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Removal of Sulphide in Tannery Wastewater by Wet Air Oxidation

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ABSTRACT

Tannery industry is one of the most important and rapidly developing industrial sectors. Anaerobic treatment of tannery wastewater in high rate close type reactors leaves Sulphide in the range89.96 mg/l, COD 360.55 mg/l, BOD,208.15 mg/l. Thus post anaerobic treatment of wastewater was required to meet discharging standards. High Sulphide concentration present in treated wastewater may render aerobic biological treatment unsuitable. Hence, it becomes essential to include Sulphide removal unit operation proceeding aerobic biological unit. Among the techniques available oxidation of Sulphide by air using activated carbon as a catalyst gained importance for its removal of COD, BOD, and TOC in addition to elimination ofSulphide in wastewater. The effect of [MnSO4/O2] ratio and hydraulic loading rate on removal of Sulphide and organics in current reactor containing activated carbon were discussed. The removal efficiency of sulphide from the wastewater was found by specified conditions. Further the parameters like pH, TDS, TSS and COD were determined from the wastewater.

KeywordsSulphide, Anaerobic Treatment, Turbidity, Activated Carbon, Oxidation, Biodegradable organics.

I. INTRODUCTION

The rapid growth of industries has not only enhanced productivity but also resulted in the release of toxic substances into the environment, creating health hazards. It has seriously affected the normal operations of ecosystems, flora, and fauna. In recent years, considerable attention has been paid to industrial wastes, which are usually discharged on land or into different water bodies.

This is likely to result in the degradation of the environment. Various physicochemical techniques have been studied for their applicability in the treatment of wastewaters. These mainly include sedimentation, screening, aeration, filtration, flotation, degasification, chlorination, ozonation, neutralization, coagulation, sorption, ion exchange, etc. Several limitations of physicochemical methods including partial treatment, higher cost, generation of secondary pollutants, higher quantity of solids, and use of chemicals agents make other methods (Zimpro Process) a favorable alternative for the removal of pollutants.

II. TANNERY INDUSTRIES

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater. The major components of the effluent include sulphide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. For every kilogram of hides processed, 30 liters of effluent is generated and the total quantity of effluent discharged by Indian industries is about 50,000 m3/day.The various components presentin the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin irritations, kidney failure and gastrointestinal problems.

III. TANNERY WASTE

Tannery waste material also varies considerably in volume and concentration due to continuous operation and intermittent discharge. Sulphide is one of the major components of the tannery effluent. It causes an irritating, rotten- egg smell above 1 ppm (1.4 mg m^{-3}), and at concentrations above 10 ppm, the toxicological exposure limits are exceeded. It is highly toxic to human beings. It can cause headaches, nausea and affect central nervous system even at low levels of exposure. It causes death within 30 min at concentrations of only

800–1000 mg/L, and instant death at higher concentrations. The upper concentration5 limit of sulfide in water intended for human consumption is 250 mg/L.

The corrosive properties of sulfide are apparent in the damage done to concrete walls of reactors, sewer systems and steel pipelines. It also inhibits the methanogens process. Soluble sulfide ranging from 50 – 100 mg/L can betolerated in anaerobic treatment with little or no acclimation. Sulfide has high oxygen demand of 2 mols O2/mol sulfide and causes depletion of oxygen in water.

IV. LITERATURE

Aravindhan et al., (2004) Tanning involves a complex combination ofmechanical and chemical processes. The preservation and processing of raw hidesand skins for tanning process cause severe pollution problem towards environmentand mankind, rather than being important from economic and employmentconsideration). The tanning operation in which organic or inorganic materialsbecome more chemically bound to the available substance and preserve it fromdeterioration. The substances generally used to accomplish the tanning process arechromium or extracts from bark of trees, such as chestnut.

Zhu et al., (2004) The complete digestion of mixture of primary and surplussludge using wet oxidation without catalysts. The wet oxidation was carried out inan autoclave at 250 °C with holding times ranging from 30 to 120 minutes. Adigestion efficiency of volatile suspended solids (VSS) of 94 – 96% was achieved.However, the organic matter content was high in the product liquid, whichnecessitated subsequent biological denitrification.

