Proceedings of the 3rd International Conference on Civil Engineering for Sustainable Development
(ICCESD 2016), 12~14 February 2016, KUET, Khulna, Bangladesh (ISBN: 978-984-34-0265-3)

ESTIMATION OF SOLUBLE SULPHIDE DISCHARGED IN HAIR BURNING LIMING OPERATION FROM TANNERIES, BANGLADESH

Md. Abul Hashem[1], Md. Shahruk Nur-A-Tomal[2], Aziza Ahsan*[3] and Syeda Anika Bushra[4]

[1] *Assistant Professor, Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh, e-mail: mahashem96@yahoo.com*
[2] *Undergraduate Student, Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh, e-mail: shahruktomal2010@yahoo.com*
[3] *Undergraduate Student, Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh, e-mail: aahsan7872@gmail.com*
[4] *Undergraduate Student, Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh, e-mail: iqrayasha@gmail.com*

ABSTRACT

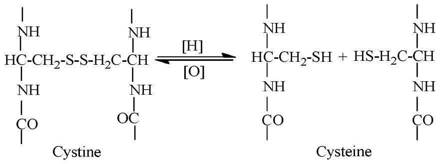
Tanning industry involves the conversion of putrescible hide or skin into imputrescible leather. In leather processing, huge amount of chemicals are employed to obtain various characteristics of the final leather or products. In tannery, liming is the first and indispensible chemical operation where hide or skin are treated with sodium sulphide (Na_2S) and lime (CaO) to dissolve epidermis, hair, wool, etc. Liming process residues release wastewater containing with sulphide (S^{2-}), high chemical oxygen demand, biological oxygen demand, total suspended solids, and total dissolved solids loads in the effluent. In this study, an attempt was made to estimate the soluble S^{2-} discharging from the tannery especially in hair burning liming operation. The sample was filtered through glass fiber filter and the filtrate was analyzed for sulphide quantification by titrimetric following SLTC official method (SLC 202). It was estimated yearly 208–6238 MT soluble sulphide is discharged only from the cowhide processing during hair burning liming. The discharged sulphide contents wastewater is mixed with simultaneously discharged the lower pH residue wastewater which emits toxic hydrogen sulphide (H_2S) gas. H_2S gas has a great negative effect on environment. Sulphide containing wastewater also causes aquatic problem. To prevent sulphide pollution from the leather processing tannery authorities should follow an alternative hair saving liming process.

Keywords: *Hair burning liming, sulphide, titrimetric, hydrogen sulphide, environment*

1. INTRODUCTION

Tanning industry is one of the most polluting obnoxious and hazardous manufacturing sectors because of producing excessive solid, liquid and gaseous pollutants. Tanning involves the conversion of putrescible hide or skin into imputrescible leather. In leather processing, huge amounts of chemicals are employed to obtain various characteristics of the final leather. In tannery at beamhouse, liming is the first and indispensable chemical operation where hide or skin is treated to dissolve the keratins (epidermis, hair, wool, etc.), non-structural proteins and subcutaneous adipose layer (Gutterres et al., 2011).

In the hair or wool, cystine is the disulphide linked amino acid which is 90% dry weight of the hair or wool (Cruz et al., 2011). After soaking, hide or skin is taken for liming operation with calcium oxide (CaO) and sharpening agents, e.g. sodium sulphide (Na_2S) or sodium hydrosulphide (NaSH) to break down the disulphide bond of cystine (Fig. 1).



$$HC\text{-}CH_2\text{-}S\text{-}S\text{-}H_2C\text{-}CH \underset{[O]}{\overset{[H]}{\rightleftharpoons}} HC\text{-}CH_2\text{-}SH + HS\text{-}H_2C\text{-}CH$$

Figure 1: Interconversion of cystine and cysteine (Covington, 2011)

The supplied hydrogen agent from the sharpening agent weaken the cystine molecular link whereby the covalent disulphide bond links are ultimately ruptured, weakening the keratin.

