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NONCONVENTIONAL USE OF BASIC CHROMIUM SULPHATE FOR WET BLUE LEATHER PRODUCTION- AN ATTEMPT FOR ABATEMENT OF POLLUTION

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ABSTRACT

Concern about pollution related problems in the global scenario are persuading all the processing industries to adopt cleaner manufacturing practices. The leather industry is also under pressure to look for effective alternative methods for abatement of pollution. In conventional chrome tanning huge amount of chromium content remains in the spent chrome liquor which increases the pollution and cost of tanning. In this study, an attempt has been made to reduce the water consumption, quantity of spent chrome liquor and overall attenuate the pollution load and cost of production. In the process soaking to pickling operation were done in conventional manner and the tanning was carried out in conventional as control and four nonconventional methods as experimental. Such an approach has resulted as the cost of tanning was reduced to a great extent without compromising leather quality by nonconventional chrome tanning method. The physical properties of experimental leathers were found better than conventionally tanned leathers. The results showed that the nonconventional tanning process is cost effective and efficient in terms of improved quality of leather and also led to reduction in total dissolved solids (TDS), total suspended solids (TSS), chloride content, COD and BOD_5 loads in spent liquor. It is also helpful to improve strength properties of crust leather. The nonconventional tanning system presented appears to be a viable option for combating pollution arising from the conventional chrome tanning system.

KEYWORDS: Basic chromium sulphate, nonconventional tanning, basification, abatement of pollution.

INTRODUCTION

Leather, a traditional export item of Bangladesh, enjoys a good reputation worldwide for their quality. This sector plays a significant role in the economy of the country in terms of value addition and employment. Export Promotion Bureau (EPB) reported that Bangladesh earned $1.13 billion from the leather sector in the year of 2014-15, which was the second highest contributor to national exports after garments (EPB 2015). Due to generation of solid, liquid and gaseous pollutant, the department of environment (DoE) categorized tannery as 'red' category industry in Bangladesh (Tigga et al. 2000). In Bangladesh there are 220 tanneries; 85% of them are located at Hazaribagh, western part of Dhaka, covering 0.25 sq.km area and others are scattered all over the country (Bangladesh INSPIRED 2013). Annually about 85,000 tons of raw hides/skins are estimated to be processed for leather production in Bangladesh, which generate huge amount of solid and liquid wastes (Paul et al. 2013). The conversion of 10 kg raw hide/skin into leather produces more than 6 kg solid waste (Boopathy et al. 2013). To minimize and manage solid wastes generated from the tanneries numerous steps have been taken (Cabeza et al. 1998; Shanmugam Horan 2009; Ravindran Sekaran 2010). It is reported that only 15 % of offered chemicals are retained in the finished leather, while the residue of 85 % chemicals enter the waste streams (UNIDO 2000). Only 255 kg of finished leather (grain and embossed split) is obtained for every 1000 kg wet-salted hides processed, i.e. just 25.5% of the raw material becomes finished leather (Aquim, et.al 2010). The leather tanning process involves the use of copious amounts of water. About 300-35l L of water is employed for every kg of hide processed (Ramasami and Prasad, 1991). Chrome tanning is the subsequent operation of pickling and is the most common technique in leather processing, 90 % tanning of industries use basic chromium sulfate (BCS) instead of other tanning agents to obtain better quality leather (Avindhan et al. 2004). BCS binds with collagen protein to make it stabilize against biodegradation. Chromium has a tendency to precipitate at pH more than 4.0 (Thanikaivelan et al. 2000). The possibility of higher penetration of chromium at pH levels 2.0-4.0 (Sharphouse 1971). Suresh et al. (2001) reported that in the conventional chrome tanning wastewater contains 1500-3000 mg/L chromium. On average, only 60 % of the chromium is up taken by the pickled pelt and the other 40 % of chromium remains in the solid and liquid wastes, especially as spent chrome liquor (Fabiani et al. 1997). It indicates that huge amount of chromium content remains in the conventional spent chrome liquor. Environmental pollution is a difficult problem for world leather industry (Kumaraguru et al., 1998 and Cabeza et al., 1998). Although many alternatives have been studied and do exist, chrome tanning offers significant economic and technical advantages, which cannot be ignored and still make it the preferred way of tanning hides. Conventional methods of pre-tanning and tanning processes discharge enormous amount of pollutants, which accounts for nearly 90% of the total pollution from a tannery (Aloy M., 1976). This work has been aimed to reduce the quantity of spent chromium and minimize the level of pollution using nonconventional chrome tanning method. It also emphasizes on the minimization of overall manufacturing cost of processed leather.

