Curing is the first process of skin treatment mainly using sodium chloride salt to prevent its decay. At soaking step of tannery, the effluents will be discharged to the environment, which contains the chloride ion, which will negatively affect our environment. Therefore, it should be either treated or reused so that it can help to reduce amount of chloride ion of the soaking effluent discharged to the environment and cost of pickling. This study focused on recycling of curing salt for sheepskin pickling and studying its effect on the pickled skin’s properties. Salt was recycled from cured skins manually, and it was purified through dilution, filtration, treatment, and drying. Five enzymatic bated sheepskins were collected from Bahir Dar, Ethiopia. The recipes were developed based on the weight of the pelt which was going to be pickled with 0.8% H₂SO₄, 0.5% formic acid, and 80% H₂O for each trial and the recycled salt at different concentrations (8%, 8.5%, 6.5%, 7%, and 7.5%) for S1, S2, S3, S4, and S5, respectively. Bromocresol green was the pH indicator. Then, properties of treated samples were measured and evaluated in line with ISO standards, and the pH of the recipe was checked. The results showed that S1 treated with the mentioned materials and 8% salt amount has highest tensile strength (80.3 N/mm²). In addition, S1 has also the maximum tear strength of 60 N/mm² and the minimum was 45.69 N/mm². On the contrary, S3 has shown the least values of tensile strength and elongations as well as least tear strength. S1 has the maximum shrinkage temperature of 107 °C and S3 has that of the least value 89 °C which is lower compared with the standard shrinkage temperature, 95 °C. The pH values were found to be within the standard for pickling. The overall result of this study was promising.
of waste water generated is 12,500 m$^3$ and there is 150 tons of solid waste from which 54.5 tones is dusted salt [4, 11]. Generally, chemicals that are used during leather manufacturing are not fully consumed by the leather and wastes are produced, which include pollutant chemicals and the liquid effluent at the level of 45–50 m$^3$ per ton of raw hide is generated with nearly 70% of the emission loads [9, 13].

Mostly curing skin is carried out using sodium chloride which is sufficiently available in nature. In this process, the salt is used to decrease the moisture of the skin from 70% to 30%, which is to retard the bacterial growth, and another advantage of sodium chloride salt curing method is its cost effectiveness and being easy to practice [14]. The salt is discharged not only from pickling and chrome tanning operation but also from curing stage in major amount of water [11, 15]. In the process of chrome tanning, transitional pickling method is usually performed before tanning which brings the whole collagen matrix to uniform conditions to stop the speedy combination of the skin substrate with a chromium compound; therefore pickling allows even penetration of chromium into the collagen matrix. Sodium chloride salt or sometimes other sodium salts are previously added to restrict the swelling of the collagen in the acidic medium [16, 17]. The pickling operation minimizes the anion of the carboxyl groups and maximizes the cat ions of the amino groups of the collagen peptides, thus making the pickled positively charged. This is as repellent effect of like charge widens the spacing of the collagen peptides resulting in collagen swelling. Moreover, crosslinking of the collagen fibers is partially destroyed and the stability of the collagen weakened. Such swelling and disruption of crosslinking can probably be avoided with the presence of neutral salt [4, 9].

Although curing using sodium chloride is effective and inexpensive, it has a serious environmental effect; it contributes to about 35% total dissolved solids (TDS) in the effluents and the TDS load in the waste water is high due to the great application of salt in preservation and leather pickling stages in the life phase of leather [5, 18]. Scholars also have tried to replace half amounts of NaCl by some other eco-friendly materials to reduce its salt effect on the environment; however, the newly added chemicals affect the properties of the treated skin due to its incompatibility [4, 19].

Kanagaraj et al. have done an investigation titled “Eco-Friendly Waste Management Strategies for Greener Environment towards Sustainable Development in Leather Industry: A Comprehensive Review.” The research highlights the effect of chrome, soaking salt effect on our ecosystem, and suggests management methods for tanning leather Industry waste [15]. However, the researchers have not tried to recycle and reuse a curing salt, for which a higher emphasis is given by this study.

