A Comparative Study on Removal Efficiency of Sulphide and Cod from the Tannery Effluent by Using Oxygen Injection and Aeration

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ABSTRACT: The effluents that are generated through Tanning process have high load of COD, BOD, Sulphides and Odour. Oxidation through aeration has been used for removing sulphide and COD in the tannery effluent. In the present study a comparison of normal aeration and oxygen injection in the presence and absence of catalyst $MnSO_4$ were carried out. The three test setup were performed side by side and endured for a fixed duration till there was no further reduction observed in COD and Sulphide. Results showed that the maximum COD and Sulphide removal efficiencies were in case of oxygen injection at 0.5 LPM and addition of $MnSO_4$ catalyst (5% of sulphide concentration) at pH 8.5. The removal of sulphide and COD through pure oxygen injection was found to be two times more effective than normal aeration. The removal efficiency of COD and Sulphide after 7 hours of oxygen injection at 0.5 LPM with addition of catalyst $MnSO_4$ was 82.68% and 76.83% respectively.

Key words: Aeration, COD, $MnSO_4$ catalyst, Oxygen Injection Sulphide

INTRODUCTION

Tanning or Leather processing Industries occupies the significant place in an economy as it provides massive employment opportunities to people. Tannery industry uses various chemicals in its process that results in releasing toxic substances which cause soil and ground water pollution. These have an adverse effect on plant growth, health of animals and people existing in that area. (Bhatnagar et al., 2013). Seed germination, growth and development of cultivable crops decrease with increase of tannery effluent concentration (Sinha et al., 2015). The Tannery waste have a strong reddish- dull brown colour, High BOD, High COD, High pH, Obnoxious Odour and High Dissolved solids (Mondal et al., 2005). These industries are characterised as highly polluting industries which generates high strength of wastewater that is difficult to treat. (Durai and Rajasimman, 2011).

Tannery operations can be divided into pre-tanning, tanning and post tanning (Sayers and Langlais, 1977). Sulphide and COD cause serious concern in tannery wastewater. Sulphide level in effluent makes external environment corrosive by making the treatment of effluent difficult. This effluent if discharged untreated in to river or stream, it results in to reduction of dissolved oxygen level. (Sayers and Langlais, 1977).

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In an Effluent Treatment Plant if, sulphide is carried to biological aerobic basin it makes it inefficient. So, it is imperative to remove sulphide before aerobic biological system. (Sanjay and Vaishnav Raj, 2014). Removal of sulphide from Tannery effluent can be attained slowly by aeration and more rapidly by aeration in presence of ferrous or manganese sulphate catalyst. (Sayers and Langlais, 1977). For oxidation of sodium sulphide in aqueous solution Manganese Oxide and mixtures of other transition metal oxide are found to be effective (Nhi et al., 2013). The duration of oxidation depends upon the amount of sulphides and pH. Oxidation duration is higher when sulphide amount and pH is higher. Optimal temperature at which the reaction takes place is 30 C. The duration of process lengthen when the temperature is lower or higher (Valeika et al., 2006). Sulphide oxidation is faster than re-reduction of oxidised sulphur species (Dores et al., 2008). Pilot studies prove that sulphide oxidation using $MnSO_4$ as catalyst is more effective than ferrous sulphate. The sum of results of wastewater from tannery and steel industry give better results in desulphurization, 60% of oxidised sulphur (Mohamed and Rachid, 2015).

In the batch experiment studies of oxygen injection conducted in sewer wastewater to control sulphide

generation, it was found that the rate of sulphide oxidation followed the power function with regards to H_2S concentration.

Kinetic expression projected for sulphide oxidation with oxygen:

$$r_{oxi,chem.} = K\max, chem. \times [H2S]^\alpha \times \frac{[DO]}{KO2 + [DO]}$$

where, $r_{oxi,chem.}$ is the sulphide oxidation rate in mgS/L/h, $K_{max,chem.}$ is the rate constant, $[H_2S]$ is H_2S concentration in mgS/L and and $[DO]$ is the DO concentration in mg/L.