MATERIALS AND METHODS

In this study, 15 (fifteen) pieces of wet salted goat skins were processed following five different method in three experiments. The size of the skin was 4.0-4.5 square feet and the selection was 'D' grade. The collected skins were first trimmed, de-salted and weighed properly. To manufacture wet blue both in conventional and nonconventional process some mechanical and chemical operations are involved. The operational sequence for wet blue process is shown in Figure 1.

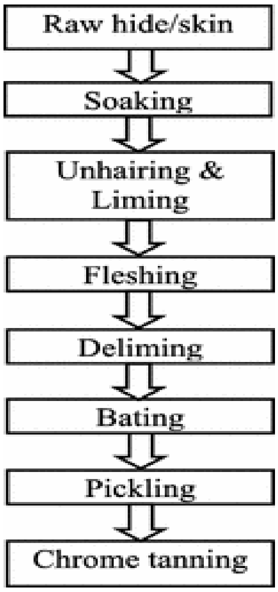

Figure 1: Operational sequence for wet blue leather production.

Soaking to pickling operation were carried out in conventional manner. In the pickling stage, float pH was maintained at 2.5-3.0 for better penetration of the chrome into pelts (Covington 2011). The pickled pelts were tanned in five methods; i.e. one conventional (Table-1) and four different nonconventional methods (Table-2). All required chemicals for tanning were taken on the basis of pelt weight.

Table 1: Recipe for conventional chrome tanning.

50% pickle liquor	
8% BCS	
1% sodium formate	The drum run for 60 minutes and complete
1 % chrome stable fat	penetration was checked.
+ 50% water	
0.5% basifying agent (MgO)	Run 5 hours
0.2% preservative	The drum was run for 60 minutes and pH was checked 3.7-3.8. Then the tanned leather was taken out and piled up for two weeks.

Method-1: Application of BCS without float

The pickled pelts were taken in a drum and treated with specified amount of BCS and other required chemicals (Table 2). The r.p.m. (rotation per minute) of drum was 5-6. The time required for full penetration of BCS in this method was 60 minutes.

Method-2: Application of BCS on flesh side

Required amount (one fifth of the chemical weight) of pickle liquor was added to make the BCS paste with required chemicals. The pickled pelts were laid on a table keeping the flesh side up and the prepared BCS past was applied on the flesh side through padding. The time required for full penetration of chromium in this method was 45 minutes.

Method-3: Application of BCS on grain side

In this method the pickled pelts were laid on a table keeping grain side up. Then the prepared BCS paste was applied on the grain side of the pelt by padding. The time required for full penetration of chromium in this method was 60 minutes.

Method-4: Application of BCS on both sides of pelts

In this method the BCS paste was applied on the flesh side first and then on grain side of the pickle pelt by padding. The time required for full penetration of chromium in this method was 55 minutes.

Table 2: Recipe designed for without float nonconventional chrome tanning.

6% BCS	
1% sodium formate	The drum run for 60 minutes and complete
1 % chrome stable fat	penetration was checked.

Fixation of all the nonconventional tanned samples was carried out together in a drum with separate identity through basification (Table 3).

Table 3: Recipe for basification of all nonconventional tanned samples.

15% pickle liquor	
35% water	
0.5% basifying agent (MgO)	Run 5 hours
0.2% preservative	Run 60 minutes

pH was checked 3.7-3.8. Then the tanned leather was taken out and piled up for two weeks. After ageing two weeks, all the wet blue was processed to crust leather following conventional method and strength performance was evaluated to compare.

