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Effect of saline water in beamhouse and wet-end processing in leather manufacturing

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ABSTRACT

Water is the most essential chemical constituent in leather manufacturing. From beamhouse to finishing a significant amount of water is used. The quality of water plays a vital role in leather production. In this study, the effect of saline water and groundwater on the leather quality and physicochemical parameters of the discharged wastewater was compared during leather production. Two freshly flayed goatskins were processed separately with saline water and groundwater to produce crust leather. The supply water from Khulna University of Engineering & Technology (KUET) and water from the SAF Leather Industries were considered saline water and groundwater, respectively. Results indicate that pH, electrical conductivity (EC), total dissolved solids (TDS), and total suspended solids (TSS) are almost the same in both discharged wastewater. However, saline wastewater contains a high amount of chloride content and biochemical oxygen demand (BOD) than conventional wastewater. In contrast, the amount of sulfide and chemical oxygen demand (COD) present in groundwater wastewater is far above the saline wastewater. The investigation indicates that the crust leather quality using industrial water exhibits better mechanical properties than the leather produced by using laboratory water.

Keywords: Leather processing, Saline water, Crust Leather, Tensile strength, Water quality

1. Introduction

Water is recognized as the most important element in leather manufacturing. Leather manufacturing consumes 30-50 L of water for the processing of 1 kg of raw hide/skin [1]. The total water required during pre-tanning operation is 44,000 L including 40% towards spillage and housekeeping which is 34 L/kg hide, and the total water required in post-tanning operation is 6,000 L including 40% towards spillage and housekeeping indicating 6 L of water per kg hide [2]. The current annual requirement of water for the leather industry is about 30 billion liters [3].

Generally, wastewater production ranges between 10-100 m^3 for each ton of hide/skin processed [4]. This wastewater is responsible for disrupting environmental balance [5]. For example, only unhairing and liming operation makes up 60-70% of the total pollution load of leather manufacturing industries [6].

Previously, some attempts were made for leather making using saline water [7]. But most of the techniques did not discuss the amount of produced wastage during the processing and the quality of such produced leathers. In the Khulna region, cations and anions present in both saline water and groundwater are within permissible limits [8]. However, due to the dominance of chloride ions over other ions, surface water obtained from the Khulna region is generally saline. On the other hand, groundwater in the Khulna region has a certain degree of salinity but not as much as compared to water obtained from the surface level.

Water hardness has a great impact on the leather quality. In wet-end operations, mostly anionic agents like syntan, resin, dyestuffs, and fat liquor are used. Hence, all these anionic agents get reacted with the cationic ions (Ca^{2+}, Mg^{2+}) of the hard water. Therefore, significant amounts of tanning agents get precipitated without any reaction or cross-linking with the collagen fibers. Thus, soft water is essential in leather processing to avoid reagents/chemical loss and quality leather. The physicochemical parameters like pH, EC, TDS, TSS, BOD, and COD were measured during saline and industrial groundwater leather processing, and their pollution load was measured and compared.

The study aims to illustrate the effect of saline water on the amount of wastage produced during the manufacturing of crust leather. The idea is to demonstrate that the choice of water for production has a significant impact on the production of good-quality leather. For this reason, two crust leathers were produced using saline water and groundwater, and the physicochemical parameters were measured during different stages of manufacturing.

2. Materials and Methods

2.1 Materials

Two freshly flayed goatskins were collected from a nearby slaughterhouse in Khulna, Bangladesh. The average weight of the goatskin was 1 kg per skin.

The saline water used for this study was collected from the campus of Khulna University of Engineering & Technology, Khulna, Bangladesh, and groundwater was collected from the SAF leather industries Ltd. Jashore.

For this study, analytical-grade reagents were used in all experiments, and commercial-grade chemicals were used in leather processing. All the chemicals used were purchased from a local scientific store in Khulna, Bangladesh.

2.2 Experimental

The physicochemical parameters of both saline water and groundwater used in leather processing were measured. Fig.1 shows the freshly flayed goatskin cut into two pieces.

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Fig.1 Freshly flayed goatskin cut into two pieces

To compare the wastage level produce, two freshly flayed goatskins were cut equally into four pieces along the backbone line. Then the pieces of goatskins were preserved for 48 hours using NaCl salt. Two equally cut pieces of the same goatskin were made into crust leather using saline water and groundwater, respectively. During various stages of the processing of crust leather, different physicochemical parameters e.g., Total Dissolve Solid (TDS), pH, Electrical Conductivity (EC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and sulfide content were measured. After the preparation of crust leather, tensile strength was also measured. All the parameters obtained during saline and groundwater leather processing were compared.