In the hair burning liming, sodium sulphide (Na_2S) is used to hydrolyze the keratin (hair/wool) and epidermis. The hydrated lime makes the float alkaline buffer at pH (12.8-13.0), which enhances to swell up the hide/skin, opening up the collagen fibre network (Thormstensen, 1993). The liming process residues release wastewater containing with sulphide (S^{2-}), high chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), and total dissolved solids (TDS) loads in the effluent. The sulphides are not dangerous when they are in strongly alkaline medium. It is reported that wastewater contains sulphide, upon acidification (8.0 < pH) sulphide emits as very poisonous hydrogen sulphide (H_2S) gas (Dixit et al., 2015) as the equation (1).

$$S^{2-} + H^{+} \rightarrow H_2S \qquad (1)$$

In Bangladesh, the conventional practice of discharging spent liquors from the tanneries is discharging both the spent lime liquor (pH > 12.0 with sulphide content) and spent chrome liquor (4.0 < pH) simultaneously at the same water stream. During mixing the spent lime liquor with the spent chrome liquor, produces poisonous H_2S and directly merge to the atmosphere.

In this study, an attempt was made to estimate the soluble sulphide (S^{2-}) discharging from tannery in hair burning liming operation. The sample was filtered through glass fiber filter and the filtrate was analyzed for sulphide quantification by titrimetric following SLTC official method (SLC 202).

2. METHODOLOGY

2.1 Sampling

The hair burning liming wastewater was collected into high density polyethylene (HDPE) bottle from the SAF leather industries, Khulna, Bangladesh and brought to the laboratory for experiment.

2.2 Reagents

All the stock solutions were prepared from the analytical grade reagents. Potassium ferricyanide (UNI-CHEM, China), barium chloride (UNI-CHEM, China), ammonium chloride (Loba Chemie, India), dimethyl glyoxime (Loba Chemie, India), ferrous sulphate (Merck, India), Ethanol (Merck KGaA, Germany), ammonia (Merck, India) and sulphuric acid (Merck, India) were used to prepare the required concentration or amount. Buffer solution was prepared using 200 g ammonium chloride and 200 g ammonia per liter deionized water. Indicator was prepared by mixing with 10 mL 0.6% ferrous sulphate, 50 mL 1% dimethylglyoxime in ethanol, 0.5 mL concentrated sulphuric acid. Barium chloride solution was prepared dissolving 12.5 g barium chloride per liter deionized water. The titrant 0.1 N potassium ferricyanide was prepared dissolving 32.925 g potassium ferricyanide per liter deionized water.

2.3 Measurement of Sulphide

The sulphide determined by the titrimetric method following society of leather technologists and chemists (SLTC) official method (SLC 202). The liming wastewater was filtered with glass fiber filter to remove suspended matter. The filtrate was two times diluted using deionized water and swirled for a while. 10 mL diluted filtrate was pipetted into 200 mL conical flask. Then 15 mL buffer, 1 mL indicator and 1.5 mL barium chloride were added and stoppered the flask. The flask was left for 2-3 minutes to precipitate the sulphite. The solution was then titrated with 0.1 N potassium ferricyanide until the pink colour was disappeared.

2.4 Measurement of pH

pH was measured by using digital meter (UPH-314, UNILAB, USA). Before measuring pH meter was calibrated in three points by using the standard solutions of 4.01, 7.0 and 9.0.

2.5 Measurement of DO

Dissolved oxygen (DO) of the liming wastewater was measured on-site by using the DO meter (HQ40d, HACH, USA). Before measuring, the DO meter was calibrated by the standard solution.

2.6 Measurement of TS

A 10 mL liquid sample was pipetted in an evaporating dish and dried in drying oven at 103–105°C until a constant weight was obtained.

2.7 Measurement of EC, TDS and Salinity

The electrical conductivity (EC), total dissolved solids (TDS) and salinity were measured by using an electrical conductivity meter (CT-676, BOECO, Germany). Before measuring, the meter was calibrated by using the standard solution.

