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Deliming process of leather fleshings as lime free feedstock for biomethanation process in tannery industry

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Abstract
Leather fleshings are the solid waste generated from the tannery industries and large-scale production of waste is associated with the land, air, and water pollution. Leather fleshings being rich in protein are most suitable for biomethanation. The main problem addressed in this research is the lime treatment of the tannery fleshings causing a high pH of 11 - 12 which unfavorable for methanogenesis. Therefore, the solution for this problem is achieved through mixing the ammonium salts as deliming agent to reduce the pH of leather fleshings. The key aim of this study is to utilize this waste from tanneries to the biogas yield as much as possible. The deliming process has been carried out using ammonium chloride and ammonium sulphate with different proportion for 30 and 60 minutes time of treatment and the results obtained that 8.15 - 8.30 for 60 minutes of treatment and pH shows 8.54 – 8.75 for 30 minutes of treatment. Hence these conditions were feasible to the anaerobic digestion of tannery fleshings to produce biogas and methane. From the batch experiments R_3(50:50) of cowdung and delimed fleshings and R_4(25:75) of bio-digested slurry and delimed fleshings yielded highest biogas of 29.37 and 31.85 l/kg of fleshings.

Keywords: leather fleshings, deliming, pH, ammonium chloride and ammonium sulphate, biogas yield

Introduction
In India, the leather sector has grown in importance on a socioeconomic level. By providing work possibilities, the leather industry has contributed significantly to economic prosperity. Among India, the leather industry is more dispersed in the unorganized sector. The country's enormous animal population is the key reason for the leather industry's development and growth. Raw hides and skins, which are the basic raw material for the leather industry, are abundant in India, accounting for almost 10% of global availability (Lie *et al.*, 2020) [4]. The tannery process involves transforming raw skin, which is a highly putrescible substance, into leather, which is a stable material that can be used to make a variety of products. A series of sophisticated chemical reactions and mechanical processes are involved in the entire process. In India, production of finished leather is increasing every year on the other hand pollution also increasing due to the presence of eco-sensitive chemicals in leathers (Want *et al*., 2013, Kong *et al.,* 2016) [5, 6]. The foul odour that pervades historic tannery clusters gives the impression that this is a severely polluting activity. Tanneries are classified as a 'red' industry in India due to their potential for pollution (Maina *et al.,* 2019) [8]. The chemicals utilised, the raw materials used, and the effluents, waste and off-gas releases generated in the tanning process all have an impact on the air, surface and ground water, and soil contamination (Skytte *et al*., 2012) [7]. Around 500-600 kg of process solid waste is created in chrome tanning plants when one tonne of raw hides/skins is processed into finished leather. 70-230 kg of the waste generated will be fleshings (Ahamed *et al*., 2014) [11]. These fleshings were utilised in industries for glue manufacturing until recently, but they are currently used on a very small scale due to the availability of other forms of glues (Dagne *et al*., 2019) [9]. Thus, the disposal of these fleshings is also a serious issue now a days. Fleshings are the highly proteinaceous and suitable for anaerobic digestion for methane production but presence of lime in these are making the fleshings not suitable for the process. Deliming is a lime neutralizing process to make fleshings to neutral pH. Hence the present study was carried out the deliming process to brings the pH of the fleshings to neutral stage and they are best suitable for anaerobic digestion process.

Materials and Methods

The deliming phase uses acids and/or acidic salts to decrease the surplus liming agents employed in the earlier unhairing procedure. Sulphate or chlorides salts of ammonium are widely employed when the pH needs to be gradually decreased. This neutralization also aids the subsequent proteolytic enzyme treatment of the skins during the bating process, that open the fibrous structure of the skins and increase their suppleness. In this study, five different proportions of water and ammonium salts was tested for effective deliming of leather fleshings.

