Tannery Solid Waste into Wealth by Non-Edible Gelatin Production from Raw Trimmings

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Abstract—During the conversion of raw hides or skins into leather involves generation of enormous amount of solid waste that has been major concern for environment and cause severe pollution. In leather industry solid wastes can be generated almost from all operations including pre-tanning, tanning, and even post tanning operation. Solid wastes are mainly unwanted materials like raw trimmings, fleshing, chrome shaving, buffing dust, keratin, finished scraps etc. This study focuses on utilization of raw trimmings into useful product like non edible gelatin those demand is going up day by day due to its versatile application in various fields. Raw trimmings are mainly originated during leather trimming skins sorting of leather before actual tanning process happens and best for non- edible gelatin production as it does not contain any harmful chemicals. This study will also describe the chemical properties of non-edible gelatin, manufacturing process of non-edible gelatin, and manufacturing parameters from the leather solid wastes like raw trimmings derived as wastes. Optimum extraction of non-edible gelatin from raw trimmings found at 75-85°C for 12 hours in slightly basic condition. This study found that huge amount of raw trimmings which generally thrown directly to environment can serve as potential raw materials for the manufacture of non-edible as well as edible gelatin. The approach could also contribute a significant reduction in the environmental impact of inevitable solid waste and decrease the costs associated with disposal

Index Terms—Leather Raw Trimmings, Collagen, Non-Edible Gelatin, Hides and Skins.

I. INTRODUCTION

Due to enhanced economic activities and rapid industrialization, tannery solid waste generation has increased dramatically in the last few decades. Tannery Solid waste generation is a continually growing problem at regional and local levels due to rapid industrialization [1]. Tannery Solid wastes are those organic and inorganic waste materials produced by various activities of the tanning processes. Improper tannery solid waste management causes all types of pollution: air, soil, and water. Tannery solid waste management is a challenging problem for developing countries. There are various types of solid waste generate from leather industry most of them are harmful if not managed properly. When tannery solid waste is disposed on land in open dumps or in improperly designed landfills (e.g., in low lying areas), it causes an adverse impact on the environment, such as ground water contamination, generation of inflammable gases, acidity to surrounding soil, release of greenhouse gases etc. [2]. Generally, 35-60% of the total solids in tannery sludge are organic matter. In chrome shaving chrome tanned leather, splits and trimmings have usefulness in obtaining glue, non-edible gelatin [3]. In terms of Socio-economic consideration this study is important because the non-edible was developed from inexpensive raw trimmings materials in short period of time. In below section raw trimmings and its characteristic, gelatin and its chemical properties are discussed.

A. Trimmings

Out of 1000 kg of raw hide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw materials is converted into leather [4]. Trimmings may be available in the raw, salted, limed, wet blue, finished leather from various stages of unit operation in the leather manufacturing. Trimmings of all types described above are suitable for gelatin production. It is also possible produce good quality technical grade gelatins from this raw material. Presence of hair on the hides and skins do not pose any problem in gelatin production as the hairs are separated and remain with the extracted residue in the gelatin kettle and settle to the bottom [5]. Very large quantity of hair may at times be responsible for imparting a darker shade to the final product. This happens when sulphide treated trimmings are present together with trimmings containing hair. The sulphides gradually dissolve some hair which imparts the color to the gelatin extract. Dew claws of sheep, goat and cattle may be present trimmings from the limbs of animal. When present very much in excess, dew claws may also impart darker color by the same mechanism, as hair in trimmings. Dew claws will significantly contribute to the weight of raw materials taken for extraction of gelatin, thus giving a lower percentage yield as these do not by themselves yield gelatin [6]. From 1000 kg of raw hides and skins approximately 40 kg raw trimmings are obtained. Head skin pieces, scrotal sacs (the bag that holds the testicles) of male animals, udders and teats of cows are also included in trimmings [7]. Head skins pieces are good raw materials for glue extraction and can be bought out for glue production. Presence of horns in the head skin pieces is undesirable as much as dew claws and hair are scrotal sacs being bag like may be poorly limbed or packed full of lime. The sacs filled with lime are difficult to wash to get rid of lime and the excess lime in the bag will cause consumption of excess acid for deliming. In either case scrotal sacs could be problematic. They are best cut along the length of the bag with a meat chopping knife before including in gelatin stock. Ear pieces can be present with trimmings but they yield very little glue or gelatin on weight basis. They contain a cartilage and resist neutralization with acid thus increasing the requirement of acid. The ear pieces cartilage gives of its

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salts, mainly phosphates or calcium which is insoluble in water and contributes to turbidity of extracted gelatin. Further, they may be increase the ash content of dried gelatin. The economic development of a country depends on the utilization of indigenous raw materials and their by-products. As the pollution reduction can be possible by formulating cost intensive non-edible gelatin production, the leather industry will be eco-friendlier and become environmentally compliant to buyers. Therefore, export earnings will be increased and the socio-economic status of people will be improved.