Xinju Jia et al. have published their research results in their research titled “A Salt-Free Pickling Chrome Tanning Technology: Pretreatment with the Collective Polyoxyethylene Diepoxy Ether and Urotropine.” The research claimed that the curing and tanning salt highly affects our environment due to the inclusion of common salt and chrome tanning agent; therefore, a salt-free chromium tanning technology should be developed using alternative materials [3]. However, as NaCl is cheap in its cost and application, it is better to recycle and reuse than searching alternative materials. This study takes those researchers’ idea positively and has tried to fill its gaps by launching an idea regarding recycling and reusing of this pollutant common salt instead of searching other costly tanning materials.

On the other hand, Vedaraman et al. have done an experiment on recovery and reuse of contaminated sodium chloride obtained from tanneries for raw goatskin preservation [17]. Although its idea is nearer to that of this study, it lacks an investigation on the effect of recycled salt on the treated skin properties compared to using fresh salt. In addition, the researchers studied referring goatskin samples but the this was focused on sheepskin.

Therefore, even though many investigators have reflected their views regarding the effect of tannery salt, most of the researchers’ concerns were only environmental issue. It is known that our environment will be eco-friendly when the possible pollutant material is recycled and reused. As stated, most of the researchers’ focuses were on the effect of chloride ion on the human health and environment from the tanneries effluent discharge. However, these researchers have not given an emphasis on how the use of recycled salt on skin pickling affects the properties of the treated skin. This research aims at recycling the curing salt from cured sheepskins for pickling and investigating on whether it has an effect on physical and mechanical properties of treated skins compared to that of conventionally pickled skin or not. Unfixed salt on cured skin was dedusted and recycled. This can be done either by using DODECA wooden frame or by hand beat up, shaking, and collecting the dedusted salt on ballast. The first method involves a simple wooden frame of a size, which can be made from easily available wood. In this method, the dedusting can be done by holding the hides at the edges and beating them on the frame and in the second way the cured salt will be highly beat up and shaken and then the dedusted salt will be collected [11].

The researchers used the second method. The salt generated by dedusting is diluted, filtered, and treated with bactericide with charcoal to remove contaminations and impurities. All research materials were collected form Bahir Dar Tannery (BDT) and Ethiopian Institute of Textile and Fashion Technology, Bahir Dar University, Ethiopia.

2. Materials and Methods

2.1. Materials. Ten cured sheepskins were collected from Bahir Dar Tannery, Ethiopia, shown in “Table 1” from which the salt is recycled. Enzymatic bated sheepskins (each weight of 1 kg and thickness of 0.7 mm) were used to be pickled by the newly developed pickling recipe. Formic acid (HCOOH) was used for fixation purpose and H$_2$SO$_4$ for lowering pH level from basic to acidic region in pickling for chrome tanning, also collected from Bahir Dar Tannery, Bahir Dar, Ethiopia. Litmus paper was used to measure the pH level of the newly developed pickling recipe by referring its result with the universal color indicator.
2.2. Methods

2.2.1. Dedusting and Recycling Methods. As illustrated in “Figure 1” the procedure used for dedusting the cured salt is beating up the cured skin and shaking it, accumulating the salt on the mat, and calculating the amount of dedusted salt based on the weight of the cured skin. The salt used in leather pickling was recovered from the preserved skin and dissolved in water to make a saturated salt solution, according to researchers who utilized the most efficient method of recovering powdered salt. Insoluble contaminants were removed from the salt solution using the filter cloth. Activated charcoal was used to remove the unwanted color from the solution. Salt solutions treated with activated charcoal were also treated with an antibacterial agent, which is used to remove bacterial contamination from the solution. Finally, the solution was exposed to direct sun light to get dried purified salt and that was used for the pickling processes [11]. This is illustrated in “Figure 1.”

