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Aquatic effluence triggered by tannery during beamhouse and chrome tanning operations at Hazaribagh, Bangladesh

Md. Abdul Zalil [1], *Md. Abul Hashem* [2*], *Abu Jor* [2]
[1] Department of Leather Engineering, Institute of Leather Engineering & Technology, University of Dhaka, BANGLADESH
[2] Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, BANGLADESH

ABSTRACT
Real time physical and chemical parameters of discharged liquid wastes have been characterized during beamhouse and chrome tanning operations. Tanning operation converts the putrescible raw hide/skin into leather. Since raw hide/skin to make finish leather involves a series of chemical and mechanical operations and every operation produces a substantial amount of liquid and solid wastes as well as gaseous air pollutants. Result indicates that physical parameter: pH was extremely low (<2) or high (>12.0); suspended solids (SS) were 18-98 times and dissolved solids (DS) were 13-41times higher than the regulations. The biological oxygen demand (BOD) (50−2300 mg/L) and chemical oxygen demand (COD) (2696−10560 mg/L) values were high; higher the BOD and COD values have the negative effect on aquatic life. The suspended matters have the possibility to deposit on the bed of stream which causes to kill aquatic organisms; floating solids affect the stream's ability for self-purification by regeneration of oxygen from the air. Authority should take initiative to minimize the waste before discharging to the environment for cleaner leather production.

Keywords: Suspended solids, Dissolved solids, pH, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD).

1. Introduction

Aquatic pollution is becoming great threat for the forthcoming generation including human, animals and plants. Due to industrialization, air, water and land are becoming contaminated from the discharged gaseous air pollutants, liquid and solid wastes. Tannery is one of the oldest aged industries; worldwide it is known one of the obnoxious industries due to generating solid and liquid wastes and gaseous air pollutants. Tanning operation involves the conversion of putrescible raw hide/skin to make finish leather where a series of chemical operations are required to hold several types of attributes. Each chemical treatment requires huge amount of water and after completing chemical treatment huge amount liquid waste is produced as waste water containing extremely high or low pH, suspended solids (SS), dissolved solids (DS), high chemical oxygen demand (COD) and biological oxygen demand (BOD), low level of dissolved oxygen (DO), coloring substance, sulphide, chloride, lime, heavy metals like chromium, rotten proteinaceous substances etc. for discharging. In beamhouse operation produces gaseous air pollutants such as hydrogen sulfide (H_2S), ammonia (NH_3), chlorine (Cl_2), sulfur dioxide (SO_2) etc. are immediately merged to atmospheric environment [1]. The produced gaseous air pollutants, solid and liquid waste are caused serious environmental hazards and public nuisance.

In Bangladesh 243 out of 270 tanneries are located at Hazaribagh, Dhaka [2], covering an area 25 ha [3], three sides are surrounded by the residential areas and the western side by the flood embankment. Tanneries of Bangladesh have gained a negative image in the society due to generating environmental pollution therefore facing a severe challenge to survive. On the other hand, it is one of the largest export earning sectors to strengthen the national economy for the country. The Export Promotion Bureau (EPB) reported that Bangladesh earned US$765 million from the leather sector in the fiscal year of 2011-2012. Besides, gradually demands of finished and fashionable leather products growing all over the world and the government of Bangladesh already declared as a priority sector [4].

Since the last few decades of development, Bangladesh has faced the environmental degradation of the river, Buriganga and supplementary linked rivers due to picking up the discharged green solids and liquids from the leather industries at Hazaribagh, Dhaka, Bangladesh [5]. None of the leather industries have effluent treatment plant (ETP) excluding for one modern tannery (Apex Tannery, Unit-2).

Many researchers have accounted on tannery wastes by characterization of the parameters and their impact assessment on the environment [6, 7]. Mostly samples are picked up after mixing of discharged waste liquid from the tanneries before falls to the river, Buriganga from where it is difficult to recognize the specific effluent load from the tannery in a specific operation as well as the real feature of the effluent.

In this study real time physical and chemical parameters of discharged liquid wastes have been characterized during beamhouse and chrome tanning operations. The obtained results were complied with the standard.

2. Experimental

2.1 Sample collection

All the year round production base big tannery at Hazaribagh, Dhaka was selected for sample collection. The samples were collected into polyethylene bottles without air gap just after completing chemical treatment and kept in the refrigerator at 4ºC until to complete the

* Corresponding author. Tel.: +88-01674590373
E-mail address: mamashem96@yahoo.com

experiment. In Fig. 1 shows the operational sequences for chemical treatment of beamhouse to chrome tanning.