The results of experiment imply that the H_2S oxidation rate was independent of the DO concentration at a DO level above 5 mg/L, below this the H_2S oxidation rate decreased with decreasing DO level (Sharma and Yuan, 2010).

The most important aspect of designing the process for removal of sulphide is proper mixing and dispersion of oxygen and catalyst homogenously. Along with the sulphide removal through chemical oxidation processes the biodegradability and toxicity of organics is controlled, which in turn will help in removal of COD. (Kabdasli and Arslan- Alaton, 2010). Sulfide needs 2 mols O_2/mol for oxidation. (Midha and Dey, 2008). The oxidation reaction of sulphide in a treatment plant would result into formation of thio compounds through sulphates $S^{2-} + O_2 \rightarrow SO_2, SO_3, SO_4$ (Sayers and Langlais, 1977).

Advance Oxidation Processes (AOPs) are used and known for removing organic contaminants. Recalcitrant pollutants are converted into biodegradable intermediates through AOPs that can be degraded in biological process. Integrated MBR – photoelectrooxidation (MBR-PEO) enhance the removal efficiency of COD in tannery effluent. The treated effluent after MBR-PEO can be recycled for the tanning and retanning step (Neoh et al., 2016). Aerobic digestion of tannery effluent using cow dung as seed demonstrated BOD removal rate of 95.8% at an optimal organic load of 0.6 Kg BOD/m³/d (Prakash, 2001). Various advanced oxidation techniques that lead to mineralization of contaminants converting them into carbon dioxide; water and inorganic compound are expensive (Schrank et al., 2004). Pure oxygen injection is found to be cost effective technique when compared with AOPs. Aeration system efficiency improves when we use pure oxygen injection in any system. By applying pure oxygen injection, it is expected that the oxygen transfer rate increases by five times. Pure oxygen injection can be effectively used for removal of toxic level i.e. Sulphide and COD in tannery effluent. (Wang et al., 2005). Sulphide concentration increases the COD load in effluent and

when it is oxidized to sulphate, it increases the TDS. (Bosnic et al., 2003). Precipitations through Calcium provide over 99% sulphate removal in raw and oxidised water (Benatti et al., 2008).

Fenton process and photo fenton process showed degradation of COD by 83% and 87% with no change in ammonia nitrogen after 3 hours of reaction. There was no change in ammonia nitrogen amount after the reactions (Dantas et al., 2003). Mn-Cu/Al$_2$O$_3$ heterogeneous catalytic ozonation process for tertiary treatment depicted that the removal efficiency of COD was 29.3% more as compared to ozonation alone after 60 minutes (Huang et al., 2016). An average removal of 96% of COD, 92% of TKN and 98% of TSS was observed in biological degradation studies on tannery effluent in Sequential batch biofilm reactor (SBBR) combined with chemical oxidation with ozone (Di Iaconi et al., 2004). The oxidised beamhouse effluent at increasing organic load rates (OLR), in the range of 0.4 to 1.6 g COD/L x day when treated through activated sludge system demonstrate overall COD removal up to 96%, compared to 60% without oxygen pretreatment (Vidal et al., 2004). The treatability study of combined tannery and domestic wastewater using Lab scale ASP under extended aeration showed that at a high HRT (30 hr) and SRT (16 days) with lower F/M ratio of 0.08 kg BOD/kg MLSS, the reduction of 92% COD. (Rajagopalu and Kanmani, 2008). The combined process of Electro and bio-oxidation recorded a 67 % COD degradation in tannery effluent (Kanagasabi et al., 2013). There are various researches that are carried in tannery effluent using different oxidation and combined processes. Catalytic oxidation in the presence of $MgSO_4$ or $NiSO_4$ is effectively used in removal of sulphide from Tannery Effluent. Electro-oxidation technique helps in the reduction of Sulphide and Chromium. Photo Fenton process removes COD. The literature review of various oxidation processes that have been researched so far are provided in table below.

