

Preparation of Sulphide-lime Unhairing Ratios for Pollution Load Reduction in the Manufacture of Shoe Upper Leathers from Tropical Goat Skins

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Abstract Preparation of sulphide-lime unhairing tannery process was carried out using nine ratios-coded as A_I – A_{III}; B_I – B_{III} and C_I – C_{III} with varied concentrations of sodium sulphide and hydrated lime. Result obtained through subjective tests and gravimetric method show differences in degree of unhairing, swelling and plumping of the pelts. The pH of wastewater generated from each ratio and weight increase of limed pelts, was observed and recorded. Analysis of pollutants from the wastewater was determined by parameters such as BOD, COD, and Sulphide generated from the wastewater. Results obtained show various levels of parameters from the studied ratios indicated that A-group had poor unhairing and liming properties. The C-group gave excellent properties but with higher pollution load. However, B_{II} (2.5% Na₂S with 2.0% Ca(OH)₂) and B_{III} (2.8% Na₂S with 2.5% Ca(OH)₂) in 200% float generated lower pollution level as determined by the parameters from their individual wastewaters. This was compared with the conventional (CTL) and that of the industry. The average sample wastewater collected from the industry indicated higher pollutants than the studied and CTL ratios. The study reveals that maximum utilization of reagents is a necessary technique for reduction of pollutants in the wastewater from sulphide-lime unhairing process known to generate 65%-70% of pollutants from the beam-house.

Keywords Preparation, Unhairing, Liming, Ratios, Wastewater

1. Introduction

Unhairing/liming is a mandatory process especially in the manufacture of full grain leathers from goat skins. The process removes epidermal structures, brings about swelling and plumping and the removal of non-structural protein of the pelts [1]. Liming process is the stage, that properties of leathers are largely determined thus “leather is made or marred during liming” [2]. The process modifies the skin fibre for subsequent penetration of other processing chemicals such as tannins which has direct bearing with both physical and chemical properties of the resultant leathers [3].

Sodium sulphide and hydrated lime combination is popularly used in this process because other methods of unhairing and liming have one setback or the other [4, 5]. However, the use of this chemical combination generates large volumes of waste that constitutes major source of pollutants amounting to more than 65-70% in combined

tannery effluent [6, 7]; Leaf, 1999. The effluent which constitutes both organic, inorganic matter and metals makes its treatment very complicated and expensive [8, 9]. If this wastewater is not properly treated before discharge may affects the ecology of agricultural land and other factors of the environment as reported by some researchers [10].

It is therefore important to prepare a sodium sulphide-hydrated lime combination ratio that will results to minimal pollutants in the unhairing-liming wastewater and consequently to the overall tannery effluent [11, 12]. Pollution load associated with tannery wastewater, has been reported as the greatest challenge in the leather industry [13, 14]. Preparation of chemical combination of sulphide-lime in unhairing-liming process is necessary for the reduction of pollutants in its effluent [15, 16].

2. Materials and Methods

Wet-Salted medium Goatskins were obtained from Tudun-wada, Zaria, Nigeria. They were soaked, washed free from dirt and other extraneous substances and drained. Each piece of skin was divided into two halves along the back-bone and weighed prior to each batch of unhairing-liming ratio. The sulphide-lime unhairing process was carried out according to standard procedures. Three (3)

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classes of ratios were drawn for this study and coded as;

Class 'A' Ratios

Class 'A' ratios used 2.5% w/w sodium sulphide for unhairing-liming process. The quantity of calcium hydroxide was varied accordingly, 1.5%, 2.0%, 2.5% and 3.0% in a float of 200% w/v for the water (all percentages based on weight of each skin). Four ratios were formulated with the fifth as conventional ratio serving as control (CTL).

- Ratio A_I: - 2.5 % Na₂S/1.5 % Ca (OH)₂,
- Ratio A_{II}: -2.5 % Na₂S/2.0% Ca OH)₂,
- Ratio A_{III}: -2.5 % Na₂S/2.5 % Ca (OH)₂,
- Ratio A_{IV}: -2.5 % Na₂S/3.0 % Ca (OH)₂
- CTL - 3.0 % Na₂S/3.0 % Ca(OH)₂
- E - Wastewater from commercial Tanneries.

