catalyzed oxidation reactions of water-miscible organic compounds. The mixture of $FeSO_4$ or any other ferrous complex and H_2O_2 (Fenton's reagent) at low enough pH, results in Fe^{2+} catalytic decomposition of H_2O_2 and proceeds via a free radical chain process that produces hydroxyl radicals which have extremely high oxidizing ability and could oxidize hard to decompose organic compounds in a short time. This work aims at highlighting Fenton's oxidation processes operating at ambient conditions viz. photo-catalytic oxidation, Fenton's chemistry and use of hydrogen peroxide & also the study for providing economic feasibility of the proposed physicochemical process.

Keywords: COD Removal, Fenton's for Color Reduction

I. Introduction

In India almost 70 per cent of its surface water resources and a growing percentage of groundwater reserves were contaminated by biological, toxic, organic, and inorganic pollutants which show water scarcity for both human use and for the ecosystem (Murty, 2011) [2]. Overall, some 5–20 per cent of total water usage goes to industry and it generates a major proportion of total waste water (Corcoran, 2010). During the past few decades Indian industries have registered a quantum jump, which has contributed to high economic growth but simultaneously it has also given rise to severe environmental pollution (Mishra A) [2]. Industrial wastewater entering a water body represents a heavy source of environmental pollution in rivers [2]. The bulk of industrial pollution in India is cause by the small and medium scale industrial (SMIs) sectors which are almost 3 million and are widely scattered throughout the country [2].

Dye intermediates mainly include four types: benzene, naphthalene, anthraquinone and heterocycle. Previously reported studies were focused on the treatment of naphthalene dye intermediate wastewater by Fenton methods [4].

Dye intermediates are important products of the chemical industry and are used extensively in the dyestuff and pharmaceutical industries [4]. The common characteristics of real dye intermediate wastewater are high toxicity and a high concentration of chemical oxygen demand (COD), as well as a low ratio of BOD5/COD (<0.1), which have potential carcinogenic, teratogenic, and mutagenic effects [4]. Due to the wide application of the dyestuff industry in the world, large amounts of wastewater are discharged without proper treatment, bringing irreversible pollution damage to the surface water, groundwater and soil, causing serious public environmental safety problems [4]. Many industrial processes use different chemical dyes for various purposes (textile, cosmetics, food, pharmaceutical, paper, pulp manufacturing, dyeing of cloth, leather treatment, printing etc.). The presence of dyes in water is most undesirable, so a very small amount of these coloring agents are highly visible and may be toxic to the aquatic environment. Dyes absorb and reflect sunlight entering the water and so they can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [1]. Also it is well known that dye effluents from dyestuff manufacturing and textile industries, may exhibit toxic effects on microbial populations and can be toxic and/or carcinogenic to mammalian animals [1]. Therefore, removal of dyes from industrial effluents before discharge is an important aspect of wastewater treatment; it is a major environmental problem. To deal with the effluent in these SSIs the concept of Common Effluent Treatment Plan (CETP) was introduced with a hope that it would help the industries in abating the pollution. The concept of CETP has only compounded the toxic content to larger volumes and various standards formulated for inlet and outlet effluent for CETPs has no mention of such toxic contents, thus it goes beyond the capacity of primary and secondary treatment in CETPs [2]. Hence there is an urgent need for Tertiary treatment options for Common effluent treatment processes to deal with the high volume of effluent loading [2].]. The study here is aimed for providing economic feasibility report of the proposed physicochemical process replacing the conventional biological treatment in the CETP [5].

The main aim of the present study is to develop an economic and effective treatment scheme and to optimize the treatment scheme for CETP wastewater.

II. Materials and Methods

A. *Water Samples*

Sample was collected from the Inlet of Vatva CETP located in Ahmedabad, Gujarat. After that characterized to identify the initial pH, COD and Colour.

B. *Experimental Set-up*

The untreated wastewater samples are to be collected from the collection basin of an ETP and are to be transferred in beaker and pH was adjusted to 4-4.5 by using H_2SO_4. Hydrogen peroxide best stabilizes the waste between PH ranges 4-4.5 in presence of ferrous as a catalyst. After aeration solution PH become 7.4 neutralizes to 7 by using concentrate H_2SO_4 then add H_2O_2 in the ratio H_2O_2: COD is 2 and ferrous in the ratio H_2O_2:Fe^{2+} is 4 now PH become 3 and then adjust PH up to 4.5 by using lime and watch clearly flocks are formed then continued on stirrer for 2 hour then again adjust PH up to flocks again starts to formed then finally neutralized and sludge out from waste water for further process [7]. Fenton treated effluent was analyzed for colour removal, residual H_2O_2, COD and mineralization [3]. All experiments were carried out in batch mode. Several set of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results. Oxidation experiments were performed with varying the reaction time [6].

