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LEATHER PROCESSING, ITS EFFECTS ON ENVIRONMENT AND ALTERNATIVES OF CHROME TANNING

Karanam Sai Bhavya, Raji P, Jenifer Selvarani A
Department of Biotechnology, School of Bio and Chemical Engineering,
Sathyabama Institute of Science and Technology, Jeppiaar Nagar, Chennai, Tamil Nadu, India

Antony V Samrot*, Pazhayakath Thevarkattil Mohamed Javad
Department of Biomedical Sciences, Faculty of Medicine and Biomedical Sciences, MAHSA University, Jenjarom, Selangor 42610, Malaysia

Appalaraju, V.V.S.S
Department of Medicinal Chemistry, Faculty of Pharmacy, MAHSA University,
Jalan SP2, Bandar Saujana Putra, 42610 Jenjarom, Selangor, Malaysia.
*Corresponding Author Email id: antonysamrot@gmail.com

ABSTRACT

There are several processes involved in leather making, one of the process is tanning. In tanning process, higher concentration of chromium is commonly used. Whereas chromium is regarded as one of the toxic heavy metal. The disposal of these chromium effluent into water bodies is known to cause various ill effects. To replace that, vegetable tanning can be practiced, where the method is easy as well as ecofriendly. In this review, we have dealt about various procedures in leather processing especially chrome tanning and health hazards caused by chromium. Also added a note on vegetable tanning using tannins to replace the chrome tanning for making better environment.

Keywords: Tanning; chromium; tannins.

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1. INTRODUCTION

Processing of skin or hides into stable material – leather is known as tanning. Leather, the primary product from the tanning industry, where the product has got its applications in making footwear, furniture, bags, etc., [1,2]. The global leather industry generated about 18

billion square feet leather in 2003 with an estimated price of US$40 billion (World Leather Magazine). Most developing countries including India is producing 60 % of world's leather needs. For making the leather, Tanning is considered as a major process which involves more chemical reactions as well as mechanical operations. During the process more chemicals including chromium, acid solvents, etc are involved, these processes release effluent of 30L/kg of processed skin [3], where tanneries of India are releasing effluent more than 50,000 mg/day with huge quantity of organic pollutants [4]. 70% of chrome (III) is usually discharged (IULTCS, 2008) and leads to heavy metal contamination in water [5,6]. Release of chromium by tanneries are higher now than mentioned parameters.

Chromium, a major heavy metal exploited in leather industry. In India, it was found to release 30 billion of waste water with 3000-5000mg/L of total solids and chromium in between 100-200mg/L on processing 700,000 tons of skins in about 3000 tanneries [7]. More than 170,000 tons of with 0.04Mt Cr (III) wastes per year are released into environment worldwide [3, 6]. With the enhancement of environment realization and change in manufacture patterns, the world industry is desirous to take cleaner and greener approaches for leather processing [8].

The global leather have been in existence during which technologists were concerned to inflict stability to raw skins and hides [9]. Until the approach of chrome tanning, there were very few options available for tanners such as aluminium tawing, smoke tanning, oil tanning and vegetable tanning. The term tannin was firstly used in 1796 by Seguin in order to specify the specific components of vegetable extracts having a potential to bind with collagen making insoluble complexes by blocking the action of other proteolytic enzymes which effect the physical condition of the skin [10]. The process of this extraction may include non-tannins and other materials which have no tanning strength which contributes in determining the functional properties of the leather. Oils of animals Leather are also smoke tanning where the oil in animal's brain used as tanning agent which gives highly durable leather [11]. Today chrome tanning is the most commonly used method which accounts for world's leather producton [12]. Although chrome tanning has many advantages like high speed, low cost, good hide storage, etc 40% of the chromium remains in the effluent which end up in sludge [13]. One of the major problem of leather industry is chromium disposal where the treatment results in chromium contaminated sludge [14]. Due to these disadvantages of chrome tanning tanners are encouraged to use the ecofriendly process of tanning like vegetable tanning.