3. RESULTS AND DISCUSSION

3.1 Physiochemical Properties of Liming Wastewater

The physiochemical parameters of the hair burning liming wastewater are inserted in the Table 1. It signifies that liming wastewater was strong pollution load because of containing higher quantity of pollutants such as dissolved keratin, non-structural proteins, lime, sulfide, etc. The values of all environmental parameters were higher than the Bangladesh standard for inland surface water except dissolved oxygen. The experimental results reveals that liming wastewater contains higher amount of total dissolved solids and total suspended solids. Total dissolved solids value was 13.2 times higher and total suspended solids value was 183.4 times higher than the permissible limit. The high amount of total dissolved solids and total suspended solids adversely affects the quality of water through various unfavourable physicochemical reactions. Electrical conductivity was found 38.7 than the permissible limit.

Table 1: Physiochemical properties of liming wastewater

Parameters	Unit	Liming wastewater	Permissible Limit*
pH		12.4 ± 0.2	6 – 9
Dissolved Oxygen	mg/L	6.51 ± 0.02	4.5 – 8.0
Total Dissolved Solids	mg/L	27670 ± 0.03	2100
Total Suspended Solids	mg/L	27510 ± 0.35	150
Total Solids	mg/L	55180 ± 0.35	2250
Electrical Conductivity	mS	46.43 ± 0.05	1.2
Salinity	ppt	27.2 ± 0.03	

* Bangladesh Standards for Inland Surface Water (MoEF, 1997)

3.2 Estimation of Sulphide in Liming Wastewater

It is reported that every year 33.80 thousand tons wet salted cow hide is taken for the leather processing (FAO, 2012). The water (100-300% of wet salted hide or skin) used in conventional liming opeartion at selected tanneries are shown in the Table 2. It is estimated that yearly 207.6–622.8 MT sulphide is discharged only from the cowhide processing. It seems that huge amount of sulphide is produced during the leather processing.

Table 2: Percentage of water used in hair burning liming at selected tanneries

No.	Observed industry*	% water used
01	S_1	100-160
02	S_2	150-200
03	S_3	100-200
04	S_4	250-300
05	S_5	200-300
06	S_6	100-150

* To maintain secrecy tannery name are veiled

3.3 Effect of Sulphide on the Environment

3.3.1 Effect of Sulphide on Human Health

Liming wastewater is the highest pH containing wastewater discharged from tannery; others having lower than this. Simultaneous mixing of liming wastewater with lower pH containing wastewater causes lowering of the pH by neutralizing charges. As upon lowering pH ($8.0 < \text{pH}$), hydrogen sulphide gas is emited. The level of hydrogen sulphide emission is pH dependent. The hydrogen sulphide is poisonous for human. Individuals of the tannery area are frequently inhaled the liberated gases and suffering in difficulties. Hydrogen sulfide can affect the nervous system, and even exposure to high concentrations (> 900 ppm) for one minute can cause instant coma and death (UNIDO, 2001).

3.3.2 Effect of Sulphide on Atmosphere

The fluxes of H_2S led to increase toxicity at atmosphere by atmospheric photochemical reaction. It also destroy ozone shield and increase the greenhouse methane gas (Kump et al., 2005).

In the atmosphere, H_2S is oxidized to sulphur dioxide in a three step process as the equation (4), (5) and (6). The hydroxyl radical ($HO^\bullet$) is the initiator for the transformation from H_2S to sulphur dioxide (SO_2). The main conduits for $HO^\bullet$ formation via the absorption of ultraviolet light by tropospheric ozone (O_3) and subsequently its break-up in the presence of water vapor as shown in the equation (2) and (3) (Fiore, 2014).