For Ratio A_I, 21.25g of sodium sulphide was dissolved in 1000 mls water and transferred quantitatively into an experimental drum (reactor). The soaked skins weighing 850 g were introduced into the vessel and agitated for 3 hours continuously at a speed of 60 rpm until the skins were unhaired. Then 12.75g of hydrated lime was dissolved in 200 ml of water and transferred into the vessel and agitated for another 2 hours. Then 500 ml of water was added and agitated for 5 minutes every one hour for the remaining 15 hours. The process was repeated for A_{II} but the percentage of lime was increased to 2.0% according to the ratio. The procedure was repeated for A_{III} and A_{IV} in class 'A'. After unhairing-liming of the skins, the degree of unhairing, swelling, plumping was assessed for each skin and recorded. Samples of wastewater from each ratio and the CTL were collected after the process period of 20 hours. The ratios coded as A_I – A_{IV} and wastewater from each was collected and refrigerated at 4°C until required for analysis. Parameters such as COD, BOD and S²⁻ were used for the determination of pollution load of the wastewater. Samples of wastewater from three commercial tanneries from Kano-Nigeria were also analysed for the same parameters.

Class 'B' Ratios

In this class, sample skins weighed 880g; the same unhairing-liming method was adopted like in class 'A' except for the increase in percentage of sodium sulphide to 2.8%.

- Ratio B_I: - 2.8 % Na₂S/1.5 % Ca(OH)₂
- Ratio B_{II}: - 2.8 % Na₂S/ 2.0 % Ca(OH)₂,

- Ratio B_{III}: - 2.8 % Na₂S/2.5 % Ca(OH)₂,
- Ratio B_{IV}: - 2.8 % Na₂S/3.0 % Ca(OH)₂,
- CTL: - 3.0 % Na₂S/3.0% Ca(OH)₂,
- E – Wastewater from commercial Tanneries.

For B_I 24.64g of sodium sulphide was dissolved in 1000 ml of water and transferred quantitatively to the reactor containing the skins and agitated for 3 hours until they were unhaired. Then 13.2g of lime was dissolved in 300 ml of water and added into the same drum and agitated for another 2 hours continuously. Finally 460 ml of water was added and agitated for 15 hours at 5 minutes every one hour. The procedure was then repeated for B_{II}, B_{III} and B_{IV}. The same variation in the percentage of hydrated lime was used; 1.5%, 2.0%, 2.5% and 3.0%. The limed pelts were assessed subjectively as previously carried out in class A. Samples wastewater from the individual ratio coded as (B_I – B_{IV}) were collected after unhairing-liming period of 20 hours and analysed for the same parameters like in class 'A'.

Class C Ratios

For class 'C' the same procedure was repeated like in class 'B' except for the increase in percentage of sodium sulphide to 3.0% w/w. The percentage of hydrated lime remained as 1.5%, 2.0%, 2.5% and 3.0%.

- Ratio C_I: – 3.0 % Na₂S/1.5 % Ca(OH)₂
- Ratio C_{II}: – 3.0 % Na₂S/ 2.0% Ca(OH)₂,
- Ratio C_{III}: – 3.0 % Na₂S/2.5 % Ca(OH)₂,
- Ratio C_{IV}: – 3.0 % Na₂S/3.0 % Ca(OH)₂,
- CTL: -3.0 % Na₂S/3.0 % Ca(OH)₂,
- E – Wastewater from commercial Tanneries