C. *Lab-Scale Set-Up*

Sr No	Instruments used
1	Thermoset
2	Magnetic Stirrer
3	Reactor Setup

Table 1: Instruments

1) *Effect of Temperature*

It showed that the effects of reaction temperature on COD and color removals were evaluated over the range of 30–60◦C. no significant differences were observed in the treatment efficiencies for the 30 to 50◦C tested temperatures; beyond that COD and color removal efficiencies decreased slightly. Temperatures higher than 50 °C may negatively affect COD removal because the flocs formed may be destabilized at high temperatures. It also reported that temperature of wastewater almost does not affected the efficiency of COD removal in Fenton's oxidation. The reaction temperature of 30◦C was considered appropriate and all experiments were carried out at room temperature, for practical and economic reasons. However, high degradation rate occurred at higher temperature, this trend can be explained by the influence of temperature in the kinetic constants according to Arrhenius law [9].

The influence of agitation rate during oxidation of leachate was studied varying the magnetic stirrer rate. The results showed varying the agitation speed had a marked effect on the COD and color removal efficiencies. High agitation rates led to more rapid and high efficient process. Increasing the rotation speed had increased the COD and color removal; however as the rotation speed was more than 400 rpm, the reduction in the COD and color was not recorded [9].

D. *Experimental Procedure*

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+$$

The procedure requires:

– Adjusting the wastewater to pH 3-5;
– Adding the iron catalyst (as a solution of FeSO4); and
– Adding slowly the H2O2. If the pH is too high, the iron precipitates as Fe(OH)3 and catalytically decomposes the H2O2 to oxygen -- potentially creating a hazardous situation[11].

The Fenton's oxidation experiments were carried out under optimal conditions established in previous work (Benatti et al., 2006): ratio [COD]:[H_2O_2] = 1:9; ratio [H_2O_2]:[Fe^{2+}] = 4.5:1 and pH 4. Experiments were carried out in 250 mL beakers with a solution volume of 150 mL that consisted of laboratory effluent without solids separation. The effluent was continuously mixed (100 rpm) in a jar test apparatus at room temperature. Firstly the pH of the solution was adjusted to 4 with NaOH (~30% w/v), and a sample was withdrawn and centrifuged at 2500 rpm for 5 min for the separation of suspended solids and COD0 was determined in Fenton´s Process for the Treatment of Mixed Waste Chemicals supernatant. The required amount of reagents was determined according to COD0 value. The amount of $FeSO_4$ was first added to the reaction mixture. The Fenton reaction was then initiated by sequential addition of the required amount of H_2O_2, in three steps of equal volume added at intervals of 20 min, to moderate the rise in temperature that occurs as the reaction proceeds and to minimize quenching of •OH. The pH adjustments were performed using H_2SO_4 or NaOH solutions before each reagent addition and then at each hour. The Fenton reaction time was initiated by the addition of the first required amount of H_2O_2 to the reaction mixture. After reactions were completed (4 h), precipitation of the oxidized iron as $Fe(OH)_3$ was performed by adjusting the pH to 8 and then about 15 h of clarification under quiescent conditions. Final samples of supernatant were taken for COD measurements and for determination of residual hydrogen peroxide. All experiments were performed in duplicate. [11]

III. RESULT AND DISCUSSION

A. *Characteristics of Inlet Waste Water*

Parameter	Avg. Value
pH	7.33
COD(mg/L)	1600
Color (NTU)	2124
TDS (mg/L)	13453

Table 2: Characteristics of Inlet of CETP- Vatva

Parameters	Initial	50 ppm	100 ppm	150 ppm
COD (mg/l)	1600	1400	1220	1000
Colour (NTU)	2124	1800	1690	900

Table 3: Effect of dosage of Hydrogen Peroxide on pollutant removal

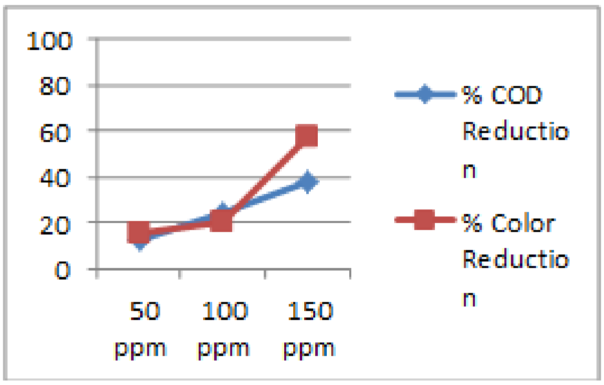

Fig. 4: Removal of COD and Color and dose indicates of Hydrogen Peroxide

B. Effect of Ferrous Sulfate Dosage

Ferrous Sulfate is a catalyst in the process. The effect of process conditions such as pH, ferrous sulfate, iron oxide nano powder and H_2O_2 doses on the efficiency of detergent decomposition was determined. It was also checked to what extent the addition of iron oxide nano powder could improve the decomposition rate and efficiency compared to the classical Fenton process.

IV. Conclusion

In this study this process was found to be an effective method for the treatment of CETP waste water containing Dyes and Dyes Intermediate member units. The effect of operational conditions such as dosage of Hydrogen Peroxide on removal of COD and Color was examined. The result showed that the removal of COD and Color increase with increase dosage of hydrogen peroxide. The highest removal efficiency of COD by 39 % and Color by 59 %. The COD removal efficiency was strongly affected by many factors such as the concentration of H_2O_2, Fe^{+2} and the ratio of organic materials to the Fenton reagents.[6]

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