MATERIAL & METHOD

$MnSO_4$ (98% pure) used as catalyst in Experimental test setup no. 2, NaOH solution is used for adjusting the pH of the sample, Pure Oxygen Cylinder (99.5% pure).

Reagents for COD testing: Mercuric Sulphate, Sulphuric acid and silver sulphate reagent, Standard $K_2Cr_2O_7$ (0.25N), Ferrous Ammonium Sulphate (FAS) (0.1N), Ferroin indicator.

Reagents for Sulphide testing: Hydrochloric acid, concentrated (sp gr 1.19), Iodine standard solution 0.010N, Potassium iodide, Sodium thiosulfate standard solution 0.010N, Starch indicator solution.

Reagents for Sulphate testing: Isopropyl Alcohol, Glycerol, Concentrated Hydrochloric acid, Sodium Chloride, Barium Chloride, Sodium Sulphate.

Table 1. Literature review for optimum conditions of Tannery wastewater by various oxidation processes (Rameshraja, D. and Suresh, S., 2011)

Type of Oxidation Processes	Pollutants	Optimum Conditions
Catalytic oxidation ($MgSO_4$ or $NiSO_4$)	Sulphide	Air flow rate = 0.8 l/min; Aeration time = 450 min; $MgSO_4$ conc. = 270 mg/l; NiSO4 conc. = 260 mg/l
Electro-oxidation	Sulphides, Chromium COD, Colour	Anode: Ti/Pt; Cathode: Ti; Current density = 5.56 A /dm^2 Ti/PbO$_2$; Ti/TiRuO$_2$
Fenton-photo Fenton process (fast and slow process)	COD	Ferrous ions =1 g/l; Hydrogen peroxide = 15 g/l; Time = 20 and 240 min
Hydrogen per oxide	Chromium COD	Time = 5 min Oxidant = Calcium Hypochloride; Time = 5 min; Temperature = 100 ^{o}C
TiO$_2$/UV	COD, TOC, + NH$_4$, SO$_4^{2-}$	Temperature = 100°C, Ozone dosage = 2.6 g O$_3$ /h; pH = 7
O$_3$/UV	COD, TOC, + NH$_4$, SO$_4^{2-}$COD	Ozone dosage = 2.6 g O$_3$/h; pH = 11 Ozone flow rate = 6 × 10^{-3} m^3/min; Ozonation time = 60 min; pH = 11
Photo oxidation	COD, Chromium Chromium and Leather	Nano-TiO$_2$ dosage = 100 mg/l; pH = 6; Radiation time = 480 min Sodium sulphate = 0.1 mol/l; Nanoporous Ti/TiO$_2$ electrode; pH = 2
Fenton photo Fenton process	COD	H$_2$O$_2$ dose = 840, 1679 mg/l; pH = 3,5; Reaction time = 90 min
Electro coagulation and Electro fenton	COD and sulphide	Electric current = 33.3 mA /m^2; Electricity consumption = 1.8 and 1.5 kWh/kg COD removed; 27.7 and 8.3 kWh/kg sulphide removed

Instruments used

pH meter: pH of the solution was monitored by using a digital desktop, pH meter and pH was adjusted with the help of 0.1 N NaOH and 0.1 N H$_2$SO$_4$. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

Magnetic stirrer: Magnetic stirrer was used during experimentation to solve the problem of mixing and solution remains in suspension.

Air/Oxygen sparger: Air/Oxygen is continuously supplied in the three test experiments setup in order to oxidize the sulphide and COD present in tannery wastewater.

Dissolved Oxygen Probe: The DO (Hach make) probe is continuously used to maintain D.O of 2 ppm in aerated/oxygenated wastewater.

UV visible spectrometer: The spectrum was taken with UV-visible Spectrophotometer by Hitachi V-500 UV/ VIS (Japan) double-beam spectrophotometer at 420 nm.