1) Composition of gelatin:
Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones and connective tissues of Animals such as domesticated cattle, chicken, pig and fish, during hydrolysis, the natural molecular bonds between individual collagen strands are broken down into a form that rearrange more easily [11]. Gelatin has proline, Hydroxyproline and glycine in its polypeptide chain. Glycine is responsible for clone packing of the chains. Presence of proline restricts the conformation. This is important for gelatin properties of gelatin. Gelatin readily dissolves in hot water and setter to a gel on cooling. When added directly to cold water, it does not dissolve well, however gelatin also is soluble in most polar solvent. The mechanical properties of gelatin are very sensitive to temperature variation and the amount of time elapsing. The viscosity of the gelatin water mixture is greatest when the gelatin concentration is high and mixture is get cool at about 4°C the gel strength is quantified during the bloom tent [12]. Gelatin’s strength declines if it is subjected to temperature above 100°C or if it is held at temperature near 100°C for an extended period of time. Typical non-edible gelatin normally contains about 15% of water and 1-4% inorganic salts [13].

- Carbon -15%
- Hydrogen -26%
- Nitrogen -18%
- Oxygen -25%
- Sulfur – 0.1%
- Phosphorus -0.3%

Gelatin is rich in protein and has a unique amino acid profile that gives it potential health benefits. There is evidence that gelatin may reduce joint and bone pain, increase brain functions and help reduce the signs of skin aging [14].

2) Types of gelatin:
There are two types of gelatin depending on the preparation methods. Gelatin is classified according to whether an acid or an alkali is used in the final pre-extraction step. If acid solution is used as the final solvent type- A gelatin (acid process). In case of alkali as the final solvent, type-B gelatin (alkali process) is obtained. Although there might be two types of gelatin extraction procedure i.e. acid and alkali gelatin but in taste and others chemical and physical properties there are no significant changes.

Type A: Produced by acid hydrolysis of bones, skins and connective tissues of pork. This type of gelatin exhibits an iso-electric point at pH 4.47 [16]

Type B: Produced by alkaline hydrolysis of bones, skins and tissues of animals. This type of gelatin exhibits an iso-electric point at pH 9.0[15]

3) Uses of gelatin:
- Edible Gelatin typically constitutes the shells of drugs and vitamins capsules to make easier to swallow.
- It is used in virtually all photographic films and photographic papers.
- It is also used as a carrier, coating or separating agent for other substance for example, it imparts a yellow color to any soft drinks containing β-carotene.

Fig.1. Typical effluent and solid waste generated from all tanning operation.

B. Gelatin
Gelatin is a product of animal origin derived from collagen by irreversible hydrolytic procedures. Collagen is a natural occurring proteins found in animals [8]. Collagen is not a uniform substance but rather a family of protein. In this study chemical structure of collagen and gelatin, the collagen-gelatin conversion, and the gelatin process will be discussed. Gelatin is a term used for a class of protein fraction that has no existence in nature. Gelatin is derived from collagen, which is a natural structural protein, predominantly found in the connective tissue of animals although also found in much other tissue [9]. Collagen is the ubiquitous of animal proteins. Gelatin is able to form a high viscosity solution in warm water, which set to gel on cooling. The chemical composition of gelatin is in many respects, similar to that of collagen. Gelatin gels generally have melting temperature 35°C that is below human body temperature, which makes gelatin unique in terms of its sensory aspects, especially flavor release which is particularly desired for some food applications [10]. Gelatin samples were prepared by thermal denaturation of the collagen fibrils at 70°C for 6-10 hours in water. Gelatin is a substance brittle (when dry) flavorless, food ingredient that is derived from collagen obtained from various animal body parts. Collagen is the source of protein from which gelatin is prepared. A gelatin is typically produced in a powdered or granulates form. Slightly yellow to light in color. It is rather tasteless and odorless substance. Gelatin is multifunctional ingredient used in foods, pharmaceuticals, cosmetics agent and film former.
Non-edible gelatin is used as binder in match heads and sandpaper.
Non-edible gelatin may serve as a binder and finish for drying. Then it is pressed into sheets Depending on its final application.

Fish skin gelatin may provide better alternatives for gelatin production. Bone broth is the original gelatin source. The hides and skins are soaked in vat lime or some other chemicals were used. List of chemicals are given below:

- Biocides, Surfactants, Lime, Sodium sulphide, Sodium hydroxulphide, Low sulphide unhairing agents, Caustic soda, soda ash, Ammonium sulphate, Ammonium chloride, Salt etc.