2. HISTORY OF TANNING

Tanning is one of the ancient trades of humanity in reference to use of leathers in archeological sites and cave paintings. Tanning had a random nature which has evolved slowly into craft in the middle age. The scientific studies on tanning started in nineteenth century and derived into present day leather technology with the development of machinery and industrial revolution. The Egyptians made long-lasting leather which is 3000 years old specimen but still in good condition which made the evidence for oil tanning [10]. The Rudimental processing of leather is mentioned in Assyrian texts and in Homer's Iliad [15]. At first the skins obtained from hunting and livestock breeding were used for clothing and tents but they became stiff at low temperatures and rotted with heat which was overcome after many attempts by a process called smoking where the animal fats were rubbed for getting more render and flexible and this process became an origin for leather processing by accident [16]. From middle ages till 17th century there was no change in skin processing. At the end of 18th century with the development of industrialisation created a demand for different types of leathers for belting in machines, leathers for textiles, footwear, fabrics, etc. Similarly, at the end of 19th century the tanning industry was developed with the discovery of various

chemicals as tanning agents and finally with the discovery of major tanning agents like chromium and alum pointed the beginning of industrial scale tanning. According to references, it is Neolithic period where man started using plant materials such as bark, pods, leaves to prevent skins from putrefaction forming the most stable and durable material [17-20]. The term skin is the one used to determine the outer part of mature animals of smaller type such as Pigs, goats, reptiles, fish, etc whereas the term hide is referred as the outer part of large animals such as buffalo and cattle [21].

3. STEPS INVOLVED IN LEATHER PROCESSING

3.1. Soaking

Soaking is the first step involved in tanning where the preserved raw skins or salted skins are treated with water to make the skin dirt free and soft [22]. The main purpose of soaking is to remove salt, rehydrate the dry skin and also to remove unwanted materials like blood, soil, dung, etc. The soaking time depends on condition of skins or hides [23].

3.2. Liming

The second operation is liming which involves the removal of hair and unwanted materials which are not transferred to leather. It also loosens the epidermis and also remove soluble skin proteins. It uses lime and sodium sulphide as liquor [24]. The hair is loosened due to increase in high pH. The higher pH also cause splitting and swelling of fibre bundles [25]. Dehairing and fleshing is also done in order to remove extra flesh and allow tannins to penetrate easily.

3.3. Deliming

Deliming is the process of adjusting pH between 8-9 which enhances the enzyme activity and converts proteins into soluble forms. It uses ammonium sulphate and results in de-swelling of pelts [26]. Deliming decreases the plumping of skin or hide.

3.4. Bating

Bating makes the grain surface soft and flexible. It prepares skin for tanning. It is an enzymatic operation which removes unwanted proteins and increases the degree of stretch [27]. It imparts flexibility and softness towards the leather.

3.5. Degreasing

Degreasing is a process used to remove extra fat and oils which allows the tannin to penetrate easily through the skin. This step can be carried out by emulsion of fats using detergents or surfactants

3.6. Tanning

Tanning is the main operation which converts skin or hide to stable material called leather. In this step tannins are allowed to interact with the prepared skin which act on collagen and make it stable.

3.7. Fixing

Formic acid is mostly used in this process which ensures homogenous tanning of hides in leather processing [28].

4. TYPES OF TANNING

4.1. Mineral Tanning

Mineral tanning is a process which uses basic chromium sulphate as tanning agent after the process of pickling. Once the desired level of penetration the pH is again increased to facilitate the process which is termed as basification and the obtained product is called as wet blue [28].

4.2. Tawing

Tawing is another practice which uses aluminum salts and alum along with other materials such as flour, egg yolk and other salts. It is an age old traditional process which gives a wet white product. In this method the skin is tawed in alum and salt solution which increases flexibility, stretchability, etc whereas egg yolk and flour enhances the handling properties [20]. Tawing was conventionally used on goatskins and pigskins [28].

4.3. Chrome Tanning

Chrome tanning is the most commonly used tanning process. It uses Chromium (III) sulfate which has been considered as the most effective and efficient tanning agent [29, 30]. It forms poly chromium compounds by a process called olation which acts as active compounds in tanning that crosslinks the collagen subunits [31]. The leather obtained by chromium contain 4-5 % of chromium [32] and its efficiency is determined by enhanced hydrothermal stability and resistance to shrinkage at high temperature. Although chrome is an effective tanning agent it is having some hazards towards human.