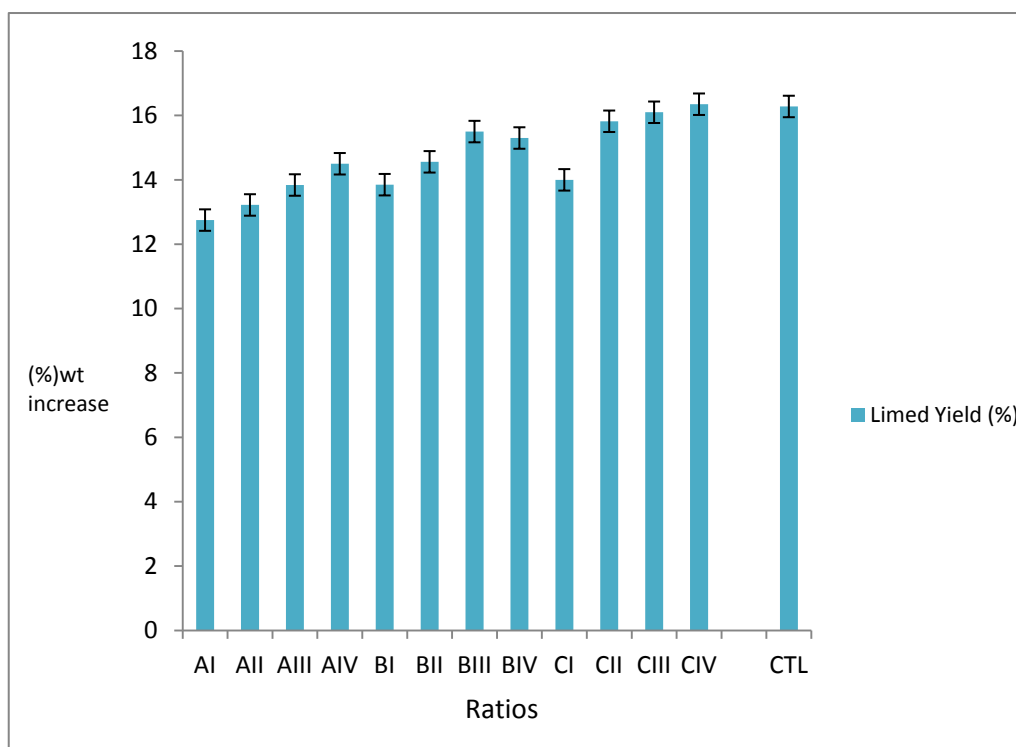
For C_I ratio, sample skins weighed 830g, the quantity of sodium sulphide required was 24.9g while hydrated lime is 12.45g. The same procedure was followed for C_{II}, C_{III} and C_{IV} ratios in the same float of 200% water. After the unhairing-liming process, degree of unhairing, swelling, plumping and change in pH of the wastewater was determined. Samples wastewater from each ratio (C_I – C_{IV}) were also collected after unhairing period of 20 hours. The wastewater was again stored until was required for analysis for the same parameters in order to assess the level of pollutants.

3. Results and Discussion

Table 1. Effects of Different Methods of Sulphide/Lime on Degree of Unhairing, Percentage Weight Increase of Pelt and pH of the Wastewater

Ratios	Percentage weight increase of limed pelt (%)	pH of wastewater	Unhairing/liming rating (%)	Observations
AI	12.75	11.5	50 – 59	Poor degree unhairing was observed with little swelling of the pelt.
AII	13.22	11.8	50 – 59	Poor unhairing was observed and swelling was fair.
AIII	13.84	12.5	60 – 69	Fairly good degree of unhairing was observed, swelling was good but pelt grain not smooth.
AIV	14.50	12.5	60 – 69	Fairly good degree of unhairing, with rough grain surface, good swelling was observed.
BI	13.85	12.5	79 – 89	Good degree of unhairing with little swelling
BII	14.56	12.0	89 – 90	Very good unhairing and swelling, with the pelt having smooth grain
BIII	15.50	12.5	89 – 90	Very good degree of unhairing with adequate swelling and plumping of pelts
BIV	15.30	12.5	89 – 90	Very good degree of unhairing with pelt well swollen and translucent
CI	14.0	12.0	90 – 100	Excellent and Complete unhairing was observed; the pelts had very smooth grain, with little swelling.
CII	15.82	12.5	90 – 100	Excellent and Complete unhairing was observed with adequate swelling and plumping of the pelt
CIII	16.1	12.5	90 – 100	Excellent and Complete unhairing was observed; the pelt was swollen and slippery.
CIV	16.35	12.0	90 – 100	Excellent and Complete unhairing was observed smooth grain and swollen pelt was observed.
CTL	16.28	12.5	90 – 100	Excellent Unhairing with smooth grain and swollen pelts were observed.