V. Valeika et al., (2006) One of the methods of detoxification of sulphidesn wastewater (WW) of tanneries could be their oxidation by use of MnO2. Thismaterial, as well as the product of the chemical reaction between sulphides and thismaterial is not left in WW and does not pollute it.The amount of sulphides and the pH of solution have an influence onoxidation process duration; it is longer when the Sulphide amount and pH in theWW is higher. Optimal temperature of the treatment is 30°c. Oxidation goes faster ifthe size of MnO2 particles does not exceed 0.1mm.The possibilities of repeated useof MnO2 were investigated. The stable efficiency of the MnO2 could be obtained byputting at first 0.5% of MnO2 and additionally 0.05% of MnO2of the solution mass

for every following cycle of the treatment.

Rameshraja, D. et al., (2011) The tannery wastewater with Sulphide as mainsources of pollutant, electro-coagulation is the best removal efficiency processamong the other oxidation processes, whereas for chromium, photo catalyticoxidation process using nano-TiO2 and wet air oxidation in the presence ofmanganese sulphate and activated carbon as a catalyst are more efficiency processes.

Kevin Hii et al., (2012) Hydrothermal processes such as thermal hydrolysisand wet oxidation technologies are becoming an essential part of sludgemanagement strategies adopted in modern wastewater treatment plants. Thesetechnologies contribute not only to the reduction of waste volume, but also to theimprovement of their environmental performance. Enhanced biogas production,energetically self-sufficient processes, value-added by-products, decreasedgreenhouse gas emissions and reduced reactor volumes are some of the benefits thatcan be expected from these technologies.

V. METHODOLOGY

Tannery wastewater can be treated by any of the Biological methods, Physico-Chemical methods as well as by Wet Air Oxidation Processes, Compared to all these methods Wet Air Oxidation Process, is found to be economical and efficient. Hence the tannery wastewater sample has been treated using (WAO) to remove the Sulphide, to improve the ground water quality, to eliminate environmental impacts, to reduce pollution of land and ground water and also to prevent water borne diseases.The most important among the chemical processes used for treatment of tannery wastewater are oxidation process. Wet air oxidation processes are divided into physical and chemical oxidation. The most commonly used methods include oxidation with oxygen and Manganase Sulphate.

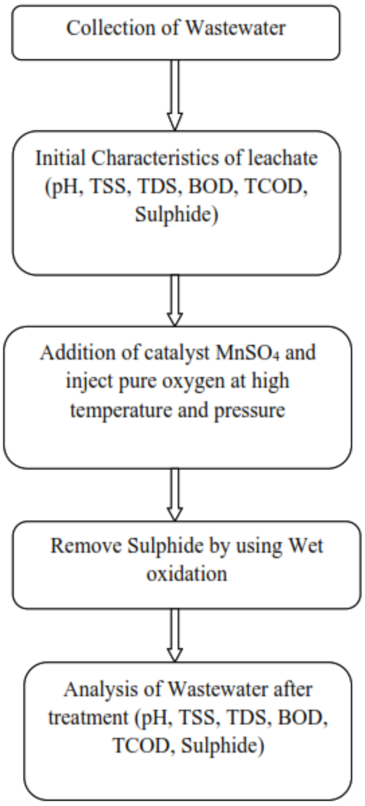

FIGURE 1

METHODOLOGY

V. MATERIAL TEST

Wastewater of each tannery process consists of pollution of varying pH values. Similarly, a large variation exists in every parameter BOD, COD, Chloride, Sulphide, etc. Discharge of these chemicals into wastewater is hazardous for the environment. Analysis of physical and chemical characteristics of the tannery wastewater collected.

TABLE 1

RAW EFFLUENT CHARACTERISTICS

S.NO	PARAMETERS	VALUE OF FRESH SAMPLE
1.	pH	11.14
2.	Total Suspended Solids	1040 mg/l
3.	Total Dissloved Solids	6395 mg/l
4.	Biological Oxygen Demand	1520mg/l
5.	Chemical Oxygen Demand	3640 mg/l
6.	Sulphide	210 mg/l