2.3 Analysis of Physicochemical Parameters

2.3.1 Determination of Chloride Content

The chloride content of the collected saline water and groundwater was determined by the Mohr method [9]. About 25 mL water sample was taken in a conical flask and about 1 mL of potassium chromate indicator was added in it and then titrated with silver nitrate until the color of the solution turned pinkish. Then, the chloride ion concentration was measured in mg/L. This experiment was carried out three times for both saline water and groundwater. A blank test was also done.

2.3.2 Determination of COD

The COD of the collected saline water and groundwater was determined by standard procedures [10]. Firstly, a 2.5 mL sample was taken with 1.5 mL potassium dichromate. In the mixture, 2.5 mL of sulfuric acid was also added. Then, the samples were heated for 2 hours at 100°C in a water bath. After 2 hours of heating, the sample was taken out of the bath, cooled and 2-3 drops of Ferroin indicator were added. The solution was titrated with the ferrous ammonium sulfate solution until the yellow-green color turned to brick red. The COD was expressed in mg/L. This experiment was carried out three times for both saline water and groundwater samples.

2.3.3 Determination of Sulfide Content

To measure the sulfide content [11], the samples were filtered rapidly through gas wool to remove suspended matter. Then 20 mL buffer solution, 1 mL indicator, and 4 mL barium chloride solution were placed in a 250 mL stoppered flask. After that, the titration was done with standard potassium ferricyanide until the pink color disappeared and the pink color did not reappear after 30 seconds. The measured sulfide content was expressed in mg/L. This experiment was carried out three times for both saline water and groundwater samples. A blank test was also done.

2.3.4 Determination of EC, TDS, and TSS

To test the water quality of the sample, a device (CT-676, BOECO, Germany) was used. The probe of the device was immersed in the water sample. The probe contains a sensor at the bottom of the probe. This sensor measures EC, TDS, and TSS of the sample in mS/cm, mg/L, and µg/L, respectively.

2.3.5 Determination of BOD

For the determination of the BOD of saline water, groundwater, and wastewater standard APHA method was followed [12]. This determination involves the measurement of the dissolved oxygen (DO) used by microorganisms in the biochemical oxidation of organic matter. BOD_5 is the total amount of oxygen consumed by microorganisms during the five days of biodegradation. For BOD determination, 250 mL of distilled water was taken into a BOD bottle where 2 mL sample, 1 mL alkaline azide, and 1 mL manganese sulfate were added. The solution became golden in color. After 5-6 minutes, 1 mL sulfuric acid was added to the solution. The rest of the BOD bottle was filled with distilled water. This is done to eliminate any air from the BOD bottle. Then 200 mL solution was taken in a conical flask. The solution was titrated with sodium thiosulfate until the color of the solution becomes pale yellow. After that, 2 drops of the starch indicator were added to it and the titration was continued until the solution became colorless. This experiment was carried out three times for both saline water and groundwater samples. A blank test was also carried out. Thus, initial dissolved oxygen (DO_o) was obtained. DO was expressed as mg/L. The same process was carried out to fill up the BOD bottles and the BOD bottles were set in an incubator at 20°C for five days. After five days the BOD bottles were taken out from the incubator and titration was done in the same way thus dissolved oxygen on day five (DO_5) was obtained. BOD was calculated in mg/L.

2.3.6 Determination of pH

The pH of different steps of crust leather processing was measured using a pH meter (Pocket Pro pH tester, Hach, USA).

2.3.7 Determination of Tensile Strength of Leather

For determining the tensile strength of the produced leather using saline water and groundwater, samples were taken according to the standard sampling location. A total of 24 samples were cut from the crust leather. Then, the tensile strength of the samples was assessed according to ISO 3376 [13].

3. Results and Discussion

3.1 Sulfide Content

In beamhouse, unhairing and liming make up 60-70% of the total pollution load of the leather manufacturing industry. Table 1 represents the comparison of sulfide content between saline water and groundwater at different stages of crust leather processing.

Table 1 Sulfide content in different operations

Operation	Sulphide content (mg/L)	
	Groundwater	Saline water
Initial	1.92±0.09	4.38±0.10
Soaking	3.93±0.06	4.32±0.05
Liming	2724.8±5	4633.33±41.63

The sulfide content of groundwater and saline water was 1.95 mg/L and 4.38 mg/L, respectively. After the soaking operation, the sulfide content increased up to 3.93 mg/L and 4.32 mg/L for groundwater and saline water, respectively. After liming, sulfide content of the discharged wastewater for groundwater and saline water increased significantly at 2725 mg/L and 4633.33 mg/L, accordingly. The sulfide content plays a vital role in the pollution load affecting the environment [14]. Increased sulfide content in the wastewater would raise the pollution load. Table 1 suggests that leather processing using saline water produces more sulfide content in both soaking and liming operations.