Key rating: – 50-59% Poor Unhairing; 60-69% -Fairly good Unhairing; 70-79% -Good Unhairing; 80-89% Very good Unhairing; 90-100% Excellent Unhairing

**Figure 1.** Effects of Different Ratios of Sulphide/Lime on percentage lime yield

Effects of Different Ratios of Sulphide/Lime on Pollutants from Class A, B, C and CTL

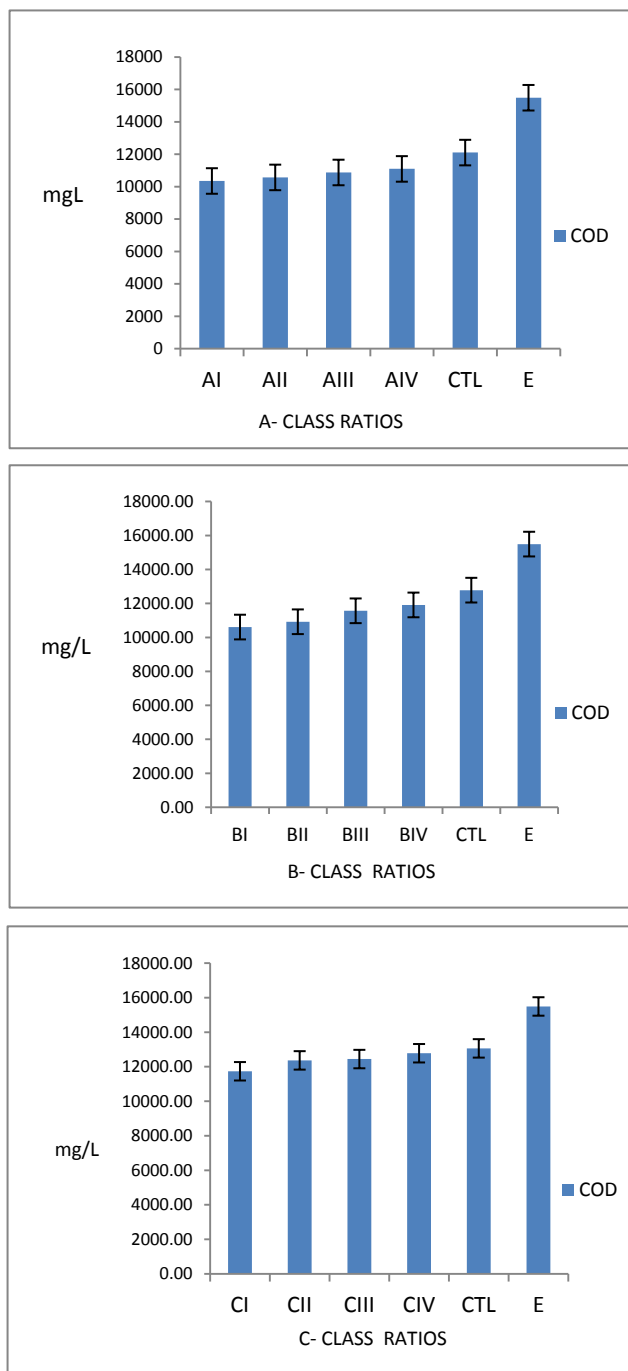


Figure 2. Concentration of Pollutants Determined by COD from Class A, B, C, CTL Wastewater and Commercial Tanneries samples

