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Advanced oxidation processes for the treatment of tannery wastewater

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ABSTRACT

This study has focused on the treatment of real tannery effluent using different advanced oxidation processes in lab and pilot scale studies. Periodic monitoring was conducted for five months to identify the performance at different stages of treatment in the CETP. Monthly monitoring analysis shows that ratio of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were about 0.1–0.25. It was observed that even after physicochemical treatment the sample had a low biodegradability index (BDI). For this reason, more efficient methods of advanced oxidation processes like Fenton, Ozonation have been experimented with primary settling tank (PST) effluent to improve the biodegradation in the successive activated sludge process and secondary settling tank (SST) effluent to remove the residual inorganics. Sample collection and analysis were performed using standard methods of analysis. Pollutant removal efficiency was measured in terms of reduction in COD and Total Organic Carbon (TOC). The purification effect obtained by Advanced Oxidation Processes (AOPs) was better in Ozone when compared to Fenton. A three step process of (coagulation + aeration + O_3) resulted in 80–90% reduction of COD. Coagulation, extended aeration followed by ozonation was recognized as the best method of treatment of tannery wastewater. Lab scale and pilot scale studies were done with real tannery wastewater effluents and the economics of the treatment processes were evaluated.

1. Introduction

Common Effluent Treatment Plants (CETPs) cater to treatment needs of clusters of small industries mostly highly polluting ones like tanneries, textiles, pharmaceuticals and etc. Even as each plant serves a specific type of such industries, the challenges are many- all the units do not employ the same production processes, demands are seasonal and so the effluents emerging from different processes are of unpredictable nature. Moreover, most of the plants find it difficult to treat the wastewater to acceptable limits using a fixed set of treatment processes. This paper deals with tannery effluent discharged from semi finished to finished leather industries. The process description of the CETP is given below. The effluent from the tanneries were collected in a receiving sump and pumped to an equalization tank. Aerators are used to mix the effluent in the equalization tank. In the primary physico-chemical treatment stage, effluent from the equalization tank was pumped to the flash mixer to which lime, alum and polyelectrolyte are added. The effluent from the flash mixer was sent to the primary clarifier via baffle channels. The sediments from the primary clarifier were removed and dewatered in a filter press before being dried in sludge drying beds. The effluent was sent to the secondary treatment stage, which was an activated sludge process. This stage comprised of a two tier aeration system, the first one with 2 aerators of 20 HP each, and the second one with 1 aerator of 20 HP. The effluent was sent to a secondary clarifier in which the biological sludge settles. Part of the biological sludge was recirculated back to the aeration tank automatically to maintain the level of MLSS in the system.

Advanced oxidation processes (AOPs) like ozonation, Fenton, and photo Fenton processes, Ozone/UV radiation are the potential alternatives for tertiary treatment of tannery effluent [1,2]. Among the existing AOPs, ozonation was an effective method to remove colour from wastewater, which cleave the unsaturated bonds in aromatic moieties found in humic substances, chromophores of dyes, and other pigmented compounds, thereby reducing the colour [3,4]. Researchers have also reported that pH and wastewater characteristics have a significant effect on ozonation and vice versa [5–7]. Oller et al. [8] in his review article has emphasized the importance on combining AOPs and biological process for treatment of synthetic and real industrial wastewater on recent studies and large-scale combination schemes reported for non-biodegradable wastewater treatment and reuse. Prashant et al. [9] evaluated the performance of chemical manufacturing and pharmaceutical industries CETP. They tried to reduce the chemical oxygen demand (cod) and biochemical oxygen demand (bod) using different chlorine, Hydrogen Peroxide (H_2O_2), Fe_2SO_4 doses, different pH values and contact time for identifying the optimum values. They have achieved COD and BOD reduction of 64.35% and 68.57% in optimized

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conditions. Dhinakaran et al. [10] conducted the feasibility studies on performance improvement for tannery effluent through chemical oxidation and biological treatment. They used solar Fenton process to enhance the biodegradability index (BDI) ratio. They achieved improved BDI ratio of 0.35–0.4. Rameshraja and Suresh [11] reviewed the treatment of tannery wastewater by various oxidation and combined processes. They reviewed the different combination of oxidation processes such as UV/H_2O_2/Hypochlorite's, Fenton and electro-oxidation, photo-chemical, photo-catalytic, electro-catalytic oxidation, wet air oxidation, ozonation, biological followed by ozone/UV/H_2O_2, coagulation or electro-coagulation.

Many of the previous studies focused on improving the bio degradability index using different advanced oxidation processes. But none of the previous studies emphasize on pilot plant studies and its difficulties involved in implementation at the field scale. Moreover a complete diagnostics of the CETP performance was done prior to AOP batch experiments to understand the spatial and temporal variations in the COD load Both the lab scale and pilot scale experiments were carried out with real tannery effluent to facilitate the AOP to be implemented at pilot scale on the site.