Quality of raw hides and skins determines the final characteristic of gelatin because poor grade or spoiled raw hides and skins do not have high gelling powder as compare to high grade raw hides or skins.

But 45% of world’s total gelatin production is obtained from pork skin followed by bovine hides with almost 30% and 23% of gelatin is obtained from bovine and porcine bones [18]. Other source includes chicken and fish but these account for only 1.5% of the world’s annual gelatin production. In Europe, pork skin is the most abundantly used raw materials for gelatin production accounting for 80% of the total followed by cattle skin with 15% of the total gelatin production [19]. Recent studies have shown that the fish skin especially might be an alternative source for gelatin production. Bone broth is the original gelatin source. Fish skin gelatin may provide better alternatives for some application because of their relatively lower gel strength and melting temperature compared to that if mammalian gelatin’s [20].

A. Production of non-edible gelatin from raw leather trimmings:
Total work is divided into three stages, those are
a) Pretreatment of hide trimmings.
b) Extraction of non-edible gelatin for four different periods at the same temperature.
c) Preparation of non-edible gelatin sheet.
Raw materials are mainly cow, goat, ship, calf, bovine raw salted trimmings, bone, eye pieces etc.

1) Washing
Wash very well to remove dirt, dung, dust, salts etc.
The hides and skins are passed under high pressure water sprays to wash away debris.

2) Soaking
They are then degreased by soaking them in hot water to reduce the fat content to about 2%. To remove full grease hides and skins are roasted for approximately 30 min at about 200°F. In soaking preservative is used to prevent fungous or bacteria attack.

- 400% H₂O at net weight
- 2.5% wetting agent
- 3% sodium carbonate
- 2.5% preservative
Left for over night
Next morning drained out and washed for 30 min.

3) Liming
The hides and skins are soaked in vat lime or some other type of lime or some type of acids for approximately five days. This process removes most of the minerals and bacteria and facilitates the release of collagen. The acid wash is typically a 4% HCl with a pH of less than 1.5. The wash is a potassium or sodium carbonate with a pH above neutral point i.e. 7.0.

- 400% H₂O
- 4% Sodium Sulphide(Na₂S) 60 min
- + 6% lime
- 0.5% liming axillary
After five days, it was washed very well with clean water.

4) Reliming (if necessary)
Generally reliming is not mandatory after liming but if collagen does not swell up properly then reliming can be done.

- 200% H₂O
- 5% lime
After 2 days, washed very well.

5) Deliming
The main aim of deliming is to remove lime residual which may create problem in the net operation by rating with other chemicals.

- 200% H₂O
- 2% Ammonium sulphate
- 1% Ammonium chloride.
Left overnight, next morning washed by clean water.

6) Melting:
Then the delimed trimmings are melted by heat into liquid. Melting is done in big boiler where delimed materials and other chemicals are allowed to react at 75-80°C. The pieces of hides, tissues and skin are loaded into large aluminum extractor and boiled in distilled water. A tube running from the extractor allows workers to draw off the liquid that now contains gelatin. The liquid is sterilized by flash heating it to about 375°F (140°C) for approximately four few minutes for high grade gelatin.

7) Drying:
From the extractor, the liquid is piped through filters to separate out bits of tissue or skin that are still attached. From the filter the liquid is piped into evaporators, machines that separate the liquid from the solid gelatin. The liquid is piped out and discarded. The gelatin is passed through machines that press it into sheets Depending on its final application. Then the gelatin sheets are passed through a grinder that reduces them to a fine powder if necessary

Drying is one of the vital parts in gelatin production. The liquid is kept into rectangular tray for drying. Then it is converting into hard board for further for drying. Depending of quality, it is kept dry for 7-12 days.

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8) Grinding:

Then the board is made to power form. This sheet form or grinding form material is called gelatin. That sheet form of gelatin in can be used as for dog feed.

Flow chart demonstrates the non-edible gelatin production from raw trimmings.

B. Chemistry of non-edible gelatin formation from collagen:

Gelatin is commonly regarded as a protein obtained from collagen present in the connective tissue, hides or skins and cartilage of animals and on hydrolysis of the collagen an impure gelatin is obtained [21]. Since collagen from any of animal usually found in admixture with other proteins and inorganic salts, some of those impurities are transferred to the gelatin. Hydrogen bonds certainly play an important role in gelation. Gelation can be considered as gelatin regaining its collagen structure but this would not be exactly correct because the conversion of collagen into gelatin is an irreversible process although gelatin can partially regain [22] some cross-linkages. The greater the amount of cross linkages recovered, the higher the gel strength and viscosity along with the melting and gelling temperatures. Traces of phosphors and sulphur also are often present in collag en. Collagen is gradually hydrolyzed by heating the collagen with water at a temperature of about 90°C [23]. The process of hydrolysis can however be appreciably accelerated by carrying out the Procedure under pressure at a higher temperature. Alternatively, the use of small proportions of other agents in the water serves to speed up the hydrolytic action because the chemical composition of collagen itself is not constant but varies with the source of the collagen; the final product gelatin will also vary slightly in its chemical composition [24].
As it is well known that, the gelatin is entirely depends on factors like gelation concentration, pH.