Deliming of Leather Fleshings

In beamhouse process the deliming is a crucial unit activity in the leather processing business, as it removes the lime from the pelt. The lime content in the fleshings will be neutralized by this method. Deliming has three key goals: eliminating lime, reducing the pH for the bating process, and deswelling the pelt. The addition of alkali chemicals like lime and sodium sulphides during the liming process renders the fleshings more basic in character and the beamhouse process was shown in the fig.1. As a result, the pH of the sample is plainly high, which is not conducive to methanogenic activity during anaerobic digestion. This required deliming of fleshings to lower the pH using ammonium salts (Mushahary *et al*., 2017) [10].

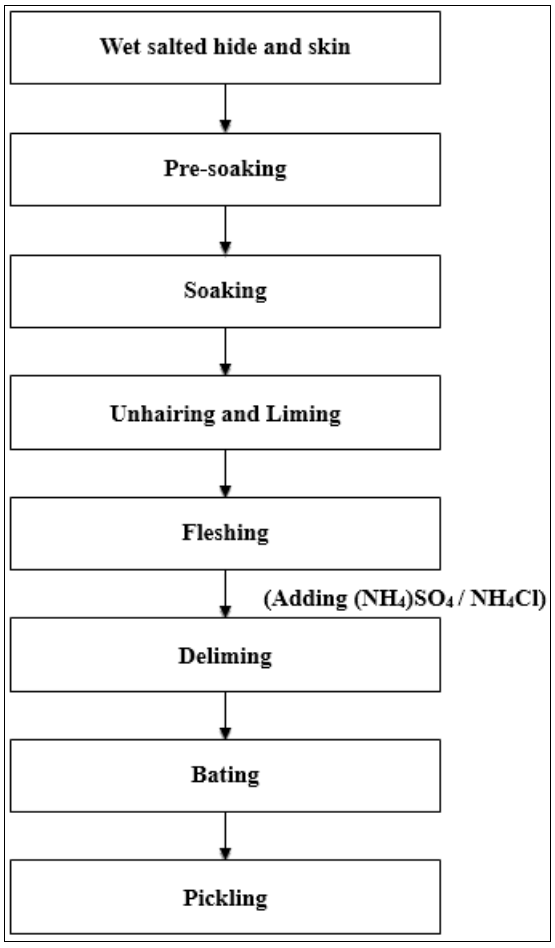

Fig 1: Flowchart for beam house process

Liming is the process of removing hair and soluble protein from hides and skins by treating them with sodium sulphide and slaked lime for about 18-20 hours before to deliming. Where pelt content lime is 0.5 - 2 wt.%, 4 - 5% lime is employed in the liming procedure (Abul hashem. *et al.,* 2014) [1]. Depending on the type of leather to be produced, this lime must be removed partially or completely. In most circumstances, traditional deliming agents such as ammonium chloride and ammonium sulphate are sufficient to remove all the lime. Boric acid is occasionally used as an experimental base; however, it is not employed for commercial manufacturing due to its high cost. To achieve some bleaching impact on limed pelt, sodium metabisulphite is also employed in combination with standard deliming agents. Based on pelt weight, 1-2% ammonium sulphate or ammonium chloride, or a combination of both, are employed as deliming agents to remove lime from the pelt. Likewise, treatment of the fleshings with different proportion of deliming salts was carried out and results are mentioned.

Liberation of ammonia in ammonium salts based Deliming process

Deliming agents such as ammonium sulphate and ammonium chloride can be utilised, and their chemistry is as follows: $(NH_4)SO_4 \rightarrow NH_4^+$ (ammonium) + SO_4^{2-} (sulphate) The ammonium ion is then free to penetrate the cross-section of the pelt and ionise further to behave as an acid. Ammonium chloride and Ammonium sulphate is used as deliming agent with different proportions, and they are represented A,B,C,D and E as a deliming salt quantity of 1, 2, 3, 4 and 5 grams per every liter of fresh water for the treatment of fleshings.

As mentioned, the deliming agent was mixed to the water then added to fleshings leave it for 30 minutes and 60 minutes as soaking condition. The water turns into milky white shows the pH of 8.0 – 9.0 then the lime water is disposed off and the fleshings can be used for the anaerobic treatment.