$$O_3 + hv \rightarrow O + O_2 \tag{2}$$

$$O + H_2O \rightarrow HO^\bullet + HO^\bullet \tag{3}$$

$$H_2S + HO^\bullet \rightarrow HS^\bullet + H_2O \tag{4}$$

$$HS^\bullet + O_2 \rightarrow HO^\bullet + SO^\bullet \tag{5}$$

$$SO^\bullet + O_2 \rightarrow SO_2 + O^\bullet \tag{6}$$

In the atmosphere, reactions of SO_2 are very complex and it proceeds in three different pathways to the sulphate ion (SO_4^{2-}) as the equation (7), (8) and (9). The SO_2 can react with the hydroxyl radical to form an HSO_3 radical which can react with another hydroxyl radical to form sulphuric acid (H_2SO_4). The third pathway to produce sulphate is when SO_2 reacts with the hydrogen peroxide (H_2O_2) form sulpuric acid as the following reactions. In the atmosphere, H_2O_2 is formed from the combination of two hydroxyl radicals (Stirling, 2000).

$$HO^\bullet + SO_2 \rightarrow HOSO_2^\bullet \tag{7}$$

$$HOSO_2^\bullet + HO^\bullet \rightarrow H_2SO_4 \tag{8}$$

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \tag{9}$$

The most common base in the atmosphere is ammonia (NH_3). Generally ammonia emits into the atmosphere from the various natural and anthropogenic sources. It is reported that $2.2\times10^6 - 8.1\times10^6$ m^3 ammonia is directly merged to the atmosphere during the conventional deliming operation in Bangladesh (Hashem et al., 2013). The ammonia reacts with the sulphuric acid to form the ammonium salts e. g. ammonium bisulphate (NH_4HSO_4) and ammonium sulphate ($(NH_4)_2SO_4$)). The formed ammonium salts are the main components of smog aerosols in the atmosphere, which effects on cloudiness as well as the earth radiation budget (Renard et al., 2004). The sulphuric acid, ammonium bisulfate and ammonium sulfate are all hydroscopic substances, readily dissolving in water and they wash out from atmosphere to the earth as wet deposition.

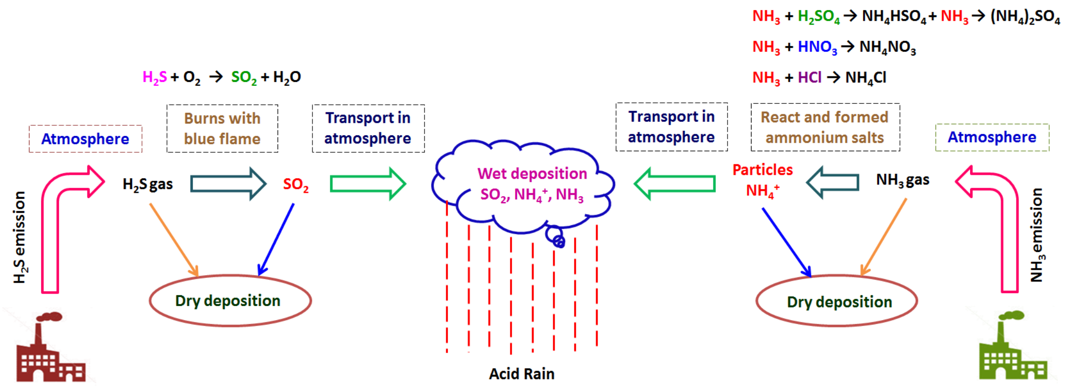


Figure 2: Effect of hydrogen sulphide in atmosphere

The exposed H_2S could be also burned with blue flame to atmosphere and produces sulphur dioxide (SO_2) (OSHA, 2005). The sulphur dioxide is the major precursors of acid rain; it reacts with atmospheric oxygen and water vapor to produce sulfuric acid, the so-called acid rain. Acid rain has the negative effect on soils, lakes and streams; it accelerates the corrosion of buildings and monuments and reduces the visibility (Padhan & Kumar, 2013). The process of dry and wet deposition of NH_3 and H_2S are illustrated in Fig 2.

3.3.3 Effect of Sulphide on Aquatic Life

The generated sulphide containing liming wastewater are discharged through drain to low lying area and finally fall in to the river, Buriganga. The spent lime liquor is highly alkaline ($pH > 12$) which has adverse effect on aquatic life. The wastewater increase biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS) and decrease the dissolved oxygen (DO) of the aquatic body. As a result aquatic balance is influenced.

