

Study of Aerial Oxidation of Sulphide Contents in Tannery Wastes

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(Received 4th March, 1997, revised 28th August, 1997)

Summary: Waste effluents from leather tanning industry contain a large quantities of sulphide salts which cause pollution in land and water channels and when come in contact with some acidic media, release a highly toxic gas hydrogen sulphide into air. Hence to protect the environment, it is desirable that sulphide content from tannery wastes should either be removed or converted to some harmless compound before leaving the waste into some water channel.

In this work aerial oxidation of sulphide has been studied by designing model experiments in laboratory. Basically oxidation was carried out by bubbling air through sulphide solution and a number of concerned parameters like the role of catalyst, temperature and time have been studied. Real sulphide samples from tanneries were also successfully oxidized by employing optimum conditions.

Introduction

In leather tanning industry sulphide salts are normally used for hair shaving of hides and skins. Sulphide is highly toxic material and has an obnoxious odour. When sulphide is released into some water channel or municipal sewer system the accumulation of sulphide gases in the pipes cause corrosion and may also release a highly poisonous gas hydrogen sulphide. In addition to the sulphide ions excess of sulphate ions is always present in tannery wastes because a large amount of sulphuric acid is consumed in leather processing. Under anaerobic conditions sulphate ions are reduced to sulphide ions, which establishes an equilibrium with hydrogen ions to form hydrogen sulphide [1]. Concentration of species like H_2S , HS^- and S^{2-} highly depends upon the pH of the solution [2]. A number of unbranched poly sulphides containing up to eight sulphur atoms are stable and have been prepared in the laboratory but no evidence has been found that higher members occur in sewerage environment [3]. Besides the serious odour problems and toxicity to animal life, hydrogen sulphide has a sufficient potential for causing corrosion to sewer pipes as well. This occurs when bacteria of the genus *thiobacillus*, which is commonly present in domestic waters, converts sulphide into sulphuric acid which attacks the metal and concrete parts of the sewer [4].

the atmosphere the probability of this reaction is almost zero [5].

At low concentration hydrogen sulphide causes irritation of eyes and respiratory tract, headache, dizziness and if exposure is prolonged bronchitis may result. Higher concentrations of the gas can paralyse the nervous system, respiratory system and digestive system. With repeated exposures to low concentrations conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision are the common findings [6,7].

Leather tanning industry is one of the high foreign exchange earning industries in Pakistan. Raw leather in the form of hides and skins is collected from all over the country and some times imported from Middle East and converted into usable form by processing with different chemicals. Certain big cities of Punjab like Sialkot, Kasur, Gujranwala and Sheikupura are famous for this industry. Unfortunately no attention has been paid so far towards the processing of tannery wastes before leaving them into some nearby water channel. The result is that the out coming waste is polluting water channels, poisoning the vast land areas and adversely affecting the health of local habitants.



Although the interaction of sulphur dioxide and hydrogen sulphide is energetically feasible but in

This work was started to develop a method to cure the sulphide content of the tannery waste. Model experiments are designed in the laboratory to oxidize sulphide by bubbling air through aqueous

solution of sulphide. Different catalysts are employed to accelerate the oxidation phenomenon and the effects of certain other parameters like temperature, pressure and mode of air pumping has been checked to investigate the aerial oxidation of sulphide content in tannery wastes.

Results and Discussion

Aerial oxidation without any catalyst

Aerial oxidation of sulphide was first performed, without the use of any catalyst, merely by passing atmospheric air at a constant flow rate through a standard solution of sulphide at room temperature. Suitable aliquots from the solution were taken after every hour and analysed iodimetrically for sulphide content. The results obtained are graphically presented in Fig. 2(a). As it is clear from the figure that in first six hours a significant decrease occurred in sulphide concentration but in the next six hours the decrease was appreciably low. This was probably due to the establishment of equilibrium between the sulphide content and the oxidized species.

Effect of temperature and air flow-rate

To check the effect of the quantity of air passing per unit time through the sulphide solution

the oxidation was carried out at different flow rates of air at room temperature. As shown by the curves 'a' and 'b', more volume of air passing through the sulphide solution per unit time significantly increased the sulphide oxidation. The volume of air passed through the sulphide solution in curve 'b' was double than the volume used for curve 'a', but, as it is clear from the figure, the quantity of sulphide oxidized in curve 'b' was slightly greater than that oxidized in curve 'a'. This reveals that the correlation between the quantity of air passed and the amount of sulphide oxidized is not linear.