3.2 Chloride Content

Chloride content represents the salinity of the water. The more chloride content is present in wastewater, the salinity is also increased. The chloride content of groundwater and saline water was 58.78 mg/L and 674.46 mg/L, respectively. It seems that the saline water contains 11 times more chloride than the groundwater.

3.3 Electrical Conductivity

Electrical conductivity is the measurement of water capacity to pass electrical flow. The electrical conductivity of different stages of crust leather production was measured for both groundwater and sample water. Table 2 represents the comparison of electrical conductivity between saline water and groundwater at different stages of crust leather processing.

The obtained values of electrical conductivity of groundwater in initial, soaking, liming, neutralization, and dyeing were 0.567, 12.14, 21.71, 6.74, and 9.65 mS/cm, respectively. For saline water, the electrical conductivity in initial, soaking, liming, neutralization, and dyeing were 1.91, 16.3, 21.2, 6.28, and 12.25, mS/cm, respectively. It seems that in every stage the electrical conductivity was higher in saline wastewater. Since the saline water contains more chloride content as dissolved solids, it increases the electrical conductivity of the saline wastewater.

Table 2 Electrical conductivity in different operations

Operation	Electrical conductivity (mS/cm)	
	Groundwater	Saline water
Initial	0.57±0.01	1.91±0.01
Soaking	12.14±0.01	16.3±1.0
Liming	21.71±0.01	21.2±0.01
Neutralization	6.74±0.01	6.28±0.01
Dyeing	9.65±0.01	12.25±0.01

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3.4 Total Suspended Solid

Total suspended solids refer to the dry weight of suspended particles that are not dissolved in water. TSS values were measured for different stages of production using groundwater and saline water. Table 3 represents the comparison of TSS content between saline water and groundwater at different stages of crust leather processing. The TSS found in groundwater for initial, soaking, liming, neutralization, and dyeing operation were 0.3, 6.43, 12.39, 3.29, and 4.61 µg/L, respectively. In addition, the saline wastewater contained 0.9, 8.6, 11.93, 3.09, and 4.84, respectively in initial, soaking, liming, neutralization, and dyeing operation. The higher the TSS values the higher the pollution of load.

Table 3 TDS in different stages of production

	Total suspended solids (µg/L)	
	Groundwater	Saline water
Initial	0.3±0.001	0.9±0.001
Soaking	6.43±0.06	8.6±0.02
Liming	12.39±0.09	11.93±0.06
Neutralization	3.29±0.001	3.09±0.001
Dyeing	4.61±0.01	4.84±0.02

It can be seen that the total suspended solids are higher in different stages of production using saline water than groundwater. Thus, it can be said that the pollution load is higher in the production of crust leather using saline water than in groundwater.

3.5 Total Dissolved Solids

Total dissolved solids represent the dissolved combined content of all inorganic and organic substances present in a liquid in molecular, ionized, or micro-granular suspended conditions.

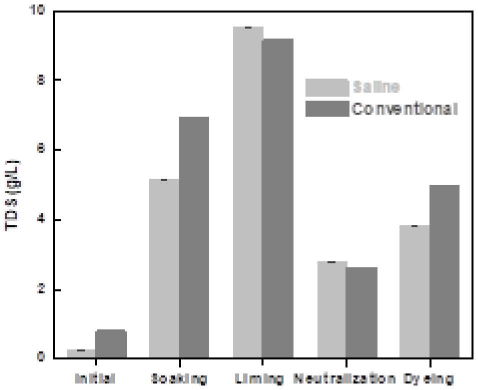

Fig.2 Comparison of total dissolved solids in different stages of production

Fig.2 represents the comparison of TDS content between saline water and groundwater at different stages of crust leather processing. TDS values measured for different stages of production using groundwater were 0.239, 5.15, 9.53, 2.78, and 3.8 g/L, respectively in initial, soaking, liming, neutralization, and dyeing operation. TDS values were also measured for the production of crust leather using saline water. The measured values were 0.802, 6.94, 9.17±0.001, 2.63, and 4.967 g/L in initial, soaking, liming, neutralization, and dyeing operation, respectively. It could be seen that the TDS are higher in different stages of production using saline water. The reason might be that in saline water the dissolved contents are higher in chloride form. Thus, it also increases the TDS in wastewater.