3.3.4 Effect of Sulphide in Plant Growth

High alkaline pH spoils the soil fertility. Wastewater contains sulfide which inhibit the growth of plants (Olson, 2012; Lamers et al., 2013). Due to its toxic effect on soil many plants are disappeared in the tannery area.

4. CONCLUSIONS

Leather processing comprise of several operational stages among them hair burning liming is the most polluting operation. The investigation reveals that huge amount of sulphide is discharged during hair burning liming operation. Wastewater containing sulphide (S^{2-}) especially liming wastewater could be transformed into H_2S or SO_2 gas. Both the H_2S and SO_2 have the negative effect on human health and in the atmosphere. Sulphide containing wastewater also causes aquatic problem. To prevent sulphide pollution from leather processing, tanneries should follow an alternative hair saving liming process such as enzymatic unhairing.

Keratins and lipids in ethnic hair

REFERENCES

Covington, A.D. (2011). *Tanning Chemistry: The Science of Leather*. Cambridge: The Royal Society of Chemistry.

Cruz, C.F., Fernandes, M.M., Gomes, A.C., Coderch, L., Mart, M., Mendez, S., Gales, L., Azoia, N.G., Shimanovich, U., & Cavaco-Paulo, A. (2013). Keratins and lipids in ethnic hair. *International Journal of Cosmetic Science*, 35, 244–249.

Dixit, S., Yadav, A., Dwivedi, P.D., & Das, M. (2015). Toxic hazards of leather industry and technologies to combat threat: *A Review Journal of Cleaner Production,* 87, 39–49.

FAO (2013). *World statistical compendium for raw hides and skins, leather and leather footwear 1993-2012*.

Fiore, A.M. (2014). No equatorial divide for a cleansing radical. *Nature,* 513, 177–178.

Gutterres, M., Bordignon, R.S., & Baur, L. (2011). Contamination of used soak/unhairing baths by nitrogen in comparison with carbon and soluble protein contents. *Journal Society Leather Technologists and Chemists*, 95, 35–38.

Hashem, M.A., Islam, A., Paul, S., & Nasrin, S. (2014). Emission of gaseous ammonia during deliming operation in tannery and its environmental effect: Bangladesh. *Proceedings of 2nd International Conference on Civil Engineering for Sustainable Development*, February 14-16, 2014, KUET, Khulna, Bangladesh, 25.

Lamers, L.P.M., Govers, L.L., Janssen, I.C.J.M., Geurts, J.J.M., Van der Welle, M.E.W., Van Katwijk, M.M., Van der Heide, T., Roelofs, J.G.M., & Smolders, A.J.P. (2013). Sulfide as a soil phytotoxin-a review, *Frontiers in Plant Sci*ence, 4, 1–14.

Lee, R., Kump, A., Pavlov & Michael A.A. (2005). Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. *Geological Society of America*, 33(5), 397–400.

Ministry of Environment & Forests (MoEF), Government of the People’s Republic of Bangladesh. (1997). *The Environment Conservation Rules*.

Olson, K.R. (2012). Mitochondrial adaptations to utilize hydrogen sulfide for energy and signaling. *J. Com. Physio. B*, 182, 881–897.

OSHA (2005). Occupational Safety and Health Administration fact sheet, U.S. Dept. Labour.

Padhan, S. & Kumar. R. (2013). SOx control during combustion of coal by adding limestone. *Int. J. Sci. Eng. Res,* 4(7), 1705–1707.

Renard, J.J., Calidonna, S.E., & Henley, M.V. (2004). Fate of ammonia in the atmosphere-a review for applicability to hazardous releases. *Journal of Hazardous Materials,* B108, 29–60.

Stirling, D. (2000). The Sulfur Problem: Cleaning Up Industrial Feedstocks. Cambridge: The Royal Society of Chemistry.

Thormstensen, T.C. (1993). *Practical Leather Technology*. Malabar, Florida: Krieger Publishing Company.

United Nations Industrial Development Organization (UNIDO) (2001). *Introduction to treatment of tannery effluents*, Vienna.