Curves 'c' and 'd' in Fig. 2. show the oxidation results at 40°C and 60°C respectively. The figure indicates that increase in temperature favourably affects the sulphide oxidation. Data reveals that if the temperature is increased 30 degrees, by using the same quantity of air, almost double amount of sulphide can be oxidized.

Efficiency of bubbling mode

To check the effect of the size of the air bubbles and the contact time and area, different bubbling systems were used for passing the air through sulphide solution. The first was a simple jet impinger with a narrow opening. Compressed air came out through this impinger in form of a stream

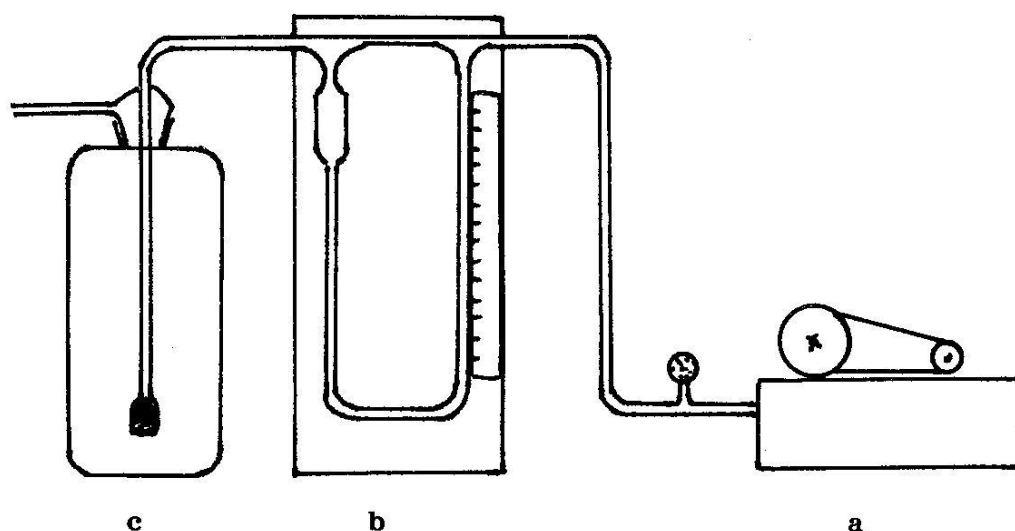


Fig. 1: Schematic Diagram of apparatus assembly for oxidation of sulphide (a) air compressor (b) manometer (c) gas wash bottle.

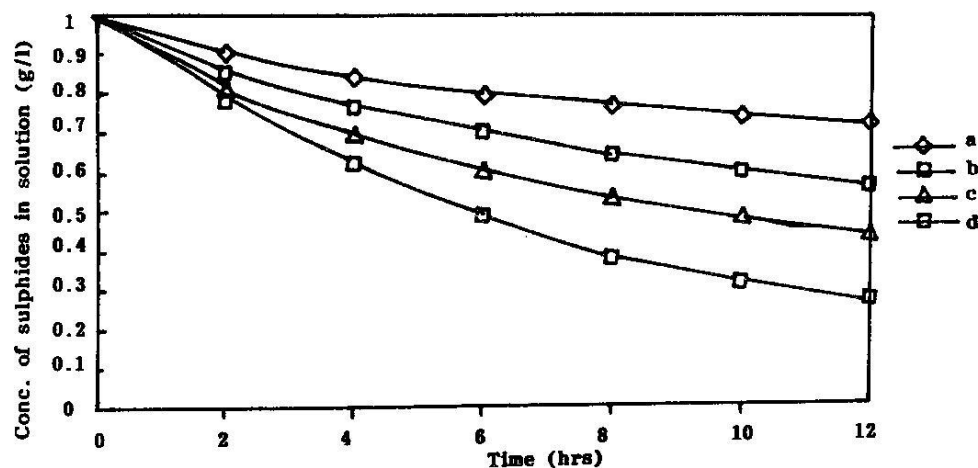


Fig. 2: Effect of time, temperature and air flow rate on the oxidation of sulphides a) room temperature: flow rate 2L/min. b) room temperature: flow rate 4 L/min. c) temperature 40°C: flow rate 2L/min. d) temperature 60°C: flow rate 2L/min.