Flow indicator: It is used to measure the flow of Oxygen into the testing equipment. The flow of pure oxygen that was adjusted into the testing equipment was 0.5 LPM.

Experimental Procedure

Collection of sample: Collection of tannery effluent for the experiment was made from the inlet stream of Common Effluent Treatment Plant. Tannery effluent that was entering into the equalization tank was collected with the help of 1000 ml beaker after every 2 hrs in a container. This activity was performed for a day (24 hrs) in order to receive the homogeneous effluent characteristics that were coming for the treatment in CETP (UNIDO, Vienna, 2011). After collecting the sample in a container it was mixed thoroughly. Test samples were separated for the container to beaker and the settle-able suspension were allowed to settle. Supernatant of the effluent was taken for determining COD, TSS, Sulphide Sulphates and pH. The following experimental setup was used for the research.

A quantity of 1000ml of effluent was taken in each testing container of three different setups. In all three setup pH was adjusted to 7.5 -8.5 using NaOH. In first experimental setup pure oxygen injection was done with the help of sparger. In second setup MnSO$_4$ solution was prepared and added to the initial sample before oxygen injection through spargers. (Addition of MnSO$_4$ shall be ~5% by weight of Na$_2$S in water sample). Dissolved Oxygen probe was used to check the DO level of effluent. Dissolved oxygen was maintained up to 2 ppm in the test sample. In experimental setup no. 3 ambient air injection was done.

Samples were taken to analyze the sulphide, COD and sulphate after every 1 hour. The test was endured until the sulphide and COD concentration becomes stable. The sulphide, sulphate and COD level was checked in the sample. Sulphide, sulphate and COD v/s time curve were created. Sulphide and COD removal rate was calculated based on the above data.

RESULTS & DISCUSSION

The Sulphide, Sulphate and COD were recorded in the three experimental setups after every hours and the Sulphide, Sulphate and COD v/s time graph was plotted. In experimental setup involving catalyst $MnSO_4$ contributes to higher Sulphide removal. There

is change in colour of the effluent to grey because of formation of Mn^{4+} or MnO_2. The reduction of Sulphide may not result in the formation of Sulphate only because there may be formation of other intermediary ions $S_2O_3^{2-}$. In all the three setup there was increase in SO_4^{2-} level. The sulphate level in experimental setup involving $MnSO_4$ + Pure Oxygen Injection was less than that of only pure oxygen/ air injection maybe due to the formation of precipitates of Calcium and Magnesium ions that were formed at the bottom of testing equipment during the test.