Deliming Agents used in the Indian tanneries

Basically, in India ammonium chloride and ammonium sulphate are used as the deliming agents and the working reactions of deliming process were mentioned in equations.

Ammonium chloride (NH_4Cl) as deliming agent

Ammonium chloride neutralizes the lime to produce calcium chloride which is completely dissolved by water **(**Sivakumar *et al.,* 2015) [2]. The reaction process is shown in below equation.

$$Ca(OH_2) + NH_4Cl \longrightarrow CaCl_2 + NH_3 + H_2O$$

Ammonium sulphate $(NH_4)SO_4$ as deliming agent

Ammonium sulphate neutralizes the lime and produce calcium sulphate which is also water soluble. The reaction process shown below equation.

$$Ca(OH_2) + (NH_4)_2SO_4 \longrightarrow CaCl_2 + NH_3 + H_2O$$

Biochemical Methane Potential (BMP) experimental setup

In order to examine the methane potential, a simple methanogenic test procedure was carried out in batch experiments using 125 ml capacity glass bottles. The composition of delimed fleshings, cow dung and bio-digested slurry were R_1(100:0),R_2(25:75),R_3(50:50) andR_4(75:25). The total gas production and methane content was measured using the saccharometer.

Results and Discussion

The deliming technique is performed to lower the pH of the limed pelt from 11.0 – 12.0 to around 8.0 – 9.0 for the bating process and to avoid swelling of pelt surfaces and the formation of H_2S gas in the leather industry (Sirvaityte *et al*., 2007) [3]. Hence, same treatment used for the tannery fleshings to decrease the pH of limed fleshings. In conventional deliming process the pH of the fleshings can be reduced to slight alkali stage and this helps to use of leather fleshings in the anaerobic treatment and the action of ammonium salts on the fleshings with respect to time of 30 and 60 minutes were shown in table 1.

Table 1: Deliming action of the ammonium salts on leather fleshings

Time (mins.)	Quantity of salt (g/l)	pH of NH_4Cl as deliming agent	pH of $(NH_4)SO_4$ as deliming agent
30	1	8.72	8.75
	2	8.68	8.72
	3	8.62	8.69
	4	8.57	8.67
	5	8.54	8.64
60	1	8.26	8.30
	2	8.21	8.27
	3	8.19	8.25
	4	8.14	8.21
	5	8.15	8.19

From the above table, leather fleshings are treated for 30 minutes showing slightly more pH compared to the fleshings are treated for 60 minutes. This is due to the lime content present in the fleshings and requires more time to remove completely and both the deliming agents like ammonium chloride and ammonium sulphate were showing almost similar results.

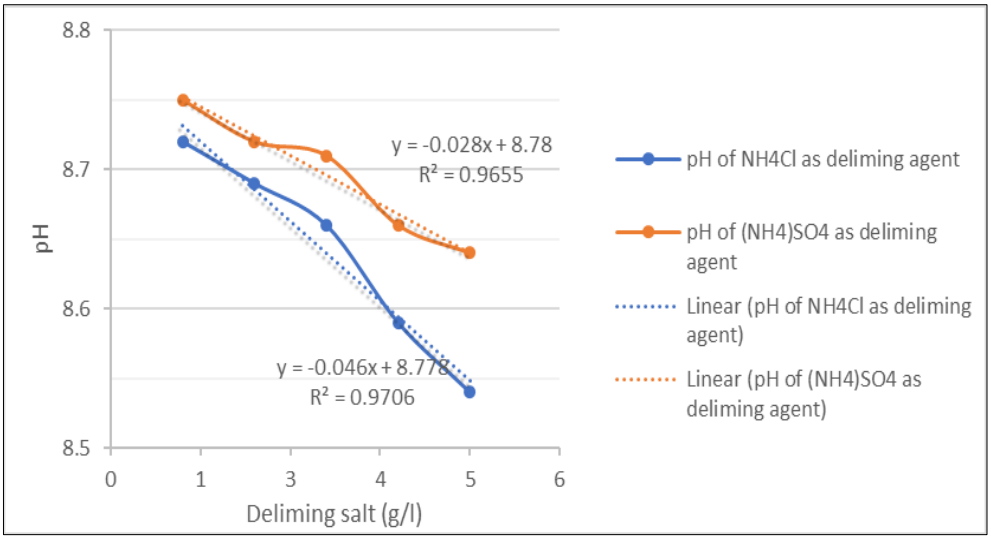

Fig 2: Variation of pH for a time period of 30 minutes at different concentration of deliming salts