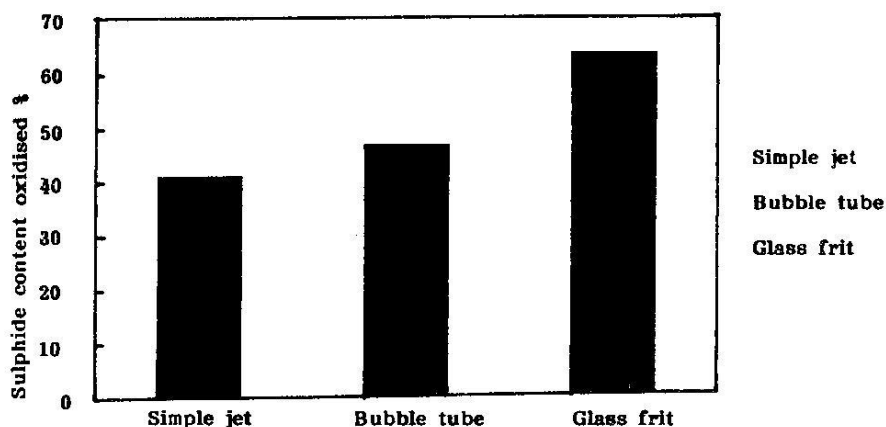


Fig. 3: Oxidation of sulphides by using different bubbling devices at room temperature for 10 hours and with 2L/min air flow rate.

of equal size small bubbles and escaped through the solution column. The second was a bubble tube with two bulges and a half-millimeter exit at the bottom. The out come of air through this device was more steady as the two bulges served as cushions for the incoming air. The third was a half-inch piece of frit fused at the end of a glass tube. Glass frit dispersed the compressed air in form of tiny bubbles throughout the sulphide solution. In this case the solution was agitated more vigorously compared to the other two devices.

The efficiency of sulphide oxidation achieved by using the three device is compared in Fig. 3. Glass frit significantly produced better results of sulphide oxidation than the other two systems. The relatively greater efficiency of glass frit was certainly due to the small size of the bubbles which provided a larger contact area and yielded oxidation to a greater extent.

As the time of air bubble contact with sulphide ions was a direct function of the height of

solution column, hence the cross-section area of wash bottle was also a considerable factor which affected the overall efficiency of the system. Bottles with smaller cross-section area proved themselves better for the aerial oxidation process.

Use of catalysts

As the basic aim of this work was to develop a simple and commercially feasible method for curing sulphide in tannery waste, hence cheaper and locally available materials were used as catalyst to oxidize sulphide. Three types of substances: inert materials, hydroxides and transition metal oxides were employed as catalysts. All the catalysts employed were added 1% by weight of sulphide content in the solution. Among the inert materials only charcoal gave an appreciable increase in the oxidation of sulphide. The other two silica and activated Fuller's earth did not produce any considerable effect on the oxidation. All the three hydroxides used, aluminum hydroxide, calcium hydroxide and chromium hydroxide gave significant enhancement in sulphide

oxidation. As shown in Fig. 4, chromium hydroxide yielded better results than aluminum and calcium hydroxides. The reason of checking the effect of chromium hydroxide as catalyst was, that chromium is usually already present in tannery wastes which could easily be converted into hydroxide by raising the pH. Among the oxides, nickel and iron oxides caused more oxidation than hydroxides and showed almost similar results, however the maximum aerial oxidation of sulphide could be found in presence of copper(II) oxide as catalyst.

Detection of oxidation products

By examining the aerial oxidation of sulphide under aforesaid conditions and analyzing the products of the reaction after suitable intervals of time it was found that at elevated temperature and in presence of suitable catalyst most of the sulphide content has been converted into sulphate, sulphite and elemental sulphur. The formation of yellowish-white turbidity due to colloidal particles in first fifteen to twenty minutes of passing air through sulphide

