

## THE USE OF OXYGEN IN CATALYTIC OXIDATION OF SULFIDES IN TANNERY WASTES

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**KEY WORDS:** *Tannery Wastewater, Sulfide removal, catalytic oxidation, natural aeration*

### ABSTRACT

With its well-known biological toxicity, the excessive concentrations of sulfide in tannery wastewaters may upset the biological treatment processes, thus leading to a substantial decrease in the efficiency of treatment plants. The presence of sulfide in wastewaters may dramatically interfere with microbial activities and consequently disturb the function of the system as a whole. In this study, the most common and reliable method of sulfide elimination by natural aeration is examined. Significant factors, such as the process efficiency, the best and most appropriate types and concentrations of the catalyst, as well as detention time of aeration are determined.

It is concluded that with an aeration time of 7 1/2 hours, sulfide removal was more than 98% effective, provided that optimum concentrations of the catalysts and adequate aeration are throughoutly maintained. The optimum concentrations of manganese and nickel are estimated to be 270 & 260 mg/l, respectively.

### INTRODUCTION

The ultimate purpose of any industrial wastewater treatment is obviously to prevent

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the health hazards associated with the environmental pollution. Industries using a diversity of processes and a variety of chemicals and generating high potential risks are commonly required to treat related waste streams, otherwise they may greatly harm all the living organisms on the earth. Because of the mentioned complexities and specificities involved, a careful study must be performed to establish the most feasible method of wastewater treatment in any group of industries or in any individual industry.

Leather manufacturing industries consuming large volumes of processing water, produce a relatively high volume of wastewater which, when discharged, may considerably pollute surface and ground water reservoirs, as well as the surrounding soils. This fact in itself is a good reason why great emphasis should be put on different aspects of treating such industrial waste streams.

Sulfide and chromium are commonly considered to be the two major obtrusive pollutants occurring in tannery wastewaters. Indeed without pretreatment of the sulfide & chrome, processes such as biological and joint treatment, following discharge into municipal sewer systems, many great difficulties are encountered.

As a hazardous substance, sulfide imparts an objectionable taste and odor, leads to corrosion of concrete and metallic parts of the apparatus used in the construction of plants and sewer systems and, finally, being a biological toxic substance it kills bacteria, consequently upsetting, the biological treatment processes. Furthermore, the presence of sulfide in waste streams leads to a substantial decrease or rapid elimination of dissolved oxygen in receiving water bodies. There are now many reported cases indicating the lethal effects of sulfide inhalation by workers during inspection and manholes cleaning (1,3,4).

Depending on whether it is economically possible for a conventional treatment plant to be constructed in an industrial site or not, two different conditions, followed by the prior segregation of sulfide-bearing wastewater and appropriate sulfide removal, may generally be considered. Generally, the former case has the merit that biological processes at the treatment plant will not be subjected to obstructive problems. In the latter case there will a rapid discharge of sulfide into municipal sewerage system for combined treatment.

The sulfide in the leather manufacturing waste streams results mostly from various procedures using lime slurry; it is also usually found in different units of beamhouse. Besides, sodium sulfide is generally added to raise the efficiency of the leather tanning process.

Of all the wastewaters generated in the tannery industry, nearly 30% is due to the liming procedure with concentration of sulfide ranging from 630 to 880 mg/l, while almost 60-65% with concentrations of 430-570 mg/l are produced in the beamhouse(1).

## **MATERIALS AND METHODS**

When an industry is confronted with sulfide problems, the most feasible method for sulfide removal is oxidation in the presence of catalysts, especially manganese sulfate. The efficiency of this procedure developed by the "British Leather Manufacturer Research Association" (BLMARA), for the tannery waste streams is now well established. Furthermore, it has been successfully applied to other industrial wastewaters, including sulfur painting liquors, cellulosic effluents (paper mills), weaving industry wastewaters using sulfur paints, sulfide-bearing effluents of oil refineries, and other related industries (2).