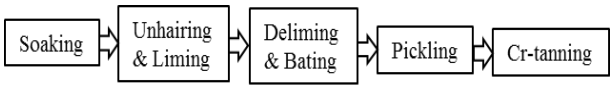

Fig. 1 Conformist beamhouse to Cr-tanning operations

3. Methodology

3.1 Determination of pH

pH of the samples was measured instantly after finished the chemical operation on that day by using pH (Orion, Model 370, USA) meter. Prior to measure the pH, meter was calibrated in three points by the standard solutions.

3.2 Determination of total solids (TS)

Total solids (TS) of the samples were determined gravimetrically as per standard methods of APHA [8]. A 10 mL liquid waste was passed through the glass fiber filter and dried at drying oven at 103 to 105°C until to obtain a constant weight.

3.3 Determination of chloride (Cl^-)

Chloride is determined by titration with $AgNO_3$ solution using ferric alum indicator. The end point is indicated by the appearance of a permanent brown red color.

3.4 Determination of Dissolved oxygen (DO)

Dissolved oxygen was measured on that day by using the DO (HQ40d, HACH, USA) meter. DO meter was calibrated before using.

3.5 Determination of BOD and COD

BOD was measured by OxiTop method. COD was determined by the titration with ammonium iron (II) sulphate $[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$ as ferroin indicator until color changes from the blue-green to red-brown.

3.6 Determination of Chromium (Cr)

After filtration the spent chrome liquor, total chromium was measured by the atomic absorption spectroscopy (Varian AA 240) at Dhaka University, Bangladesh.

4. Results and Discussion

4.1 pH level

The level of pH at different stages from soaking to chrome tanning is shown in Fig. 2. The pH in soaking, liming (unhairing & liming), deliming & bating, pickling and Cr-tanning was 7.7, 12.1, 7.7, 1.9 and 3.5, respectively. It seems that pH level was neutral to high alkaline (7.7−12.13) for soaking to liming. On the other hand in pickling pH (< 2) was extremely low; in Cr-tanning pH (< 4) was also acidic. The pH for liming, pickling and Cr-tanning was beyond the standard levels (pH 6–9) [9]. After completing chemical or mechanical operation liquid waste is discharged through drain and all these liquid waste is allowed to be mixed prior to fall the river, Buriganaga. The liquid waste contains sodium chloride, unused sodium sulphide, calcium hydroxide, dissolved hide/skin proteins, ammonium salts, keratin protein, etc. are causing aquatic problem.

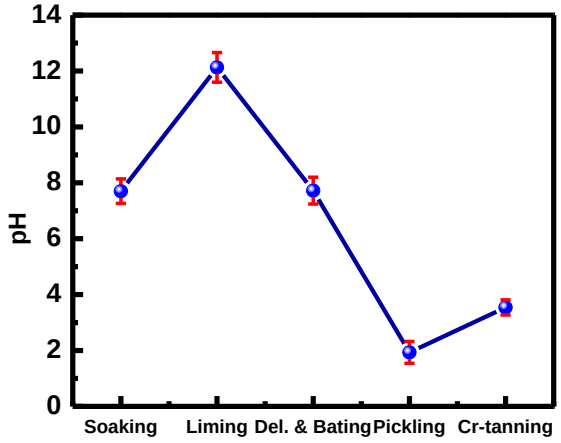

Fig. 2 pH level in beamhouse to Cr-tanning operations

4.2 Total solids (TS)

The total suspended solids (TSS), total dissolved solids (TDS) and total solids (TS) are shown in the Fig. 3. The suspended solids (SS) and dissolved solids (DS) value were so high and in some cases the level was several times higher than the standard level. Especially in soaking, liming and deliming & bating the suspended solids level was 70, 66, and 98 times higher than the standard level (Table 1), respectively.

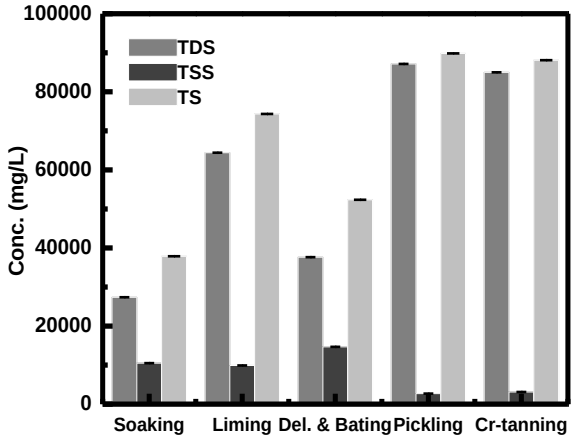

Fig. 3 The level of TSS, TDS and TS

The TDS level was 18-40 times higher the standard for beam house to Cr-tanning operations. The discharging solids substances get deposited on the bed of the stream and kill aquatic organisms of the stream bottom. The

floating solid interfere the streams ability for self-purification by re-generation of oxygen absorbing from the atmosphere. It also effects on the photosynthesis activity of the stream plankton and aquatic plants. The suspended solids (SS) are caused the turbidity which decreases the infiltration of sunlight into water thus reduces photosynthesis activity of aquatic plants.