2.3. Pickling Methods. As shown in “Table 2” five enzymatic bated sheepskin samples, each about 1 kg with thickness of 0.7 mm, were collected. Then these skins were placed in a solution that contains recycled curing salt, formic acid, and sulfonic acid. In each experiment, the amount of recycled salt was different but the same amounts of other materials as used in conventional method of pickling were used, as detailed in “Table 2”; all experiments were done at Bahir Dar Tannery, Bahir Dar, Ethiopia.

2.3.1. Pickling Procedure. As demonstrated in “Table 2” 80% water was added to the drum together with recycled curing salt in the amount mentioned. Then the test drum was run for 10 minutes and then 0.5% formic acid was added and the drum was run for an hour. Then H₂SO₄ was added and drum was rotated for 3 hours; the reason to add H₂SO₄ later is to avoid rapid swelling of the skin by the strong acid. The same order of producer is repeated for pickling of all the five samples by varying the mentioned amount of recycled salt on the table.

2.4. Testing Methods

2.4.1. pH Measurement. The pH values of pickled skin samples were measured according to ISO 9001. The indicator is placed on the pickled skin and the color change is read to know whether the medium of the recipe is within the required medium, acidic medium.

2.4.2. Tensile Strength and Elongation Test. Samples were cut using cutting die. The length of each samples was 110 mm and the width of the griper in both sides was 25 mm and then tensile strength and elongation of the treated samples were evaluated according to ISO Standard 3376 with serial number 1076 using universal strength testing machine (Mesdan model: Tenso-Lab).

2.4.3. Tear Strength Test. Tear strength is the force per unit area of the cross section required to cause the rupture of the specimen. During the experiment, the skins resistance to tearing force was assessed as per ISO 3376. Test specimens were cut using a cutting knife (50×25 mm size) having a central slot with 0.5 mm thickness from all the five samples. The tests were conducted by operating the tester at the rate of 250 ± 10 mm/minute speed until the test pieces were torn apart. Then the values were calculated using the following formula:

\[
tear\ strength = \frac{\text{max} \cdot \text{tear force (N)}}{\text{thickness (mm)}}
\]  

2.4.4. Shrinkage Property Test. The samples shrinkage temperatures were measured according to the standard of SATRA TM17; a ribbon of leather samples was immersed in water and gradually heated until a sudden shrinkage occurred. The temperature at which this shrinkage occurs indicates the characteristics of the pickled skin related to temperature resistance.

2.4.5. Subjective Assessment. The properties such as softness, uniformity, smoothness, and fullness of pickled samples were assessed visually and by feeling the touch.

3. Results and Discussion

3.1. Production Yield. 0.0592 kg pure salt was recycled from 10 cured sheepskins. The percent of salt recovered per ten samples based on total weight of samples is 7% including impurities and that of purified salt is 5.63%. The recycled salt is seen in Figure 2(b) and the fresh salt is seen in Figure 2(a). Therefore, it is feasible to reuse, if the minimum of 5.63% of salt is recycled from ten cured skins, and it is easy to imagine how it is affordable and how we can reduce its environmental effects as well as how salt cost can be reduced in pickling.

From the data presented in “Table 1,” the amount of salt recovered and purified from ten cured sheepskins, Bahir Dar Tannery, Ethiopia, shows that about 6% of salt can be
The recycled salt amount was calculated as follows:

$$\text{average salt recovered} = \frac{\text{total salt recovered}}{\text{number of samples}}$$

(2)

Thus, it is possible to recycle 7.346% of salt on the weight of the raw skin taken for soaking operation. Moreover, after applying the necessary treatment, it is possible to obtain 5.92% on the weight of the skin. This amount of salt can affect the environment largely if not managed properly by different ways like recycling and reusing.