It is to be noted that since the oxidation rate of sulfide by  $O_2$  in the absence of catalysts is relatively low, using an appropriate catalyst, increases the reaction rate and decreases the energy required for aeration.

As the schematic diagram (Fig.1) illustrates, the treatment pilot system consisted of a glass-type aeration reactor with dimensions  $H=40\text{cm}$ ,  $W=30\text{cm}$  and  $L=60\text{cm}$ , equipped with a 250-liter capacity air-compressor, transparent rubber tubes, a dry air flow-meter, air-dividing valves. A thermometer to measure the temperature fluctuations, a digital PH meter to determine PH of wastewater flows, and other conventional equipments were arranged to aid the process. An air-regulating valve was placed at the outlet of the air-compressor and one at the inlets of the flowmeter. The aeration reactor was connected to the air-compressor through a transparent rubber tube.

In a conventional test for sulfide depletion and removal, the most important steps in

this study may be outlined as follows:

Mixed samples of lime-bearing wastewaters were collected from outflowing wash-water effluents. The washing process was typically performed for a continuous two-hour period. Samples were taken by means of containers of 20-liter capacity and conveyed to the laboratory, and the wastewaters were discharged into the barrel of 80-liter capacity in which the presedimentation occurred.

The collected samples were then transferred to the aeration reactor and beakers. During the aeration process, large amounts of foam were generated, but the problem was solved by using appropriate defoaming materials. A good reason why samples were collected from the liming process was that generally this process is assumed to be a major source of sulfide production in tannery waste-streams with concentrations higher than those in the beam-house effluents.

Wastewaters were tested for sulfide prior to aeration, and also the samples were tested during aeration to find out the effects of aeration on sulfide removal. They were measured for dissolved sulfide, according to the standard method of iodometry. Sample collection was generally regulated by using a chronometer to measure the aeration periods to make the monitoring of sulfide decrease or removal as accurate as possible when the concentrations of different catalysts and times of aeration were changed.

Experiments were done according to the standard methods, so that after the application of aluminum chloride for coagulation and sedimentation of suspended materials of the wastewater, zinc sulfide was precipitated. Sediments of zinc sulfide were, then, separated on filter papers and titrated by sodium thiosulfate in an acidic medium in the presence of a standard iodine solution.

## RESULTS

The experimental results indicating sulfide removal at different catalyst concentrations and various aeration periods are given in Tables 1 & 2. Practical conditions and limits in this study may be outlined as follows:

1) Changes in the volume of air flowing to the aeration reactor ranging from 0.12 to 1.9

liters for one liter of wastewater per minute.

- 2) Changes in the types of catalysts using either manganese or nickel sulfate.
- 3) Changes in concentrations of catalysts ranging from 5 to 359 mg/l.
- 4) Changes in aeration times ranging from 6 to  $19 \frac{1}{2}$  hours.

The main reasons for aeration time changes were (a)- that the Winkler Method could not measure the dissolved oxygen accurately and (b)- that the oxygen meter was practically out of order. The air flow was increased so that the dissolved oxygen would not be a rate limiting factor.

The catalytic aeration process of the tannery wastewater was repeated 30 times. The results are as follows:

- a. The optimum air-flow of the aeration process was found to be 0.8 liter of air for one liter of wastewater per minute.
- b. The optimum concentrations of manganese sulfate and nickel sulfate were found to be 270 mg/l & 260 mg/l, respectively.
- c. The optimum aeration time, using catalysts and sufficient air at optimized levels, was estimated to be  $7 \frac{1}{2}$  hours.
- d. Sulfide removal, at an optimum concentration of catalyst and with adequate time of aeration, was more than 98 percent effective.
- e. With no catalyst used in the process, the sulfide removal was found to be 80% effective with an 8-hour aeration period.