FIGURE 2

pH Measured on the Tannery Wastewater

V. RESULTS ANALYSIS

I. PRIMARY RESULTS

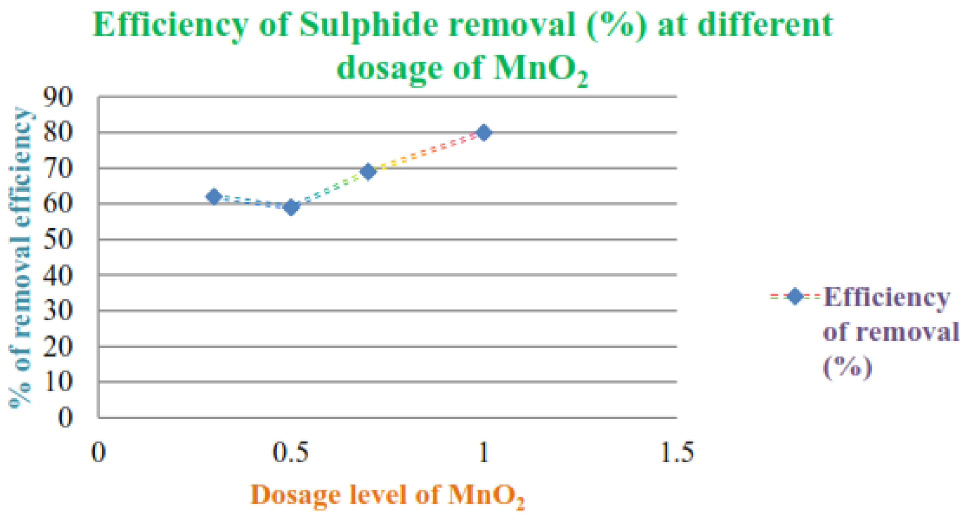

FIGURE 3

REMOVAL EFFICIENCY OF SULPHIDE AT DIFFERENT DOSAGES OF MNO2

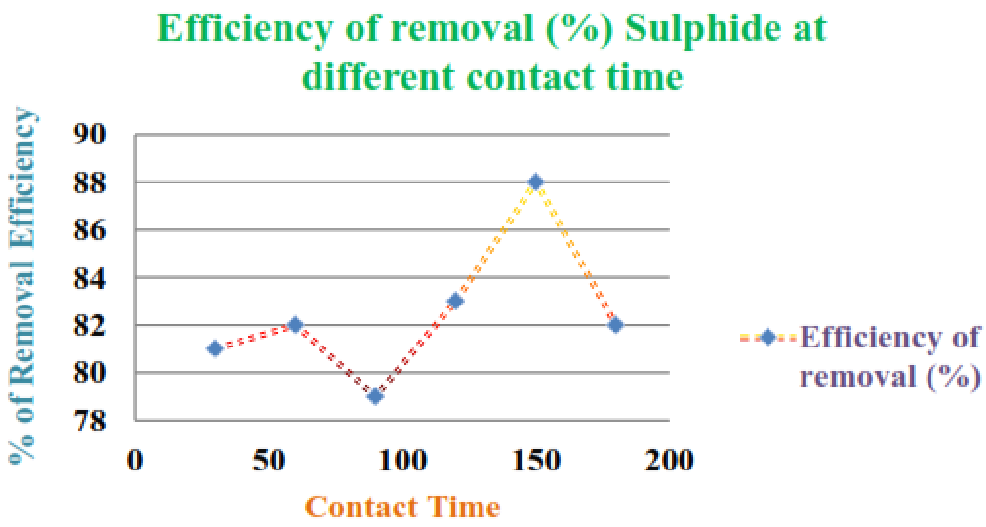

FIGURE 4

REMOVAL EFFICIENCY OF SULPHIDE AT DIFFERENT CONTACT TIME WITH1MG/L MNO2

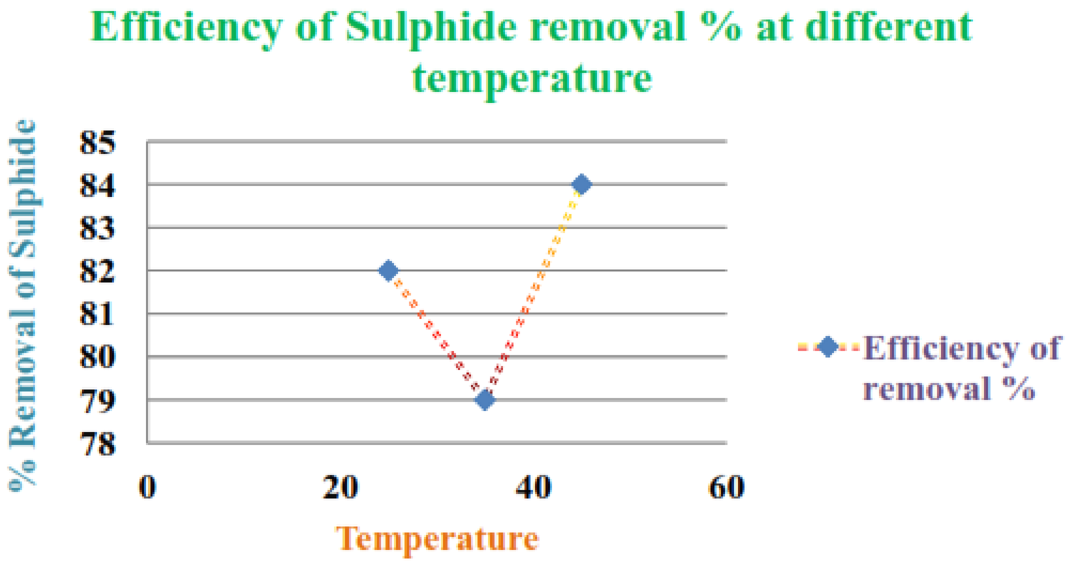

FIGURE 5

REMOVAL EFFICIENCY OF SULPHIDE AT DIFFERENT TEMPERATURE WITH1MG/L MNO2

II. RECYCLING THE OXIDIZING MATERIAL

MnO2 and the product of the oxidation MnOOH are not soluble in alkalinemedium. This property has two advantages: it is easy to separate the MnOOH fromthe treated solution (therefore, this material neither gets into WW nor pollutes it);the possibility to use MnOOH repeatedly gets possible after the separation (theprocess becomes cheaper).It is known that activity of a catalyst changes when it is used for a long time. To establish how the activity of MnOOH changes when it is used repeatedly, theunhairing liquor containing 23.6 g/l Ca(OH)2, 2.51 g/l Na2S (pH was 12.4) wastreated. For first-time treatment the amount of MnO2 added to unhairing solutionwas 0.2 and 0.5%. Control treatment proceeded without MnO2. Temperature was18-20°c. Treatment continued until sulphides were not found in the solution. Afterthat the treated solution was left at rest for about15minutes for sedimentation of thecatalyst to the bottom of the vessel. The solution was carefully poured out, leavingthe solid catalyst (to leave the maximum quantity of this, about 5% of the treatedsolution was left altogether).

After that a new portion of WW was poured on the used catalyst fortreatment. As one can see from this table, the efficiency of the catalyst decreaseswhen it is used repeatedly. We used it until the duration of treatment reached 10hours. From the technological point of view, it is a long time for treatment. Thisduration when adding 0.2% MnO2was reached the 5th time of catalyst use, and onthe 10th time, when adding 0.5% MnO2.We suppose that the efficiency of the catalyst decreases due to the effect oforganic and inorganic materials found in the liquor. But it can be said that it still iseconomical to use the catalyst a few times though its efficiency decreases.