3.6 Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is the measurement of the amount of oxygen absorbed by bacteria and other microorganisms during the decomposition of organic matter under aerobic conditions at a specified temperature. The wastewater produced in commercial, industrial or institutional facilities often has higher BOD levels than domestic water.

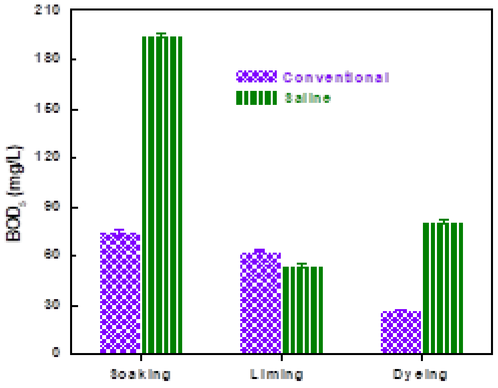

Fig.3 Comparison of biochemical oxygen demand in different stages of production

Fig.3 represents the comparison of BOD content between saline water and groundwater at different stages of crust leather processing. Biochemical oxygen demands in a different stage of crust leather production using groundwater were: soaking at 74.33 mg/L; liming at 63 mg/L; dyeing at 26.83 mg/L. Moreover, the values of BOD in different stages of production of crust leather using saline water were: soaking 194.83 mg/L; liming: 53.67 mg/L; dyeing 81.33 mg/L. The higher the values of BOD, the higher the pollution rate and the lower the amount of dissolved oxygen.

3.7 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) represents the amount of oxygen required to oxidize the organic material and inorganic material present in water. The value of chemical oxygen demand is generally higher than biological oxygen demand because COD involves both organic and inorganic substances. Table 4 represents the comparison of COD content between saline water and groundwater at different stages of crust leather processing.

Table 4 COD values in different operation

	COD (mg/L)	
	Groundwater	Saline water
Initial	107.03±1.56	24.23±1.68
Soaking	279.9±1.61	267.23±1.60
Liming	38080±3200	22720±3200
Dyeing	1600±320	8640±320

It can be seen that the COD value was highest in liming operation and in comparison the COD values were higher for saline water in every stage. The higher the COD value the higher the pollution. Thus, the production of crust leather using saline water produces more waste.

3.8 Tensile strength

Tensile strength is the ability of a material to withstand the force applied per unit area. The tensile strength of leather gives an idea about the quality of the leather. For comparing the quality of produced crust leather tensile strength of the butt portion and butt-belly portion were measured.

Table 5 Tensile strength of crust leathers

	Groundwater	
ID	Butt (N/mm)	Butt-Belly (N/mm)
Sample 1	33.28±0.26	38.38±0.31
Sample 2	43.43±0.32	42.48±0.32
	Saline water	
ID	Butt (N/mm)	Butt-Belly (N/mm)
Sample 1	22.57±0.17	27.43±0.22
Sample 2	28.45±0.41	27.34±0.23

Table 5 shows the tensile strength values of the butt portion and butt-belly portion of the leather. From Table 5, it can be noted that both halves of crust leather produced using groundwater have a higher tensile strength in both butt and butt-belly portions than the crust leather produced with other halves of these leathers using saline water.

3.9 Elongation at Break

Elongation at break is the determination of the stretchiness of a material as a percentage of the original dimension before it breaks. A higher percentage usually indicates a better-quality material. Table 6 shows the elongation at the break of the butt portion and butt-belly part of the leather.

Table 6 Percentage of elongation of produced crust leathers using conventional water and saline water

	Groundwater	
ID	Butt (%)	Butt-belly (%)
Sampe1	34.51±0.23	28.83±0.09
Sample 2	36.33±0.25	42.39±0.24
	Saline water	
ID	Butt (%)	Butt-belly (%)
Sampe1	25.43±0.32	32.67±0.22
Sample 2	42.96±0.57	28.72±0.13

From Table 6, it can be observed that the crust leather produced using groundwater has a higher elongation at break in both butt and butt-belly portions than the crust leather produced using saline water. Thus, it can be said that the production of crust leather using groundwater gives good quality crust leather compared to saline water.

4. Conclusion

The main objective of this study was to compare the influence of saline water and industrial water in the case of the quality of the produced leather. The pollution load in different stages of the production of crust leather using saline water was found to be higher than the production of crust leather using groundwater. Moreover, the leather quality was also better using groundwater i.e., industrial water in terms of tensile strength and percentage of elongation. It was observed that the quality of water played a vital role in the overall quality of crust leather as well as the pollution load in the discharged wastewater. This present study shows that the choice of good-quality water for leather production is as much important as the selection of good-quality raw material.

5. References

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