2. Materials and methods

2.1. Tannery wastewater characterization

Tannery CETP consists of various unit operations like equalization, primary treatment, extended aeration and secondary treatment with filtration. Wastewater used in the experiments was collected from the tannery common effluent treatment plant. Monitoring samples were collected at the rate of three per day- morning, afternoon, night. COD, BOD and Total Suspended Solids (TSS) were analyzed based on the procedures given in American Public Health Association (APHA, 2012) [12]. pH, ammonia, chloride, sodium, Dissolved Oxygen level were analyzed using HACH probes. Characteristics of the primary and secondary treated wastewater was given in Table 1. The schematic representation of process flow diagram and the details of advanced oxidation processes carried out in the tannery effluent treatment plant, photographs of the different unit operations are given in Figs. S1–S5.

GC–MS studies of tannery effluent was done using a HP-5 (30-m × 0.25-mm) silica based cross-linked column. The injector and detector temperatures were set at 300 °C. The initial temperature was kept at 50 °C for 1 min, ramped to 110 °C at 10 °C/min and held for 2 min, then ramped up to 250 °C at 5 °C/min and held for 2 min and to 300 °C at 3 °C/min and held at that temperature for 15 min. A 1 μL aliquot was injected in the splitless mode. Helium was the carrier gas at 1 mL/min. The MS was scanned from 35 to 550 amu at 1.562 u/s by selecting full-scan mode. MS source temperature was 230° C and MS quadrapole temperature was maintained at 150 °C.

Table 1
Characteristics of primary and secondary treated tannery effluent.

Parameters	Primary treated tannery effluent	Secondary treated tannery effluent	Discharge standards
pH	7.8–8.8	6.5–7.5	6.0–9.0
Total Suspended solids (mg/L)	200–1000	60–100	100
Total dissolved solids (mg/L)	3000–5000	4000–5000	2100
BOD (mg/L)	150–250	30–50	30
COD (mg/L)	1500–2500	250–350	250
Sulfate (mg/L)	2100–2760	2280–2420	1000
Chloride (mg/L)	1360–1740	1390–1680	1000

Table 2
Ozonation studies on PST and SST effluent.

	COD(mg/L)					
	PST effluent			SST effluent		
Time (Min)	Run-1	Run-2	Run-3	Run-1	Run-2	Run-3
0	2138	2405	2271	313	281.6	1600
15	1802	2253	1603	147.2	236.8	987
30	1736	2200	1950	44.8	121.6	450

2.2. Batch studies on advanced oxidation processes

In the present study, AOP methods, Fenton's reagent, Ozonation, O_3/Fenton combination of processes were evaluated in primary and secondary settling tank effluent. Different molar ratios of Fe^{2+} and H_2O_2 in the Fenton reagent, O_3/Fenton in different pH were added to the Primary Settling Tank (PST) and Secondary Settling Tank (SST) effluent and COD values were analyzed at different time intervals. For Fenton Processes- Fe^{2+} concentration varies from 120 to 300 mg/L. H_2O_2 concentration was varied from 600 to 2000 mg/L at pH 4. The secondary treated tannery effluent after biological treatment was subjected to ozone treatment in a bubble column reactor for further reduction of pollutants like color and residual organics in terms of COD at an ozone flow rate of 1.0 L/min was analyzed and the results were shown in Table 2. Ozone was produced from commercially available oxygen cylinder in an Ozone generator (Ozone Engineers, India) with the fixed current intensity at 0.8 A and oxygen flow rate as 1.0 L/min, was bubbled for 1 h into the ozonation reactor (0.5 L, working volume), where a ceramic fine bubble diffuser located at the bottom of the reactor and the wastewater was thoroughly mixed with magnetic stirrer to provide efficient mixing conditions in order to ensure the homogeneous distribution of the ozone in the liquid phase. The combination of ozone at a flow rate of 1 L/min and Fenton reagent (1:5 ratio) was used for the experiments. The results are given in Table 3. Samples collected at different time interval were analyzed for the reduction in COD and TOC.

2.3. TOC measurement

Total organic carbon of treated tannery effluent samples was measured using TOC analyzer (Shimazdu, TOC-Vcph, Japan). The TOC was determined by subtraction of inorganic carbon from total carbon. The instrument was calibrated by using standard solution of potassium di hydrogen phthalate along with sodium carbonate for measurement of total carbon and inorganic carbon, respectively. High pure zero-air was used as a carrier gas. Pressure of the carrier gas was maintained at the recommended level of about 200 kPa and gas flow rate at 150 ml/min throughout the analysis.

2.4. Pilot scale studies on ozonation with SST effluent

A pilot plant studies on ozonation of secondary settling effluent was set up in the CETP site. Oxygen was supplied from pressure swing

Table 3
TOC measurement for different AOP treatment with PST and SST effluent.

		Fenton			
S. No	Time (min)	PST	SST	Ozonation	Fenton + Ozonation
1	0	110.21	39.19	71.42	70.58
2	15	100.4	28.91	49.2	31.61
3	30	95.9	19.85	37.1	28.94
4	60	80.2	10.32	29.3	14.09