RESULTS AND DISCUSSION

The values of some parameters such as shrinkage temperature, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), chloride content, total suspended solids (TSS), total dissolved solids (TDS), percentage of chrome uptake by the pelt, Cr_2O_3 content, tensile strength, etc. were assessed for all samples. To justify the pollution parameter, required amount of water added with the spent liquor in the case of nonconventional tanned leather.

Shrinkage temperature of wet blue

The principle of this method is to suspend the test piece in water in the form of a strip then to heat at a rate of 2°C per min. The shrinkage temperature is noted when the sample visibly shrinks (Covington t., 2011). Table 4 represents the shrinkage temperature of chrome tanned wet blue for different experimental and control.

Table 4: The result of shrinkage temperature wet blue (^oC).

Serial no.	Method	First experiment	Second experiment	Third experiment
1	Conventional	105	104	105
2	Without float	107	106	106
3	Flesh side	106	104	105

4	Grain side	104	103	103
5	Both side	107	105	106

Table 4 shows that the shrinkage temperature of chrome tanned wet blue in three experiments are above 100^0C in all cases. Although in nonconventional method the amount of chromium input was lower than conventional tanning method, the results of shrinkage temperature were quite satisfactory.

COD value of conventional and nonconventional spent chrome liquor (mg/L).

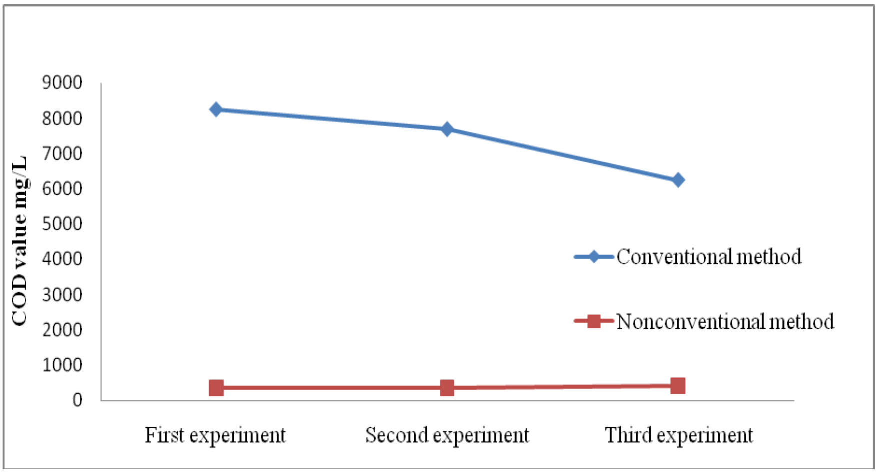

Figure 2: COD value of conventional and nonconventional spent chrome liquor.

COD indicates the amount of oxygen required to oxidize the organic matter and inorganic matter present in that solution with the help of microorganisms. In the figure 2, the COD values nonconventional tanned spent liquor were 360 mg/L, 420 mg/L and 355 mg/L respectively which were significantly lower than the conventional spent liquor.

BOD_5 value of conventional and nonconventional spent chrome liquor (mg/L).

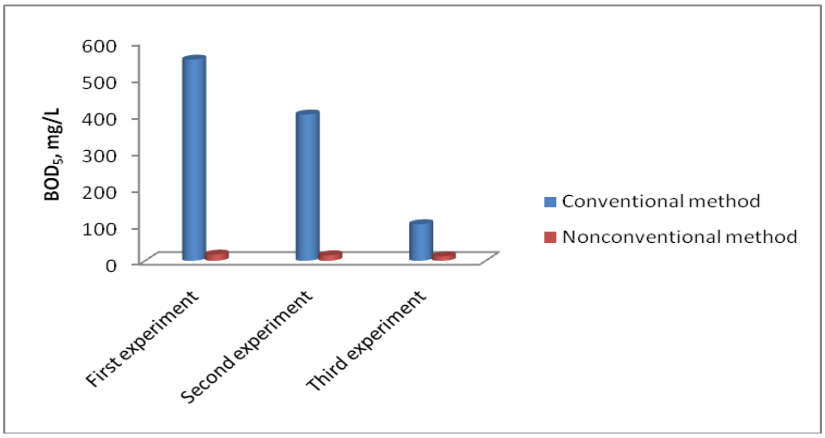

Figure 3: BOD_5 value of conventional and nonconventional spent chrome liquor.