## **DISCUSSION**

The results indicate the importance of catalysts in sulfide oxidation through aeration. In actual practice, for instance, when a catalyst such as nickel sulfate is applied, a period of only 3 hours of aeration suffices for 82% removal of sulfide. In the absence of catalyst, however, sulfide elimination is only 64% effective.

In general, the rate of sulfide removal depends substantially on its concentration. At early stages of the aeration period, in which the sulfide concentration is still high, the rate of removal is correspondingly high, but this condition is reversed at the end of the

process. For example, during the first hour of aeration, a conventional wastewater treatment depletes sulfide content by almost 36% to 38%, but in the 7th hour the aeration process is much less effective.

As it is evident from the curves and data obtained, optimum concentrations of both catalysts were nearly the same, but manganese sulfate is assumed to be a little more advantageous.

The results also indicate that when there is no catalyst present, sulfide oxidation through natural aeration brings about an 80% removal after 8 hours and complete (100%) removal after 24 hours. There are, therefore, three significant procedures to be economically considered:

1. A complete 24-hour aeration period with no catalyst present.
2. A  $7\frac{1}{2}$  - hour aeration period with nickel sulfate as a catalyst.
3. A  $7\frac{1}{2}$  hours aeration period with manganese sulfate as a catalyst.

So far as economic and cost-related considerations are concerned the first alternative, which requires a longer period of time but no catalysts is preferred, since it saves the cost of catalysts. Taking the overall practical aspects into account, the third alternative costs roughly 1.3 times as much as the first one. The second alternative is economically unacceptable, since it costs twice as much as the first. Cost estimations for other sulfide-bearing wastewaters depend obviously on the conditions, processes and factors involved.

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**Table (1) The results of catalytic oxidation of sulfide  
in different conditions**

AERATION TIME (hrs.)	Sulfide Concentration (mg/L)		
	WITHOUT CATALIST	WITH MnSO <sub>4</sub> 270 mg/l	WITH NiSO <sub>4</sub> 260mg/l
0	645	645	645
1	547	453	447
3.5	384	91	85
5	314	51	49
6.5	227	24	20
7/5	186	1	1

The Constant conditions: Temp. = 21 c; PH = 13; Consumed Air = 0.8 L/min/L

**Table (2) the mean results of Aeration of leather industry waste water  
in different conditions.**

AERATION TIME (hrs.)	Mean Sulfide Removal (%)		
	WITHOUT CATALIST	WITH MnSO <sub>4</sub> 270 mg/l	WITH NiSO <sub>4</sub> 260mg/l
1	18.6	36	37.9
2	28.1	57.4	58.6
3	44.2	78.9	82.1
4	46.6	-	83.6
5	55.5	88.3	91.3
6	64	94	96.5
7	71.9	96.8	98.2
7.5	-	98.4	98.2
8	97.8	-	-
9	82.4	-	-