![Fig. 9. Hydrolysis of collagen in acidic/alkali medium](image)

Reaction involved in gelatin production is not a very complex rather simple hydrolysis reaction at elevated temperature

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\begin{align*}
C_{102}H_{149}N_{31}O_{38} + H_2O & = C_{1102}H_{151}N_{31}O_{39} \\
\text{Collagen} & \text{gelatin} \\
C_{102}H_{151}N_{31}O_{39} + 2H_2O & = C_{55}H_{85}N_{17}O_{22} + C_{9}H_{70}N_{14}O_{19} \\
\text{Gelatin} & \text{Semiglutin} \\
& \text{Hemikline}
\end{align*}
\]

### III. RESULT

A systematic study was undertaken to produce non-edible gelatin from leather trimmings. Study on non-edible gelatin has shown that there are clear connections and extraction conditions while higher extraction temperature and durations result in higher yield, the gelation process occurred due to damage to the collagen fractions. Similarly, higher acid or alkali concentration result in higher yield along with purer material but the non-edible gelatin obtained lacks necessary functional properties. Therefore, an optimization of manufacturing process of gelatin is needed to get a final product with desired properties.

#### A. Effect of temperature on gelation formation.

Trimmings were extracted by boiling with water (float ratio 1:1) at temperature of 75-85°C for fixed periods of time. The extract was collected from each batch and its variation with temperature, float ratio, effect of Na₂S on clarity determined.

![Fig. 10. Effect of temperature](image)

As the temperature increases percentage of gelatin yield also increases but temperature above 90°C denaturation of collagen occurs thus yield percentage declined. It is found that optimum temperature for gelation formation was 80-85°C.

#### B. Effect of float ratio on degradation of collagen structure:

The specific interaction between water and collagen at different levels of float ratio will induce characteristic structural changes at each level float; however, in gelatin, the lack of conformational specificity means that changes in water content can be described by the relative level in the proximity and entanglement of the collagen polypeptide chains.

At high volume of float ratio i.e. (raw trimmings: water) 1:4, 1:5, 1:6, there was a negative correlation between the degree of collagen degradation and float ratio. The reduction of bond disintegrate was observed at high float ratio. Maximum degradation of collagen happens at float ratio of 1:1.

![Fig. 11. Effect of float ratio](image)

#### C. Effect of heating time on gelatin solution:

When the collagen is heated for prolong period of time its structure becomes weaken and started to dissolve rapidly. It is observed that heating up to 72 hours can also dissolve collagen but actual dissolution happens within 12 hours but heating after 12 hours do not yield as much as gelatin solution as 12 hours do. Heating for long period time can reduce quality of gelatin solution because it completely destroys gelling power of solution by diminishing its viscosity.

Viscosity is the second most important physical parameter. It is determined by measuring the time of flow of 100ml of 6.67% gelatin solution at 60°C from a special pipet. Viscosity is the main identification marks of gelatin but they do not adequately characterize the materials for particular applications [25]. Attention has been directed to the fact that gelatin solutions increase in viscosity for a period of time, reach a maximum and then diminish in viscosity. It has been found that the maximum viscosity is attained in about 12 hours after extraction.

![Fig. 12. Effect of time on gelatin solution](image)
IV. CONCLUSION

The paper has summarized the tannery solid waste could be managed via non-edible gelatin production and various processing parameters to extract non-edible gelatin from raw trimmings that can tackle solid waste pollution problems. It can be concluded that it is possible to produce non-gelatin by boiling leather trimmings with water at temperature range 75-85°C for any length of time, the optimum time being 12 hours and the maximum yield being approximately 46%. The non-edible gelatin obtained by hydrolysis with water is not high molecular weight as indicated by the comparatively low values of intrinsic viscosity. However, it is interesting facts that intrinsic viscosity of the observed gelatin is quite small compared to that of many edible-gelatin. Hence raw trimmings can be utilized for the production of non-edible gelatin which will surly reduce solid waste load on environment. It is expected that effective use of raw trimmings into useful products will facilitate solid waste management and will meet the ever growing demand of non-edible gelatin and contribute towards economy by creating employment opportunities. For production of edible gelatin from raw trimmings it is necessary to update facilitates like extraction bath, filtration, dust free dying etc.

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