BOD_5 is a measure of the quantity of oxygen used by microorganisms (e.g. anaerobic bacteria) in the oxidation of organic matter. The BOD values of spent liquor of nonconventional tanning were 17 mg/L, 15 mg/L and 12 mg/L respectively, which were drastically reduced as compare to the conventional method.

Chloride content in spent chrome liquor (mg/L).

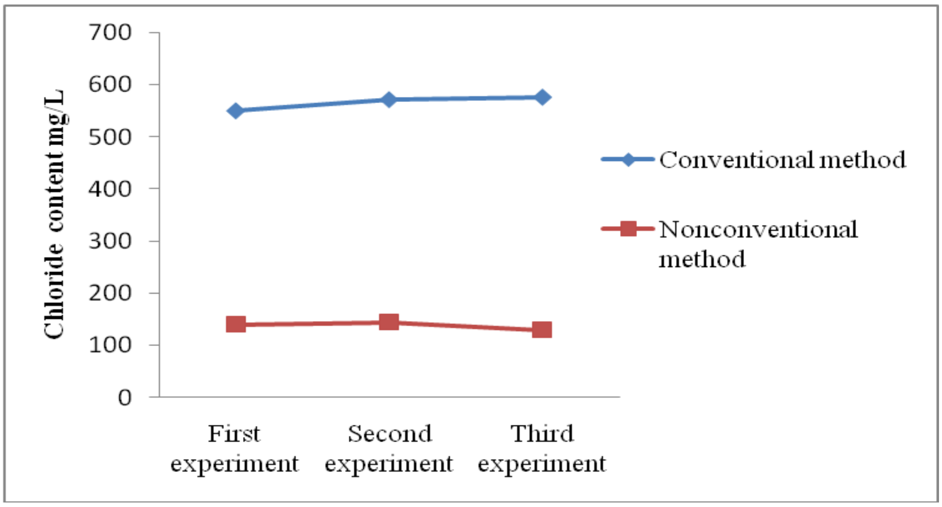

Figure 4: Chloride content in spent chrome liquor of conventional and nonconventional method.

It was found in the figure 4 that the chloride content derived from spent chrome liquor in nonconventional method were 140 mg/L, 143.91 mg/L and 129.87 mg/L respectively. These values were much lesser than the conventional method.

Total dissolved solids in spent chrome liquor (ppm)

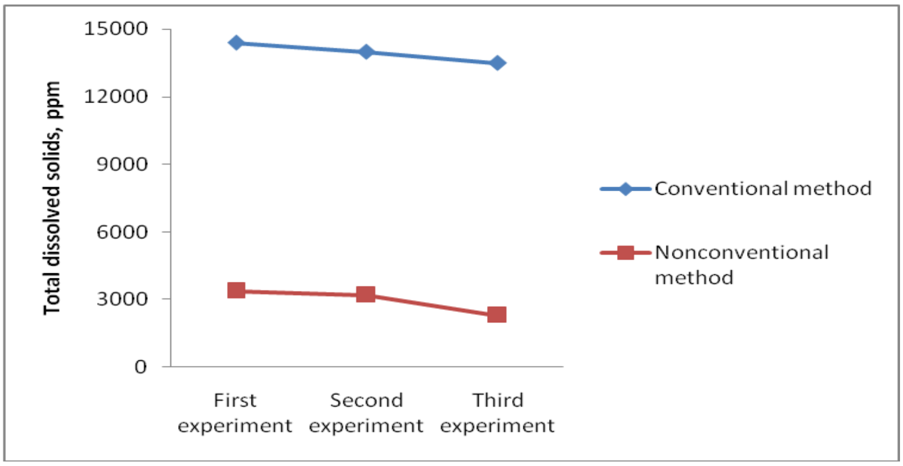

Figure 5: Total dissolved solids in spent chrome liquor of conventional and nonconventional method.