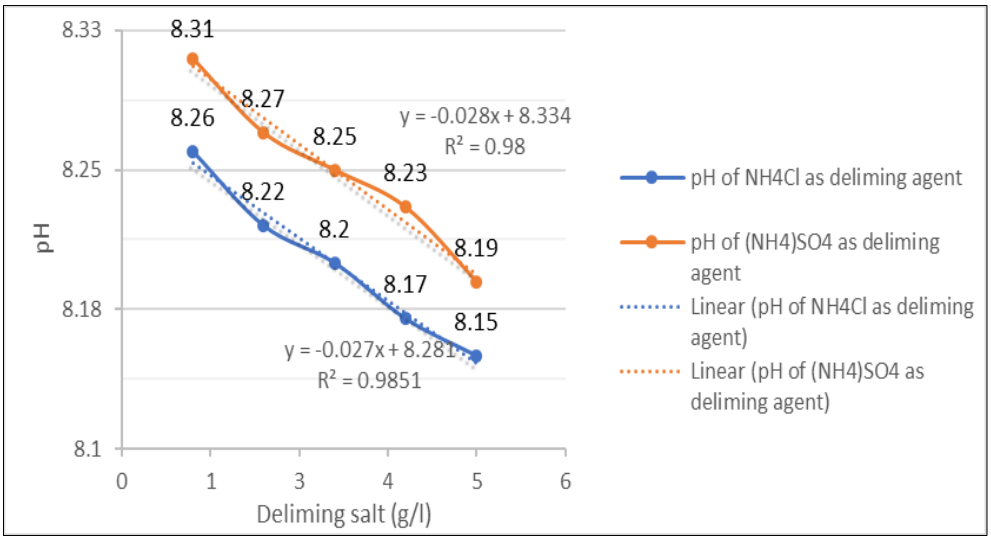

Fig 3: Variation of pH for a time period of 60 minutes at different concentration of deliming salts

Biogas production and methane content

The batch scale experiment carried out for a retention period of 45 days and the total gas production and the methane production from each treatment were shown in the table 2.

Table 2: The batch scale experiment carried out for a retention period of 45 days and the total gas production and the methane production from each treatment were shown

Treatment	I/S ratio	Total gas production (l/kg)	Methane content (%)
DLF:CD	R_1(100:0)	5.82	29.8 – 36.7
	R_2(75:25)	21.34	56.2 – 61.6
	R_3(50:50)	29.37	58.0 – 60.7
	R_4(25:75)	14.29	55.3 – 58.0
DLF:BDS	R_1(100:0)	8.34	32.3 – 39.2
	R_2(75:25)	24.27	59.0 – 62.1
	R_3(50:50)	19.49	56.3 – 62.7
	R_4(25:75)	31.85	59.7 – 63.9

Conclusion

Deliming process for leather fleshings were carried out by using the ammonium salts like ammonium chloride and ammonium sulphate to reduce the pH of the fleshings for anaerobic digestion process. The studies were carried for 30 and 60 minutes with a different proportion of salts like 1, 2, 3, 4 and 5g/l to check the better deliming proportion for further continuation experiments the pH of the fleshings shows 8.15 – 8.30 for 60 minutes of treatment and pH shows 8.54 – 8.75 for 30 minutes of treatment. From the batch experiments R_3(50:50) of cowdung and delimed fleshings and R_4(25:75) of bio-digested slurry and delimed fleshings yielded highest biogas and methane as 29.37 and 31.85 l/kg of fleshings and 60.7 and 63.9% respectively.

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