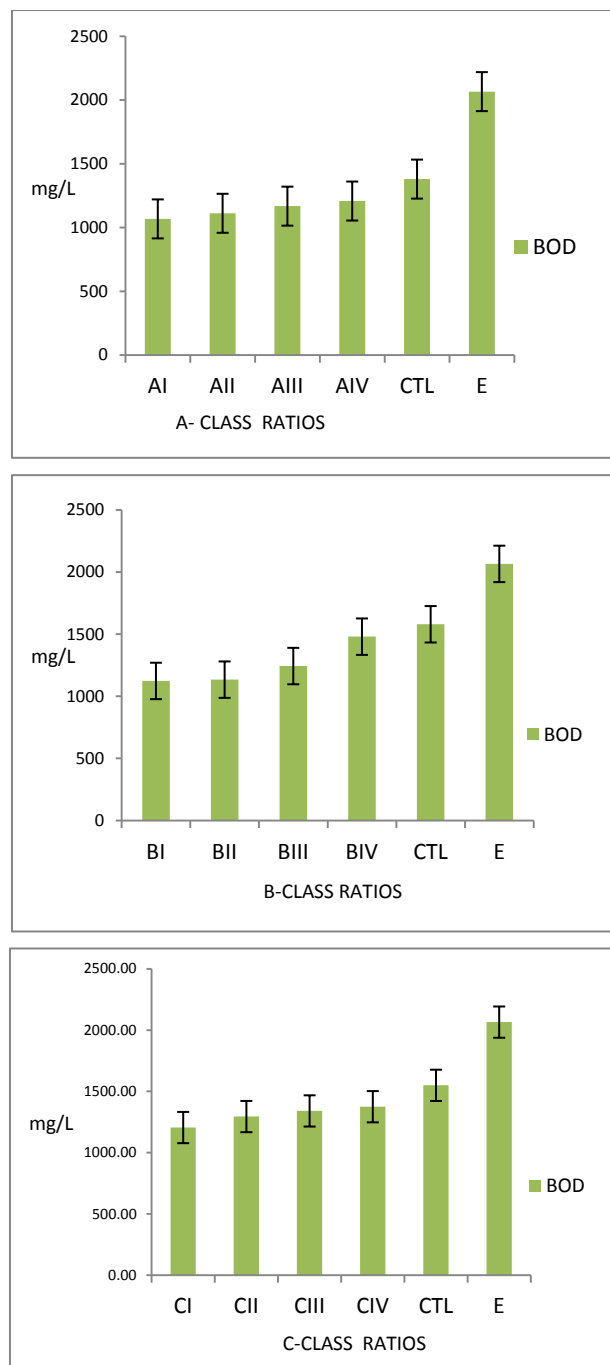


Figure 3. Concentration of pollutants Determined by BOD from Class A, B, C, CTL Wastewater and Commercial Tanneries samples