According to the figure 5 the total dissolved solids derived from nonconventional tanning spent liquor were much lower than the conventional. Nonconventional methods could be more eco-friendly if it would properly be maintained.

Suspended solids in spent chrome liquor (mg/L)

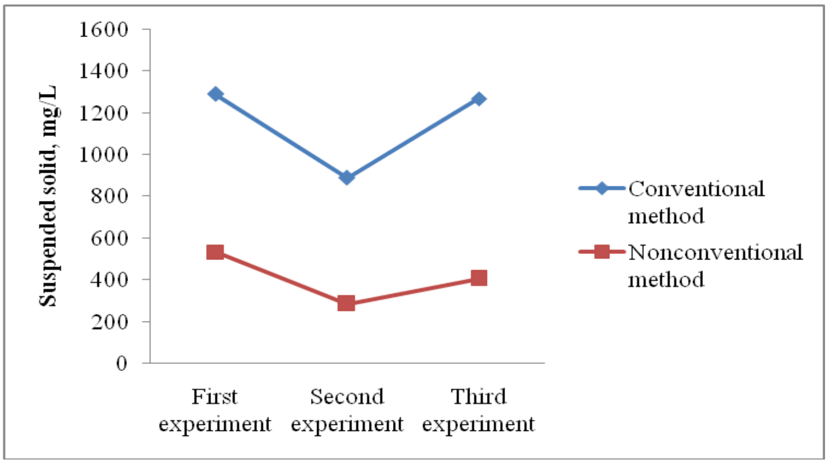

Figure 6: Suspended solids in spent chrome liquor of conventional and nonconventional method.

The figure 5 indicated the values of suspended solids derived from nonconventional spent chrome liquor were 535 mg/L, 285 mg/L and 406 mg/L respectively, which were much lower as compared to conventional spent liquor.

Chromic oxide content of wet blue (%)

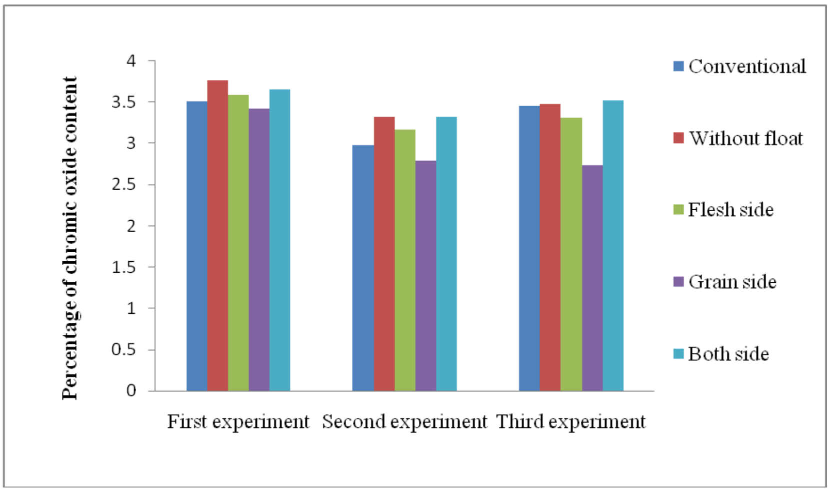

Figure 7: Chromic oxide content in wet blue produced by different method.

The chromic oxide content of wet blue is defined by the quantity of chromium compounds found in it calculated as chromic oxide (Cr_2O_3). The figure 7 represented the chrome uptake of wet blue in three experiment of conventional and nonconventional tanning method. It was found from the entire experimental data chromium uptake by nonconventional tanning method were quite satisfactory.