5. EFFECTS OF CHROME TANNING TOWARDS HUMAN

Chromium in its +6 oxidation state is referred to as Hexavalent chromium. It is mainly used for coatings, wood preservation, dyeing, etc [28]. The chromate mimics the sulphate in its structure and surface charge which can enter the cell and cause cancer, eye irritation and skin allergies. There is a high risk of getting cancers to the workers exposed to hexavalent chromium for a prolonged time. It has been reported lung cancer among workers in chromium chemical production [33]. Repeated exposure to hexavalent can also damage the respiratory tract and may also cause nasal cancer [34]. Direct eye contact of chromate cause permanent eye damage and eye irritation [35]. Prolonged exposure to skin cause skin allergies, dryness, fissured skin, skin ulcers and swelling [36]. In other way some workers may develop allergic sensitization where exposure to small amount cause serious skin rash. Other effects of chromium include dizziness, growth problems, reproductive disorders, discoloration and erosion of teeth [34, 35].

6. VEGETABLE TANNING

Vegetable tanning is the most suitable ecofriendly process which results in release of less pollutants to the environment [37]. Vegetable tanning involves usage of tannins extracted from various parts of a plant. It mainly depends on amount of tannins in the extract which can be determined by various methods such as Folins Denis method, Mass spectrophotometer, UV detection, Reverse-phase High pressure liquid chromatography (HPLC), Mass spectrophotometer, nuclear magnetic resonance and Circular dichroism [38,39]. Vegetable tanning is a two stage tanning which includes fixing and penetration. Penetration involves diffusion of tannins into the skin whereas fixing makes the penetrated tannins bind with collagen forming stable material. It is mainly affected by several factors such as temperature, pH, mechanical actions and particle size [40, 41]. The pH is the most important factor that

affects the penetration and fixing of tannins. The reduction of pH in tanning liquor increases the potential of collagen fibres to swell and increasing the tendency of tannins to bind with collagen [42]. Temperature is another most important parameter which affects the vegetable tanning. Increase in temperature results in high diffusion of tannins and gives high degree of tannage [43]. Acid and salt content in tannin liquor greatly influences the physical condition of leather [42]. Control of these parameters results in production of most stable and flexible leather which results in release of less contaminants and thereby protecting the environment. Hence the current study is an eco-friendly approach which reduces the toxic waste generation when compared to chrome tanning process and thereby reducing environmental impacts by contributing towards greener or cleaner development of leather processing

6.1. Types of Tannins

Tannins are water soluble phenolic compounds that are capable of animal skins or hides to leather [44]. They are mainly grouped into two types, condensable and hydrolysable tannins based on their structural properties.

6.1.1. Hydrolysable Tannins

Hydrolyzable tannins have a molecular weight of 500-3000Da and it has a gallic acid esterified with glucose [45]. These tannins are found only in dicotyledonous plants. They are subgrouped in to gallotannins and ellagitannins [46]. These tannins have D-Glucose at the centre where hydroxyl groups of carbohydrates are partially or completely esterified with phenolic group's i.e ellagic acid in case of ellagitannins and gallic acid in case of gallotannins [47].

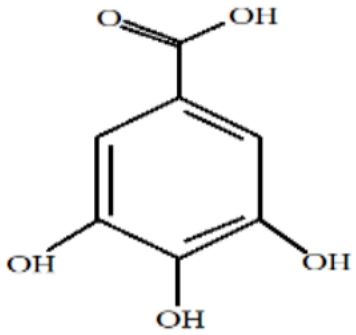

Figure 1 Structure of hydrolysable tannins

Gallotannins are the polymers of galloyl units that are bound to many polyol units which are derived from D-Glucose where the hydroxyl functions of polyol may be substituted by galloyl units [44]. Ellagitannins contains galloyl units along with hexahydroxydiphenol units (HHDP) which is formed by oxidation of galloyl groups [48, 44].

6.1.2. Condensed Tannins

Condensed tannins are non-branched polymer of flavanoids having a high molecular weight of 1000-20,000 Da [49]. The monomers of condensable tannins include catechin and epicatechin [45]. Condensable tannins are the most common tannin found in almost all families of plants [45].