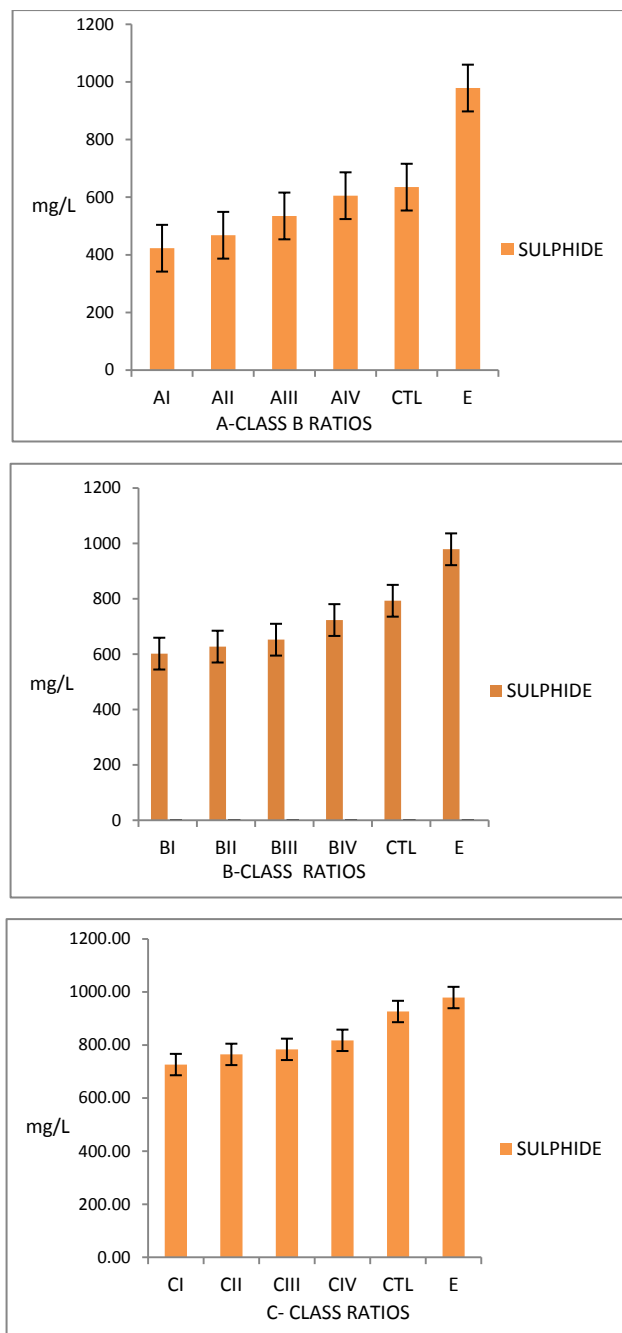


Figure 4. Sulphide (S^{2-}) Concentration of Wastewater from Class A, B, C, CTL Ratios and Commercial Tanneries samples

4. Results Description

Results on degrees of unhairing-liming, swelling and plumping, though by subjective test and percentage weight increase after sulphide-liming process were observed. The pH of unhairing-liming wastewater indicated, differences depending on the process ratio, (Table 1). It was observed that class 'A' ratios did not show effective unhairing and liming, leaving trace of short hairs and other epidermal structures. The class 'B' had good unhairing and liming as well as swellings and plumping of the pelts, except for B_I.

Other ratios in the class indicated very good unhairing and liming results. Finally group 'C' ratios gave very good and excellent swellings and plumping on the pelts. Fig. 1 also illustrates lime yield of the various ratios which indicated good results.

The wastewater from different groups (A – B) ratios indicates increasing concentration of pollutants with the class 'A' ratios having the least and 'C' the highest pollution load. All pollutants determined from the wastewater were expressed in mg/L and plotted as shown in Fig.2 - 4 above.

5. Discussions

Effects of Class 'A' Ratios on the Wastewater

Fig. 2 show the level of pollutants determined by BOD of wastewater from class A - C ratios. It is observed that A_I ratio had the least BOD ($6068 \pm 75.57 \text{ mg/L}$), while wastewater from A_{III} had the highest value ($7068 \pm 735.17 \text{ mg/L}$) in the group. Consequently these values were observed to be below the CTL and commercial tannery sample wastewater with BOD value of $9880.00 \pm 406.36 \text{ mg/L}$ and $11366 \pm 792.21 \text{ mg/L}$ respectively. The COD from commercial tannery wastewater had the highest value ($32220 \pm 961.12 \text{ mg/L}$) while the least was A_I ($22055 \pm 410.36 \text{ mg/L}$). It was also observed that COD of wastewater from group A' study ratios was lower than that of the CTL and the industry as expected. Generally the concentration of pollution load was observed to increase with increase in the percentage of chemicals offered.

Sulphide concentration from sample wastewater in class 'A' ratios was witnessed to increase from A_I - A_{IV}. CTL and sample wastewater from commercial tanneries indicated higher sulphide concentration of $486.33 \pm 13.43 \text{ mg/L}$ and $579 \pm 23.87 \text{ mg/L}$ respectively. This is expected because commercial tanneries are very likely to offer higher quantity of chemicals in order to facilitate chemical reactions to meet the demand of their customers and undermining the effects of these pollutants to the environment.

Effects of Class 'B' Ratios on the Wastewater

Fig. 2: shows results of BOD analysis of sample wastewater from class "B". B_I has the least value of $7024 \pm 520.88 \text{ mg/L}$ while B_{III} having the highest value of $8144 \pm 240.67 \text{ mg/L}$. Like in group "A," values of BOD from the commercial tannery and the CTL were higher than the studied ratios except for B_{III} ($8144 \pm 240.67 \text{ mg/L}$) which was higher than the CTL. This is not expected and might be attributed to the complexity in tannery wastewater [17, 18] or might be due to genetic differences between the raw skins used in this particular experiment [19, 20].