Chromic oxide content of spent liquor

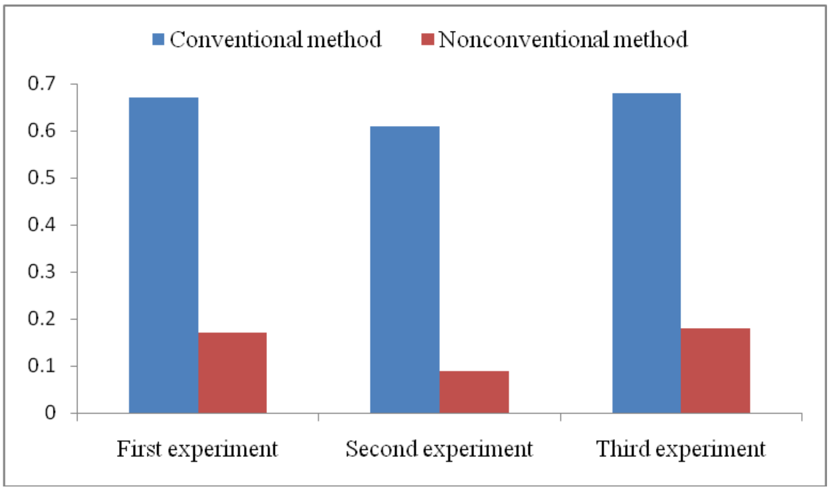

Figure 8: Chromic oxide (Cr_2O_3) content of spent chrome liquor.

Chromic oxide (Cr_2O_3) content of liquor was determined by oxidizing the liquor and iodometric titration of the hexavalent chromium ions (SLC- 8, 1966). It was observed from the figure 8 that the chromic oxide content was much higher in the spent liquor of conventional chrome tanned method which polluted the environment.

Tensile strength of crust leather

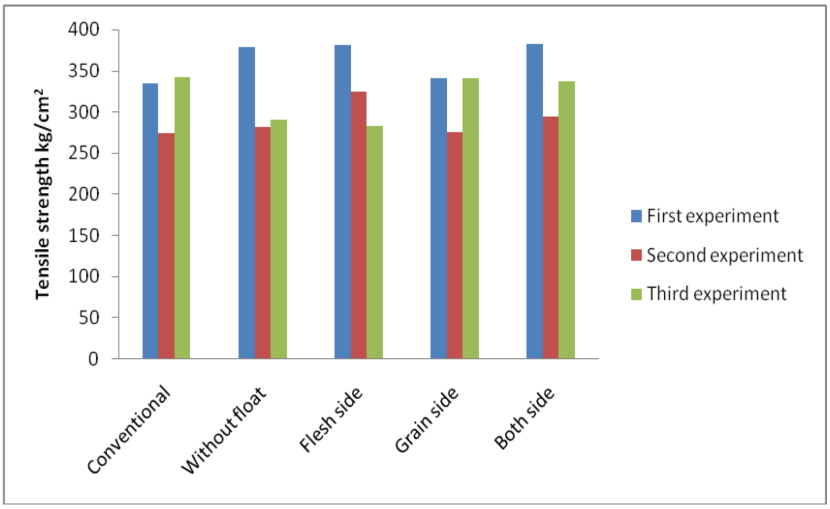

Figure 9: Tensile strength of crust leather made from conventional and nonconventional wet blue.

According to SATRA the standard value of test result of tensile strength is 200 kg/cm^2 (Venkatappaiah, 1999). The laboratory experiments shows that in each method the value of Tensile strength is higher than the standard value and the values are almost the same as the conventional method. However, it is clear that using less percentage of chromium in nonconventional method the satisfactory leather strength can be obtained.