The repeated use of the catalyst with an additional amount of MnO2 at eachew cycle of treatment was investigated. WW and conditions of the treatment werethe same as in the previous experiment. The considerable difference was that forthe first time of treatment we added 0.5% MnO2, and 0.05% MnO2 additionally onthe second and every subsequent time. 22 portions of WW were treated by thisway. Treating the first 2 cycles the duration was 2 hours, treating next 20 times itwas 2.5-3 hours. This means that stable efficiency of Sulphide oxidation wasachieved. It was calculated that when treated 22 times, the amount of MnO2required for one cycle of treatment was only 0.07%.

VI. CONCLUSION

This project deals with the removal of sulphide and toxic pollutants from the tannery wastewater. Tannery industry wastewater is difficult to treatbecause of complex characteristics like high BOD, COD, suspended solids, sulfideand chromium. The main source of sulfide in tannery industry effluent is beamhouse operations.Wet air oxidation was effectively used to remove Sulphide in wastewater.We conducted experiments for different conditions. The pollutants were reducedbecause of adding catalyst and continuous supply of air or oxygen (at hightemperature and pressure).The COD and Sulphide removal efficiency weredetermined. Hence, the Sulphide is removed in wastewater sample using WAO toimprove the ground water quality, to eliminate environmental impacts, to reducepollution of land and ground water and also to prevent water borne diseases.

WAOS are sufficient treatment methods to convert refractory organics to simplerforms in wastewater, COD and BOD can be taken under control.Wet air oxidation process is one of the most effective methods for removalof Sulphide in the tannery wastewater. The optimal temperature of the treatment is30°c at this temperature the oxidation proceeds more rapidly. The process becomesa little longer if the temperature is lower or higher than 30°c.Not only the amountof MnO2,but also the size of MnO2 particles has an influence on the duration of thesulphide oxidation process.The removal efficiency of sulphide from tannery wastewater is 80% with1mg/l of MnO2. The efficiency is also done with different contact time andtemperature.

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