4.3 Chloride (Cl^-) concentration

The chloride concentration in beam house and chrome tanning operation is shown in Fig. 4.

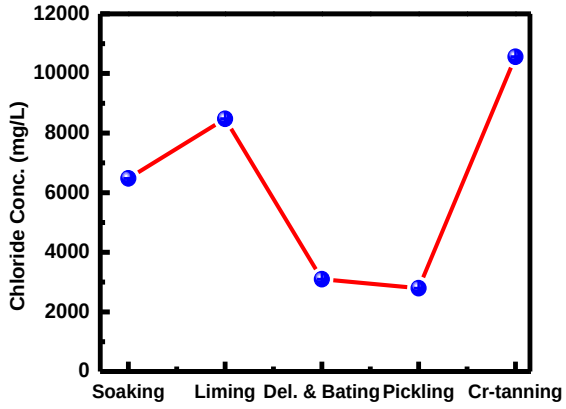

Fig. 4 Chloride levels in beamhouse and Cr-tanning

Chloride increases the electrical conductivity of the water and thus increases the corrosivity. Due to its corrosivity metal vessels of tanning react with chloride ions to form soluble salts [10] as a result increasing levels of metals in the water bodies. In some cases wastes water containing chloride is discharged through lead pipe which enhances the galvanic corrosion [11]. Finally all the metal containing waste water falls to low lying area to river, Buriganga.

4.4 Level of Dissolved Oxygen (DO)

In Fig. 5 represents the dissolved oxygen levels in the beamhouse to chrome tanning operations.

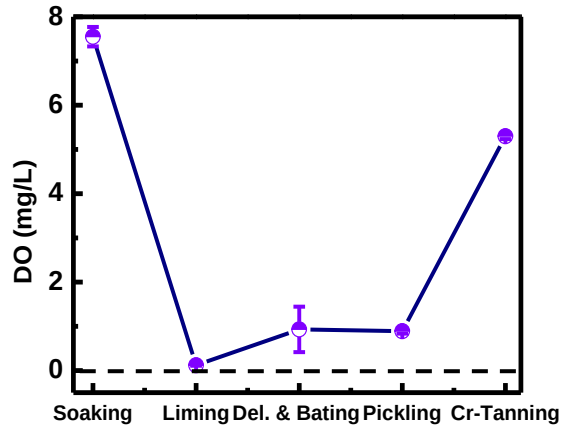

Fig. 5 DO level in beamhouse to Cr-tanning operations

DO levels were placed between 0.9 mg/L–7.6 mg/L. In the surface water DO level is 8.5 mg/L at 24ºC [12] and standard for waste from the industrial unit is 4.5–8.0 mg/L. In case of soaking and Cr-tanning DO values were between the ranges for industrial unit. The rest of operations DO values were very low; in case of liming DO was extremely low (<1). The lower DO values containing waste liquors are directly discharged to environment. Liquid waste from the various operations as well as from the different tanneries falls to the river, Buriganga which is one of the most reasons to decrease the DO level. Resulting numbers of fishes as well as aquatic plants are disappearing due to lack of DO.

4.5 Level of COD and BOD

Fig. 6 shows the BOD level in beamhouse to Cr-tanning operation. The liquid wastes are enriched with high BOD_5 except in pickling (50 mg/L). The BOD_5 level in Cr-tanning, deliming & bating, soaking and liming is (2-45) times higher than the tannery effluent standards in Bangladesh. The higher BOD_5 indicates the higher concentration of organic substances existing in the liquid wastes which consume DO. As a result, aquatic livings are getting suffocation due to lack of oxygen.