Stitch tear strength of crust leather

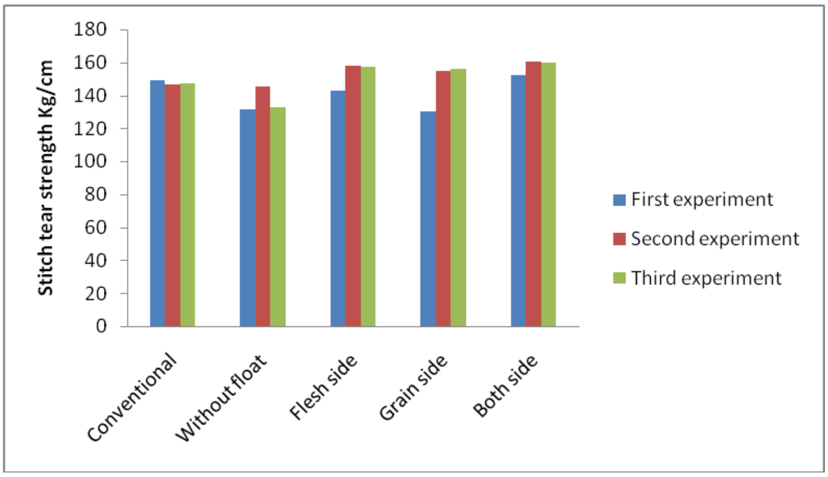

Figure 10: Stitch tear strength of crust leather made from conventional and nonconventional wet blue.

It has been observed that in the first experiment the stitch tear strength of crust leather produced from conventional method was 149.30 kg/cm, 146.39 kg/cm and 147.21 kg/cm respectively, whereas in non-conventional methods it was quite higher.

Tongue tear strength of crust leather

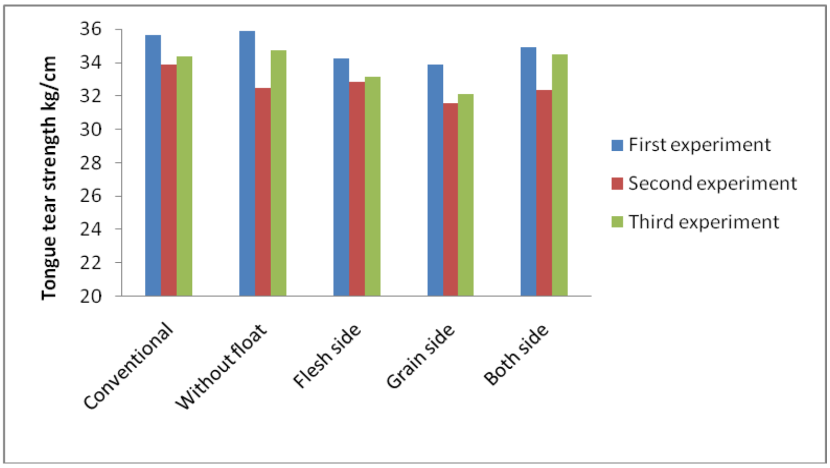

Figure 11: Tongue tear strength of crust leather made from conventional and nonconventional wet blue.

Tongue tear test is a simple tear test where the tearing takes place through the weakest region of leather specimen. The tearing strength actually indicates about the strength of the fibers and their cohesive force (Dutta, 1990).The standard value of Tongue tear strength is 25-30 kg/cm. From the above figure 11, it has been found that the result of both the conventional and nonconventional tanning methods were quite higher than the standard of upper leather.

COST CONTROL OF THE EXPERIMENTAL PROCESS

The amount of chromium required in nonconventional method was 2% lesser than conventional and cost could be minimized at least BDT 5 per square feet.

CONCLUSION

From the environmental parameter test result it has been found that the COD value for conventional chrome tanning method was 6240-8240 mg/L whereas it was only 355-420 mg/L in case of nonconventional chrome tanning method. The chrome uptake by experimental process was far better than the conventional. The chromic oxide content of tanned leather for conventional tanning method was 3.51% whereas nonconventional without float method was 3.76%. From the experiment it has been found that the chrome penetration of all nonconventional tanning methods was satisfactory with very less amount of water. As a result, evolvement of effluent reduced and the cost of tanning was minimized to a great extent without compromising quality of leather.

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