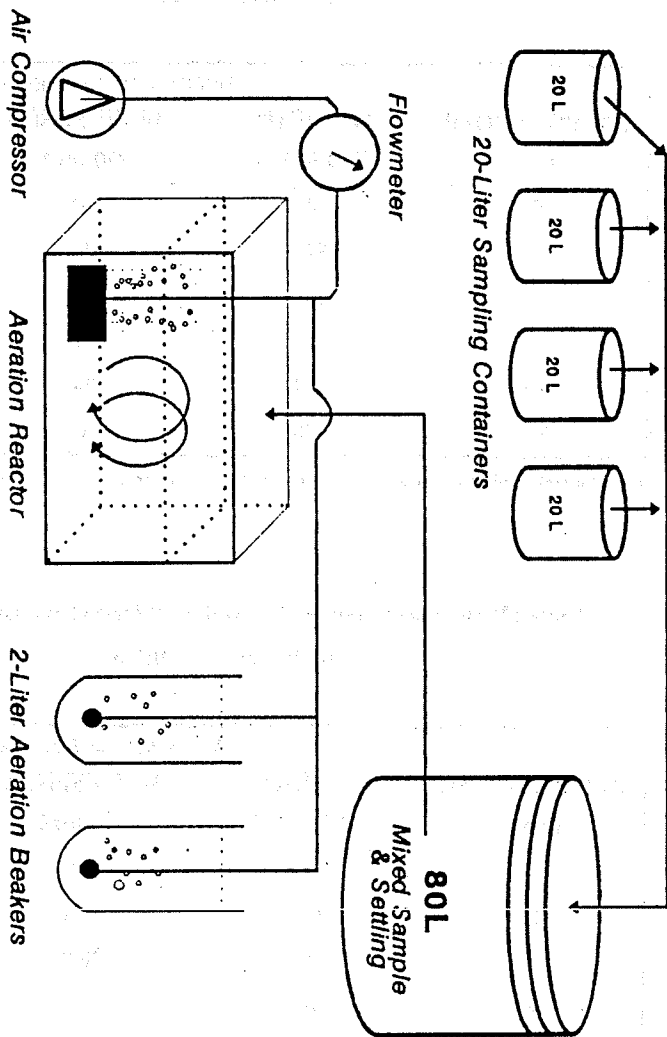


Fig.(1) Diagram of the pilot system



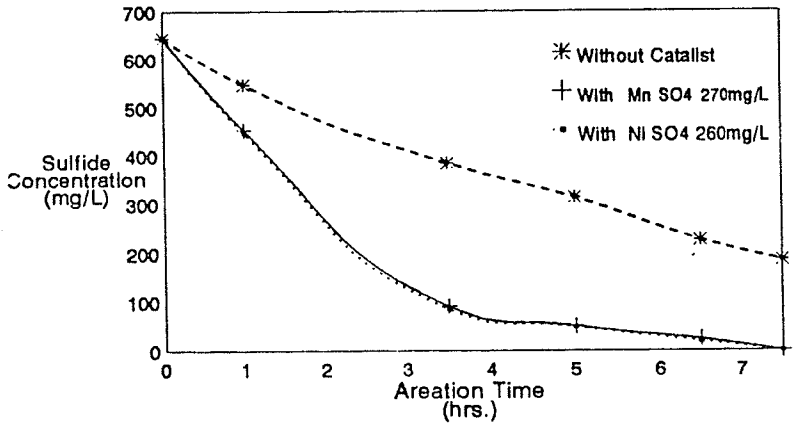


Fig. (2) Remained Sulfide concentration in different conditions

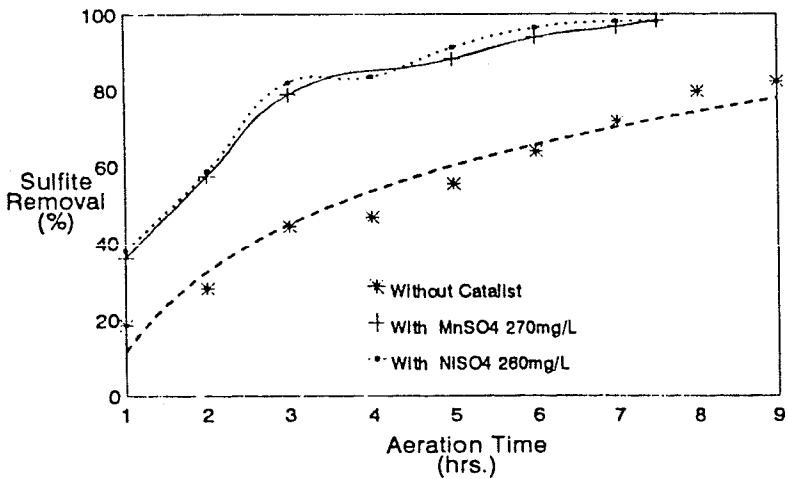


Fig. (3) Sulfide removal efficiency