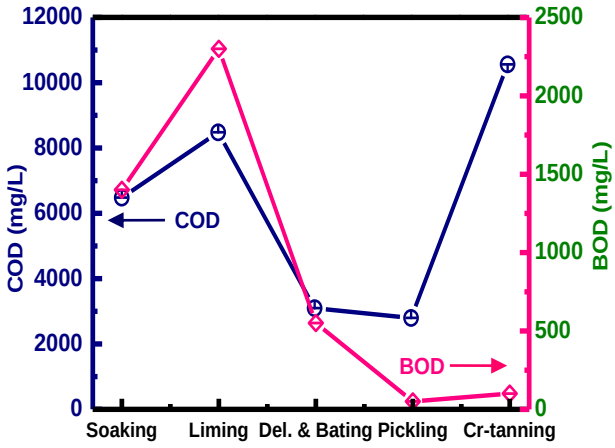

Fig. 6 BOD and COD in beamhouse to Cr-tanning operations

It is clear from the Fig. 6 that the COD values in the liquid wastes range vary from 2796−10560 mg/L. The ratio between COD: BOD of untreated tannery effluent is in the range 2:1 to 3:1 [13]. The higher the ratio between COD and BOD implies that bacteria cannot easily break down organic contaminants in the effluent or it could be said that in the biological treatment unit less organic substance will be break down. As a result, the ratio of COD and BOD has the negative effect not only in aquatic life also in the treatment technologies.

4.6 Total chromium (Cr) concentration

The concentration of total chromium (Cr) in the spent chrome liquor was 2656 mg/L. The level of chromium concentration was extremely high and it was 1328 times

higher than the industrial standard (2 mg/L) [9]. Prior to chrome tanning, during pickling stage pH is maintained at 2.5–3.0 for better chrome penetration into pelts [14] and subsequently chrome tanning the pH is raised ~4 to fix chromium with collagen [15]. In that context in pickling pH is low (< 2) thus limiting the fixation of chromium into the pelt resulting discharged as waste. The high concentration of chromium is discharged directly from the tannery without applying recover or reuse system.

During carrying the discharged spent chrome liquor through the drain; it mixes with simultaneously discharged lime liquor (pH 12.13) which produces toxic hydrogen sulphide (H_2S) gas; a fraction of chromium is precipitated as chromic hydroxide or absorbed by soil/sediment or carrying as liquid phase and falls to the low lying adjacent areas. Onset of favorable condition the adsorbed chromium could be desorbed/leached from the soil/sediment to ground water that might be a great threat in the near future of the adjacent residential area.

4.7 Effect of physiochemical parameters on aquatic life

The pH is vital for aquatic organisms and physiological process which can be activated under a relatively wide pH range 6.0−9.0 [16]. Elsewhere this pH range is stressful and potentially lethal to fish; if the pH is getting too far from optimal range even organisms may die. The extremely low pH (< 2) in pickling is contained chloride ion which could dissolve the metals from tanning vessels or from the sediment which may be taken up by the aquatic animals or plants [17]. The pH below 5.0 productivity of aquatic ecosystems is significantly reduced which successively reduces the food supply for higher organisms [18] as a result reduction the number of fish or growth rates.

Dissolved oxygen is essential for survival of aquatic livings. Low dissolved oxygen (DO) primarily results from the excessive algae growth; resulting insufficient amounts of dissolved oxygen available for fish and other aquatic lives. Deficiency of DO also occurs death of submerge plants.

The suspended substances can be altered the taste, temperature, odor and reduce the levels of DO particularly in deeper. The higher the total solids (TS) are responsible for turbidity of water which causes the photosynthesis process because turbidity impedes deep penetration of light in water [19]. The total dissolved solids (TDS) causes toxicity by increasing the salinity, changes the ionic compositions of water and toxicity of individual ions [20]. The quality of the river water, Buriganga is becoming worse due to receiving tannery liquid wastes.

4.8 Comparison data with standard

In Table 1 data was obtained from the experiment comparison with the tannery effluent standard in Bangladesh. Obtaining data exceeds the standard level which means the liquid waste is directly contaminated the receiving aquatic bodies.

Table 1 Comparison the parameters with standard

Parameters	Obtained	Standard
pH	1.9-12.1	6-9
SS	2693−10498	150
BOD_5 20°C	2796−10560	100
Sulphide (as S)	Not detected	1
T. Chromium (as Cr)	2656	2
TDS	27378−87145	2100

* The unit of the parameters is mg/L except pH

5. Conclusions

In beamhouse to chrome tanning operations substantial amount of liquid wastes are produced which contain high or extremely low pH, high TDS and TSS. The ratio of COD and BOD is also high. The spent chrome liquor contained high amount of chromium. The entire waste liquids' final reservoir is the river, Buriganga which has a great adverse impact in aquatic life. Due to deficiency of oxygen aquatic livings are becoming disappear, suspended matters obstacle to infiltrate the sunlight in the photosynthesis process. Authorities have to be minimized the liquid wastes to follow the environmental regulation before discharging to the environment. In case of spent chrome liquor it could be reuse or recover system for environmental friendly leather production.

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