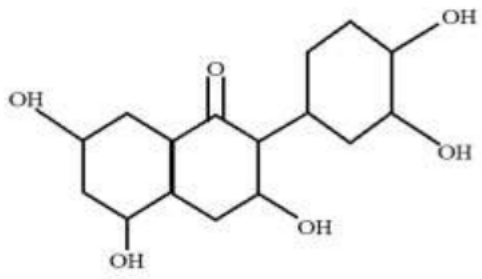

Figure 2 Structure of condensed tannins

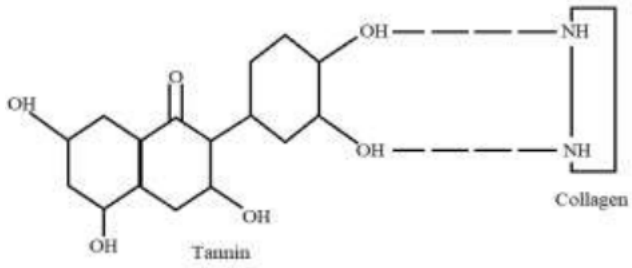

Figure 3 Mechanism of tanning

6.2. Vegetable Tanning and the Mechanism of Tanning

Vegetable tanning refers to tanning of skins or hides using the tannins obtained from barks and leaves [50]. Tannins are astringent, water soluble polyphenolic compounds with a molecular weight of 500-20,000and have an ability to precipitate proteins [49]. Tannins can be found in different parts of plant like fruit, seed, pod, stem, leaves, tuber, etc [50]. There are mainly two types of tannins based on their properties and structure. Both hydrolysable and condensed tannins are used in tanning process. The quality of leather differs based on the source of tanning materials. The tanning materials also affects the physical characteristics of leather which are taken from same origin [51]. Vegetable tanned leathers were found to have high wear resistance, molding properties, solidness and flexible endurance [52, 53]. Vegetable tanned leather is highly used in making shoe upper leather, furniture leather and garment leather.

The mechanism of vegetable tanning involves interaction of basic group's collagen protein with the acidic group of tannins by polyfunctional cross-linking [54]. The interaction between protein and tannin is mainly hydrophobic and hydrogen bonding as shown in Fig. 2.3. They form hydrogen bonding between peptide oxygen of collagen and polyphenolic -OH groups or between oxygen atoms of phenolic -OH groups and protonated amino groups [55, 56, 32]. The factors that are mainly responsible for tanning mechanism are pH, temperature, tannin concentration, salt content and condition of hide [54].

6.3. Commonly Used Vegetable Tannins

Various vegetable tanning materials are used in leather processing all over the world based on tannin concentration and also their availability in plants. Some of the plants used for tanning are quebracho (20 %), chest nut (10.7 %), behra nuts, etc [57]. Most of the acacia species are used for tanning due to the presence of high tannin concentration [57, 58].

7. NANOTECHNOLOGY IN LEATHER PROCESSING

Nanoparticles,because of their small size and their ability to combine with polymers shows its potential for the application in tanning [59]. Introduction of nanoparticles into tanning agents enhances the physical and mechanical properties of leather [60]. In order to this, silver nanoparticles due to its properties against bio-activities they can even impart some functional properties such as anti-microbial, UV-resistance and fungal resistance of leather [60-63]. Raji et al (2019) used various tannins mediated silver nanoparticles for tanning process and able to produce a stable leather [64].

8. LEATHER AND ENVIRONMENT

Global environment is continuously deteriorating due to many socio-economic activities of human [65]. Processing industries are causing much damage to the environment. Leather processing is one such industry which takes skins from meat industry and processed to produce leather through tanning process [66]. It gained negative impact in society because of its pollution. Leather processing involves various operations which include many chemicals that are expelled out in processing [67]. 40 litres of water is required for processing 1kg of skin which results in generation of large amount of effluent leading to increase in Biological oxygen demand, Chemical oxygen demand, Dissolved oxygen, etc [5,68,69]. It also results in emission of chromium and sulfate ions [70]. Leather industry also emits obnoxious smell due to protein degradation of the skin and results in generation of toxic gases such as ammonia, H_2S,etc [71]. According to the research data only 20% of the raw hide is used for production of leather where the remaining is generated as waste [72]. Hence leather industry is considered as one of the major polluting industries which generates huge amount of solid and liquid wastes. The most important approach for prevention of environmental pollution is getting an idea prevention is better than reuse which is better than disposal of wastes [72]. There are various recycling methods to make generated leather wastes into eco-friendly useful bi-products such as production of fatliquoring oils and bio-diesel from pre-fleshing wastes [27,73], production of activated carbon [74,75], gelatin, retanning agents [76,77] etc., from shavings and trimmings, production of grease, methane gas, fertilizers, etc., [78,79] from fleshing waste. Hence cleaner production and recycling are the best options in order to control environmental pollution.

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