3.1.1. pH Value Result. Knowing the pickling PH value is very important as it has a big effect on the next process, tanning of the pickled skin. The universal color indicator of pH is numbered from 1 to 14. A pH litmus paper is a material which will give different colors when it is placed on the pickled skin. It will be red if the indicator is 1, red if it is between 2 and 2.5, light yellow if it is 3, deep yellow color if it is 4 and 5, and so on as shown in Figure 3(a). With regard to this research, since pickling should be in acidic medium for chrome tanning, a required pH should be between 2 and 3.8, and hence it gave a red to yellow color as illustrated in Figure 3(c). If the pH is basic, medium fixation may not take
place, and if it is too acidic, the skin will shrink, and rapid acid swelling may occur due to the effect of strong sulfuric acid.

3.2. Tensile Strength and Elongation. The effects of using recycled salt in sheep skin pickling on the tensile strength and elongation of treated skins compared to conventionally pickled skin are discussed based on the results presented in Figure 4.

As shown in “Figure 4” the tensile strengths of treated skin samples 1 and 2 are almost the same and their salt used contents are 8% and 8.5%, respectively, which are both the same amount as that of fresh salt in conventional pickling. Salts in this amount gave a very good strength to the skins compared to treated samples S3, S4, and S5 with salt concentrations of 7.5%, 7%, and 6.5%, respectively. This is due to the salt used in pickling of these skins being out of the standard requirements. If the salt is too low, unwanted skin swelling will occur, which makes the skin weak, and if it is too high, the treated skin becomes highly dehydrated and becomes less in its tensile strength and elongation. Elongation of leather is the measure of its stretchiness in the direction of force applied and is the indication of the leather’s resistance to breakage. From the result presented in “Figure 4” tensile strength and elongation of each pickled sample are directly proportional. Elongation of sample S1 has the highest value, which means it can stretch more before it ruptures, whereas that of sample S3 is the lowest; it is easily ruptured in very less stretching force. It will tear easily if salt content is below the standard and the skin will be so dried if the salt amount is above the standard requirement. Other experimental samples S2, S4, and S5 have intermediate properties between S1 and S3. However, the salt amount used for these trials is still not correctly formulated and should be compromised for better skin properties. Generally the sheep skin pickled by curing salt, recycled salt, has shown interesting tensile strength and elongation properties. The pickling operation minimizes the anion of the carboxyl groups and maximizes the cat ions of the amino groups of the collagen peptides, thus making the pickled skin positively charged.

If improper salt amount and extreme acid are used in pickling, the crosslinking of the collagen fibers is partially destroyed and the stability of the collagen weakens. Such swelling and disruption of crosslinking can probably be avoided with the presence of neutral salt which greatly affects the leather’s tensile strength [4,9]. Therefore reusing of the recycled curing salt is highly recommended for pickling, which can save salt costs and reduce environmental pollution.

3.3. Tear Strength. As shown in “Figure 5,” S1 has a tear strength of 60 (N/mm²) at 8% percent salt content, which is better value than the standard minimum tear strength criteria for conventional pickling with fresh salt (above 50 N/mm²). As a result, the pickled skin in the first trial can withstand an external force that could cause it to break, and sample 5 (49.31 N/mm²) is extremely close to the pickling minimum requirements.

The rest of the treated samples, S2, S3, and S4, are below the standard requirement; they are therefore sensitive to tear if force is applied on a small crack of the skin in opposite direction. This implies that the amount of salt used in these samples’ pickling is not correctly formulated and, hence, it should be compromised, whereas pickling using the recipe used in the first experiment is highly advisable. Thermal stability results of the samples are different. One of the reasons for this difference is the difference in salt content used during samples pickling and another possible reason is that the collagen structure of the skin may vary from sample to sample; if the collagen fiber of the skin is highly cross-linked in nature, it greatly affects the mentioned property [1, 4]. Generally, by recycling the salt from cured skin, it is possible to it for pickling purpose and it has a positive effect on tear strength of the treated skin compared to conventionally pickled one. Moreover, recycling and reusing of the salt can reduce environmental pollution.
3.4. Shrinkage Property Testing. Shrinkage temperature in context of leather material is the temperature at which collagen fibers contract. The values of the shrinkage temperature of the treated samples are presented in Figure 6.