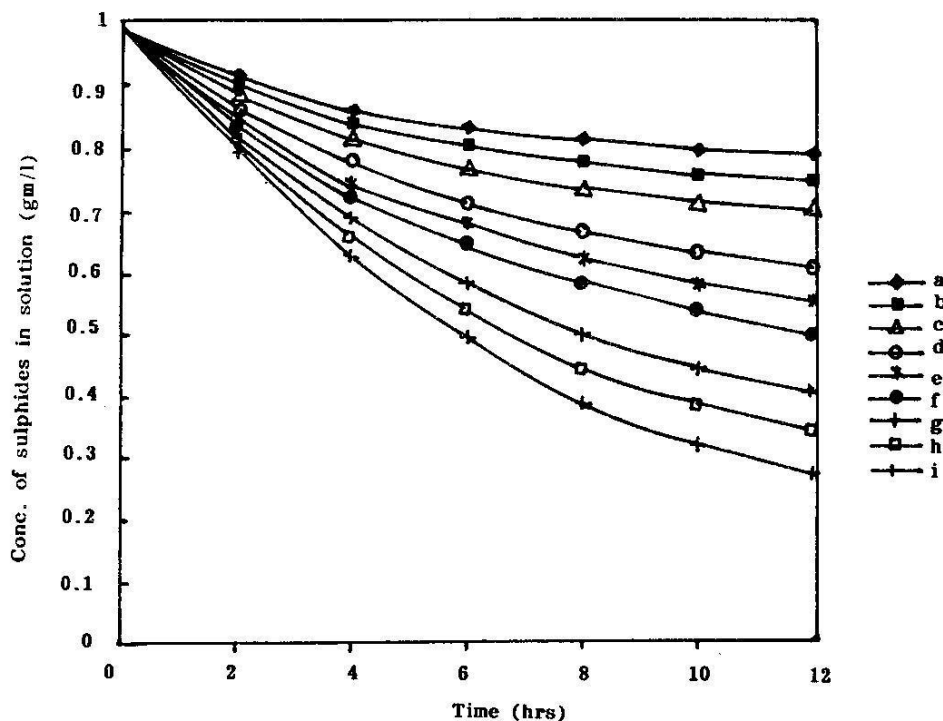


Fig. 4: Effect of various catalysts on the oxidation of sulphides at room temperature with air flow rate of 2L/min. a) Silica b) Fuller's Earth c) Charcoal d) Calcium hydroxide e) Aluminium hydroxide f) Chromium hydroxide g) Nickel hydroxide h) Ferric oxide.

solution revealed the presence of elemental sulphur. However, the solution became relatively clearer when the air was passed for a longer period. The final solution showed strong positive tests of sulphate and sulphite. This reveals that as a result of aerial oxidation at elevated temperatures and in presence of a suitable catalyst a significant part of the sulphide has been oxidized to sulphite and sulphate.

Real samples of tannery wastes

Six real samples from different tanneries containing sulphide, chromium and other contents were collected. After removing the suspended material by filtration the amount of soluble sulphide in each sample was determined titrimetrically. Then after 1:1 dilution with distilled water, each solution was oxidized at room temperature by passing air for six hours using glass frit bubbler in presence of 0.1% copper oxide as catalyst. After the oxidation the sulphide content was again estimated. As shown in Table-1, in all the samples the sulphide concentration has been reduced almost to one fifth of the original concentration.

Table-1: Aerial oxidation of sulphide in tannery waste samples at room temperature using copper oxide as catalyst

Sample	Amount of Sulphide (found)	
	Before Oxidation	After Oxidation
Sample A	650 mg/L	145 mg/L
Sample B	810 mg/L	162 mg/L
Sample C	646 mg/L	132 mg/L
Sample D	448 mg/L	118 mg/L
Sample E	1050 mg/L	286 mg/L
Sample F	610 mg/L	140 mg/L

Experimental

Standard sulphide solution

For preparing the standard solution of sulphide some crystals of AnalaR Grade sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were rinsed with ethanol and dried them on a filter paper to remove the excess of ethanol. One gram of dried sodium sulphide was dissolved in 100 mL of deionized water and a portion of it was standardized iodometrically.

Apparatus set up for oxidation and procedure

As shown in Fig. 1, the basic experimental set up consisted upon three components: 'a' an air

compressor to maintain the air supply 'b' a calibrated manometer to assess the air flow rate and 'c' a gas wash bottle in which the air was bubbled through sulphide solution.

Calibration of manometer

A laboratory made monometer, as shown in Fig. 1, filled with 1:1 ethanol-water mixture and a little dye (to give the colour) was used for measuring the air flow rate. The manometer was calibrated with the help of 2 liter standard flask, a stop watch, suitable length of rubber or plastic tube and a rubber cork with two glass tubes passing through it. One of the glass tubes was long enough, reaching to the bottom of the flask while the other just crossed the cork. The flask was completely filled with water and fitted with the cork. One end of the rubber tube was attached to the longer glass tube in the cork and the second to the bulb side of the manometer. The other end of the manometer was open to suck the air. Then the flask was inverted and let the air replace the water in the flask. While the water was being replaced by air, there was a significant difference in the levels of manometer. This difference was marked on the scale attached on one side of the manometer for this purpose. On the other hand the time taken by air to replace the water completely was noted with the help of a stop watch. The experiment was repeated several times to confirm the flow rate and the difference in fluid levels in the manometer. The difference in fluid levels was used as indicator of flow rate in later experiments.

A known volume of standard sulphide solution (100 mL of 0.05M) was taken in the wash bottle and the compressed air was bubbled under different sets of conditions like time, temperature, catalyst and pH through sulphide solution. To monitor the oxidation rate, aliquots (1-2 mL) of sulphide solution from wash bottle were taken out time to time, diluted appropriately and titrated against standard solution of iodine.

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