Pure oxygen reaction was found to be two times more effective than aeration. The reduction level that was observed in the setup was as below:
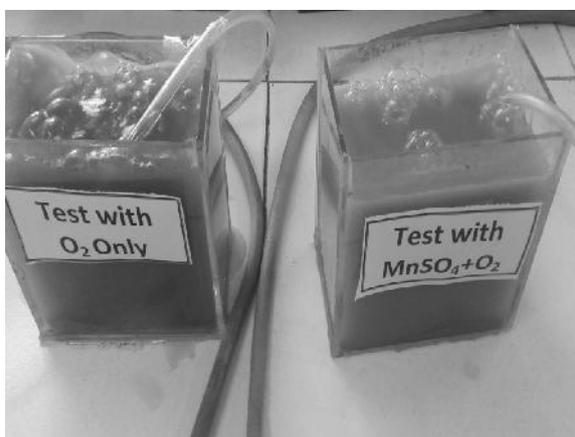
Fig. 1. Illustration of the experimental Test setup: (I) Tannery Effluent + Pure Oxygen Injection at 0.5 LPM (7 hrs duration), (II) Tannery Effluent + $MnSO_4$ addition (once) before start + Pure Oxygen Injection at 0.5 LPM (7 hrs duration)
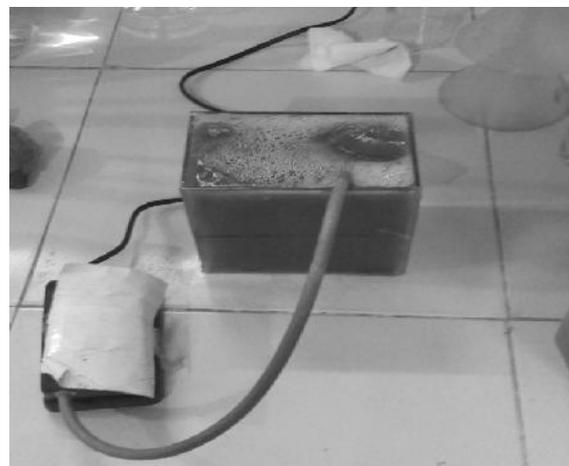
Fig. 2. Illustration of the experimental Test setup Tannery Effluent and Aeration (7 hrs duration)
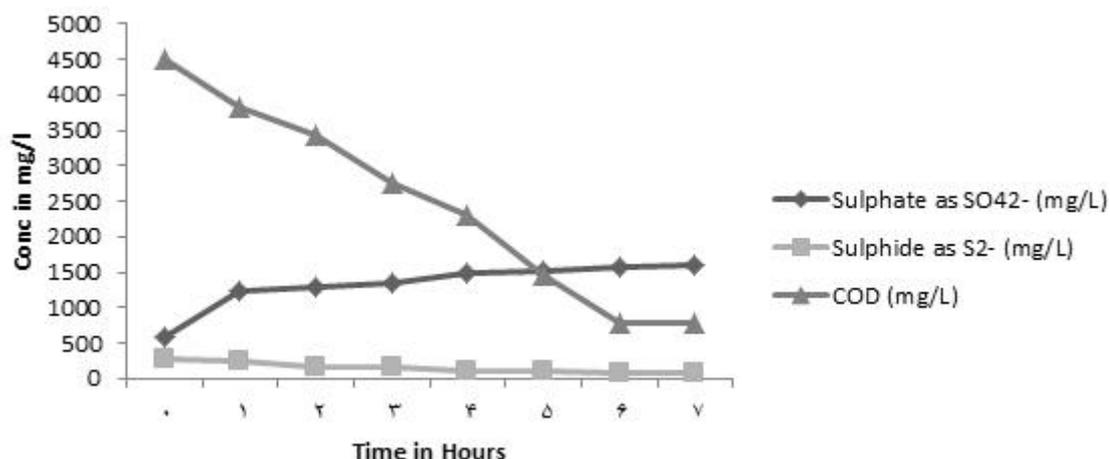