From the result shown in Figure 6 the shrinkage temperature of S1 has the highest value and that of S3 has the smallest one and the others have intermediate values; except for shrinkage temperature of S3, the values fall within the standard conventional temperature requirement (above 95°C). This difference is due to the fact that the amount of recycled salt used varies from pickling liquor of each sample, keeping chemicals other than the salt same in amount and type for both conventional pickling using fresh salt and that using recycled salt. S1 has the best heat resistance compared to the other samples as the higher the shrinkage temperature is the better the heat resistance is as there would be higher crosslinking reactions between the collagen fibers of the skin being treated. This is because contraction of collagen fibers in a highly cross-linked fibers manner is higher than that of low cross-linked fibers [6].

In addition, if shrinkage temperature of treated skin raises pickling materials are highly fixed on and/or in the skin. Therefore, the collagen fibers of the skin treated with the first recipe are cross-linked higher than other treated skin samples. On the contrary, the 3rd sample’s value is lower than standard shrinkage temperature of conventional pickling and has comparatively the lowest ability to resist heat due to very shrinkage temperature. Other samples’ values are fall within those of experiments S1 and S3; the effect on treated leather is also intermediate. Hence, the measurement and understanding are valuable for judging the suitability of the leather at which most heat may be applied, for example, in footwear manufacturing process. All these variabilities in shrinkage properties of the treated samples depend on the properness of treatment materials used, appropriate content of salt, and the nature of collagen fiber crosslinking degree of samples as the more cross-linked the collagen fiber is the more it resists the temperature.

3.5. Subjective Assessment. The properties such as softness, uniformity, and fullness of the experimentally treated samples were assessed visually and by feeling a touch. Among all the experimental samples pickled with different proportion of recycled salt, most of the samples have shown the same subjective valuation result and it is indicated that these properties can be achieved in an effective way whenever the proportion of salt and another pickling material are compromised.
4. Conclusion

Recycling curing salt for sheepskin is recommended to reduce pickling cost and its effect on the environment. This research focuses on recycling of the sheepskin curing salt and analyzes its effect on properties of pickled skin compared to that of conventionally treated skins. It is found that about 6% curing salt can be recycled and reused for pickling. All samples, S1, S2, S3, S4, and S5, were treated using 0.8% H_2SO_4, 0.5% formic acid, and 80% H_2O. These amounts are the same in type and amount of materials used in conventional pickling method for each trial and different concentrations of recycled salt content (S1 = 8%, S2 = 8.5%, S3 = 6.5%, S4 = 7%, and S5 = 7.5%). After treatment, all the treated skin properties were measured and analyzed using ISO standards.

The results showed that S1, treated with the mentioned materials and 8% salt amount, has given higher tensile strength of about 81 N/mm^2 with 45.7% elongation, where the conventional standard tensile strength and elongation value requirements are 75 N/mm^2 and 40%, respectively. In addition, S1 has also the maximum tear strength of 60 N/mm^2 and the minimum is 46 N/mm^2. On the contrary, S3, treated with 6.5% salt content, has shown lowest values of tensile strength and elongation, 64 N/mm^2 and 23.1%, respectively, and its value of tear strength was about 46 N/mm^2. The shrinkage properties of treated samples are also maximum at S1 and minimum at S3 compared with the standard shrinkage temperature requirements of pickled skin, 95°C. Generally, the properties of pickled skin using recycled salt are effective as those of the skin using fresh salt; moreover, recycling the cured salt can reduce the salt cost and make an eco-friendly environment keeping pickling materials other than the salt [20–22].

Data Availability

The data collected and analyzed during this study are included in the paper and more can be accessed from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

All authors have played their own role in the completion of the research.

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