For COD, B_I had value of $22107.67 \pm 1301.24 \text{ mg/L}$ as the least while ratio B_{IV} had the highest value of $23120.33 \pm 949.29 \text{ mg/L}$. COD values for CTL sample effluent and that of industry had higher values of $27363.33 \pm 988.72 \text{ mg/L}$ and $32220.00 \pm 961.12 \text{ mg/L}$ respectively indicating higher pollution load. The trend for

COD results indicates steady increase ($B_I - B_{IV}$), might be as a result of increase in hydrated lime (1.5 – 3.0%) in the ratios. The use of sodium chloride for preservation of the raw skins and disintegration of sulphur containing amino acids during unhairing may also contribute to high COD, as sulphide requires high quantity of oxygen for its complete oxidation. [21]

Sulphide concentration in sample effluent from class 'B' ratios show no significant differences in values from $B_I - B_{III}$, except for B_{IV} as observed in Fig. 2. This is understood, as equal percentages of sodium sulphide (2.8%) was used in this class of ratios. However, the difference observed may be due to complexity of tannery wastewater as reported earlier. The high concentration of sulphide observed in effluent from CTL and that from the industry is indicative of higher offer of the chemicals.

Effects of Class 'C' Ratios on Wastewater

Fig. 3 shows concentration of pollutants determined by BOD, COD, Sulphide (S^{2-}) in wastewater from group 'C' ratios. The average BOD value (8464.00mg/L) obtained from the studied ratios is significantly lower than values reported for typical sulphide-unhairing wastewater [14, 22] Sample wastewaters from the commercial tannery had a higher value (11366.00 ± 792.21 mg/L) of BOD compared with other class 'C'. The increase in pollution load of wastewater from this class of procedures is expected because besides increase in percentage of hydrated lime from 1.5 – 3.0% and sodium sulphide from 2.8 – 3.0%, the increased saponification and dissolution of more organic matter from the skins could increase the BOD values.

For COD in this group, it is observed that effluent from C_I ratios was the least value of 23137.33 ± 852.8 mg/L while, C_{IV} 25337.33 ± 762.81 mg/L as the highest. However it can be observed that the wastewater from C_{IV} and CTL has insignificant difference in COD values of 25337.33 ± 252.81 mg/L and 25363.33 ± 537.54 mg/L respectively. This is expected as the same ratios were used for both CTL and C_{IV} . The COD value from the commercial tannery (32220.00 ± 961.12 mg/L) wastewater has consistently observed to be higher than other classes even the 'C' class studied ratios.

From Fig. 3 the concentration of sulphide in wastewater shows little differences between the class 'C' ratios. This suggests that only optimal percentage of chemicals required for the process of unhairing-liming was actually used, the excess goes into the wastewater. Meanwhile, wastewater from C_{IV} method remains higher in sulphide concentration (487.67 ± 26.84 mg/L) than those from the same group. But the average sample effluents from commercial tannery had 579 ± 46.54 mg/L higher than those in the entire class. The fluctuations noted of this pollutant in the class 'C' ratios may be attributed to genetic differences from the skins as earlier observed, the sample skins could be more hairy.

Preparation of unhairing-liming ratios has shown good prospects for the reduction of pollution load in the unhairing-liming process in the manufacture of upper

leathers. Although the quality of the final leathers are yet to be determine, it is not expected to be lower than the standard specifications. This approach has reduced pollutants in the tannery wastewater and is likely to lessen the cost of treatment chemicals. The difficulty often experience in the handling of large volumes of complex liquid waste will also be eased, particularly from the unhairing-lime process that generates most noxious waste in any given tannery [23-25].

6. Conclusions

Results of pollutants determined from wastewater generated from the individual studied ratios indicated that B_{II} and B_{III} actually had lower pollutants compared to the CTL and commercial industry. It was observed that the prepared ratios led to percentage reduction of pollutant determined by COD to 19.16% for B_{II} while ratio B_{III} indicated 22%. For BOD reduction, it was found to be 24% and 17.6% for B_{II} and B_{III} respectively. It is imperative to recommends the said ratios for adoption as optimal for unhairing and liming of goat skins for the production of upper leathers. As the wastewater produced in the use of these ratios was observed to constitute fewer pollutants.

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