**Fig. 3. Experiment setup no. 1, Oxygen Injection in Tannery Effluent**

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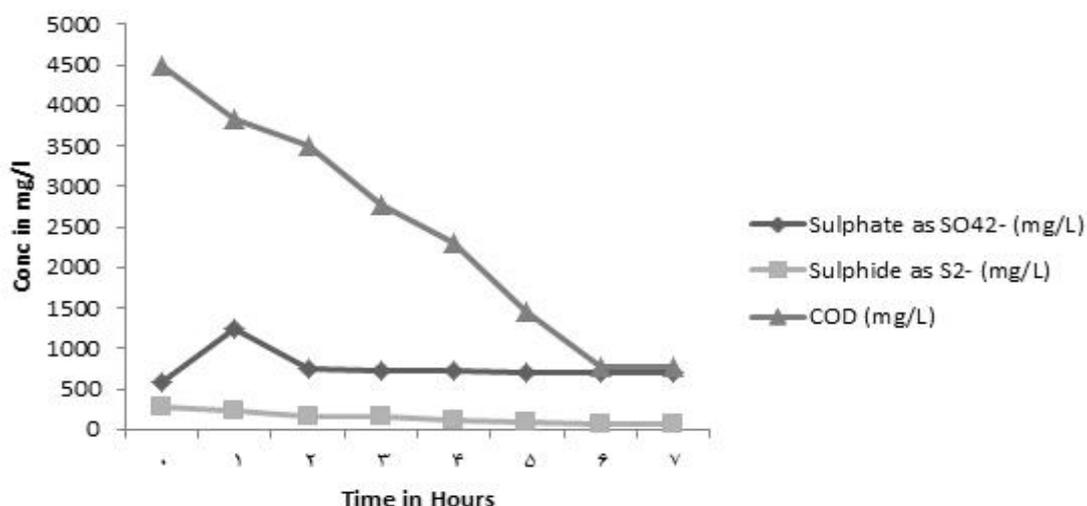
Fig. 4. Graph of Experiment setup no. 2, Tannery Effluent addition of MnSO₄ (once) before start and oxygen injection
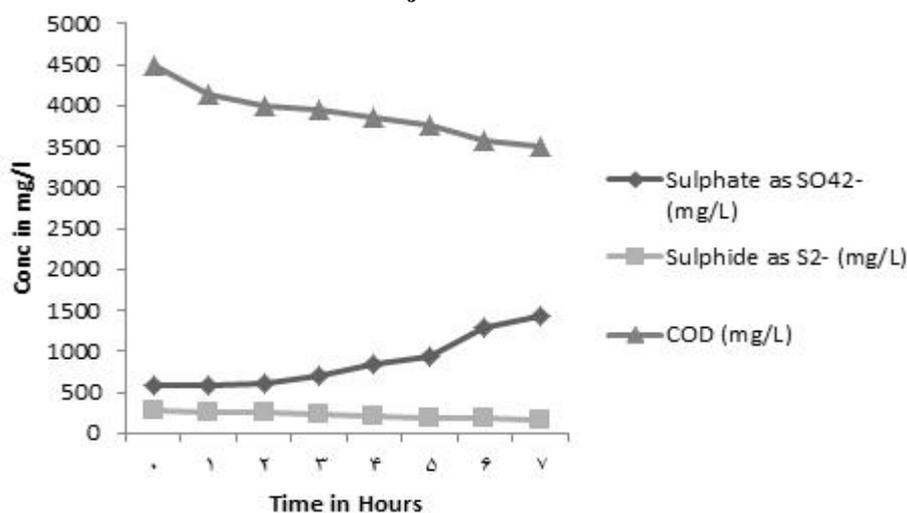
Fig. 5. Graph of Experiment setup no. 3, Ambient Air injection in Tannery Effluent

Table 2. Test Results of all three Experimental Setup

Parameters	Tannery Effluent	Tannery Effluent + Aeration (7 hrs duration)		Tannery Effluent + Pure Oxygen Injection at 0.5 LPM (7 hrs duration)		Tannery Effluent + MnSO₄ addition (once) before start + Pure Oxygen Injection at 0.5 LPM (7 hrs duration)	
		Value	%Reduction	Value	%Reduction	Value	%Reduction
COD (mg/L)	4500	3506	22.09%	784	82.58%	779	82.69%
Sulphide (mg/L)	272	163	40.07%	72	73.53%	63	76.84%
Sulphates (mg/L)	592.9	1438		1586		692	

CONCLUSIONS

Tannery Effluent is highly toxic due to presence of high Sulphide and high COD. Catalytic Oxidation technique is the simplest technique that can be used to remove sulphide present in tannery effluent. The removal of COD is complementary to sulphide removal. On testing for the oxidation of sulphide through aeration and pure oxygen injection, it was found that the removal of sulphide level in case of catalyst

(MnSO₄) with pure oxygen was more than that of aeration and oxygen injection technique only. COD reductions were also more in case of catalytic oxidation reaction than that of others. The removal of sulphide and COD through pure oxygen injection was two times more effective than aeration. Sulphide content is toxic for biological growth. Hence this technique has to be implemented before the biological (aeration) treatment process. Use of pure oxygen injection in tannery

effluent for removal of sulphide and COD is an efficient technique. It will not only help in saving power and energy expenses that are incurred by running surface aerators, blowers and diffusers but also keeps biological treatment (aeration) in good health.

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