Chapter 6

Bioremediation for Tanning Industry: A Future Perspective for Zero Emission

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Abstract

Bioremediation is one of the recent technological advancements for treating heavy metals containing industrial wastes. Leather industry utilizes almost 90% of chromium-based tanning agent for converting raw skins/hides into leather. Apart from chromium, metals such as aluminum, titanium, iron, and zirconium are widely used for various end applications. Hence, effluent after tanning processes contains higher concentration of heavy metals. Though Cr(III) is less toxic than Cr(VI), there is higher possibility of oxidation during subsequent treatment processes. Therefore, several methodologies have been developed to remove the heavy metals from the effluent before processing it for common effluent treatment. Phytoremediation is one of the eco-friendly techniques to remove the heavy metals from soil and wastewater. It is commonly used to remediate the unfertilized lands to fertile lands for agriculture. Moreover, metal absorbed plants are used for various applications such as tanning and preservative agent in the leather industry. Hence, metal absorbed plants are not dumped as solid waste. Similarly, algae and fungi are used to remove the heavy metals from the tannery waste and can be as metal-polysaccharide auxiliary chemicals during post-tanning processes. Utilization of nonpathogenic bacteria is also used for the absorption of heavy metals. In this case, the handling of biomass is easier compared to other methodologies owing to less time duration and labor friendly, whereas, in the case of phytoremediation, absorption rate directly depends on the growth duration. In the present chapter, detailed case study is carried out to compare the advantages and disadvantages of various bioremediation technologies employed for treating leather wastewater.

Keywords: bioremediation, bacteria, tannery wastewater, chromium, phytoremediation

1. An overview of tanning

Leather industry is one of the fast-growing traditional sectors with high environmental challenges. Leather manufacture deals with the conversion of putrescible material such as skin/hide to non-putrescible material. During the conversion, series of chemical processes and physical operations are carried out to attain the final desired properties of leathers. Pre-tanning, tanning, and post-tanning are the major steps involved in the leather processing. One of the major challenges of leather processing is generation of high solid and liquid wastes that makes it more an environmental concern [1].

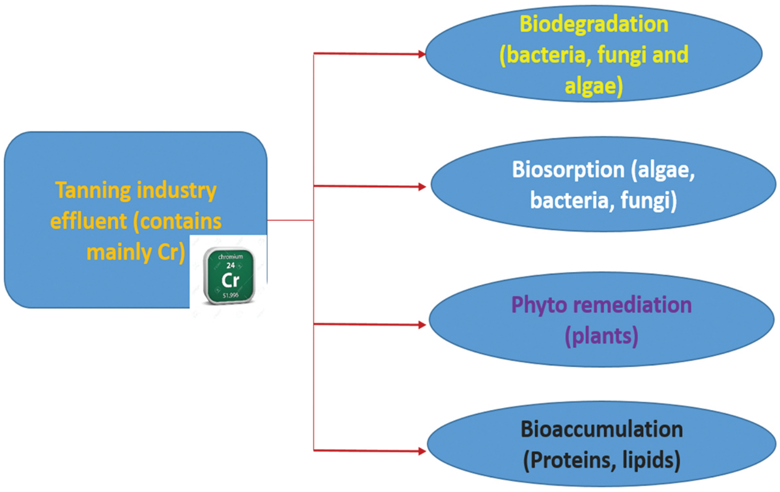

Figure 1. Scheme of bioremediation employed for the removal of heavy metals.

Pre-tanning involves the preparation of skin material tanning; hence raw material undergoes extensive cleaning and removal of unwanted material from the matrix. Soaking, liming, unhairing, reliming, fleshing, deliming, bating, and pickling are various steps involved in pre-tanning. Solid wastes such as hair, lime sludge, interfibrillary materials, and adipose tissues are the major components during this step. Liberation of toxic gases such as hydrogen sulfide and ammonia is also noted. Liquid wastes are generated in all unit processes contributing to the chemicals used in the respective steps. To combat the heavy pollution load, leather researchers have developed several cleaner/greener leather processes to counteract conventional leather process. Enzymatic unhairing and fiber opening, CO_2 deliming, and pickle-less tanning are major alternate processes to reduce the pollution loads. Chrome tanning is widely practiced globally due to its unique leather properties. However, generation of Cr(VI) in the waste stream causes a serious alarm to the environmental engineers due to its high cancer-causing nature (carcinogenic). Next to chrome, vegetable tanning is practiced owing to its nontoxic nature; it is considered as an alternate to chrome tanning. However, the vegetable tanned leathers are unable to match the propertied chrome tanned leathers. Several other tanning agents such as phosphonium, oxazolidine, and silica-based tannings are carried out with their merits and demerits. Bioremediation possibilities and the scheme of tanning process are given in **Figures 1** and **2**.

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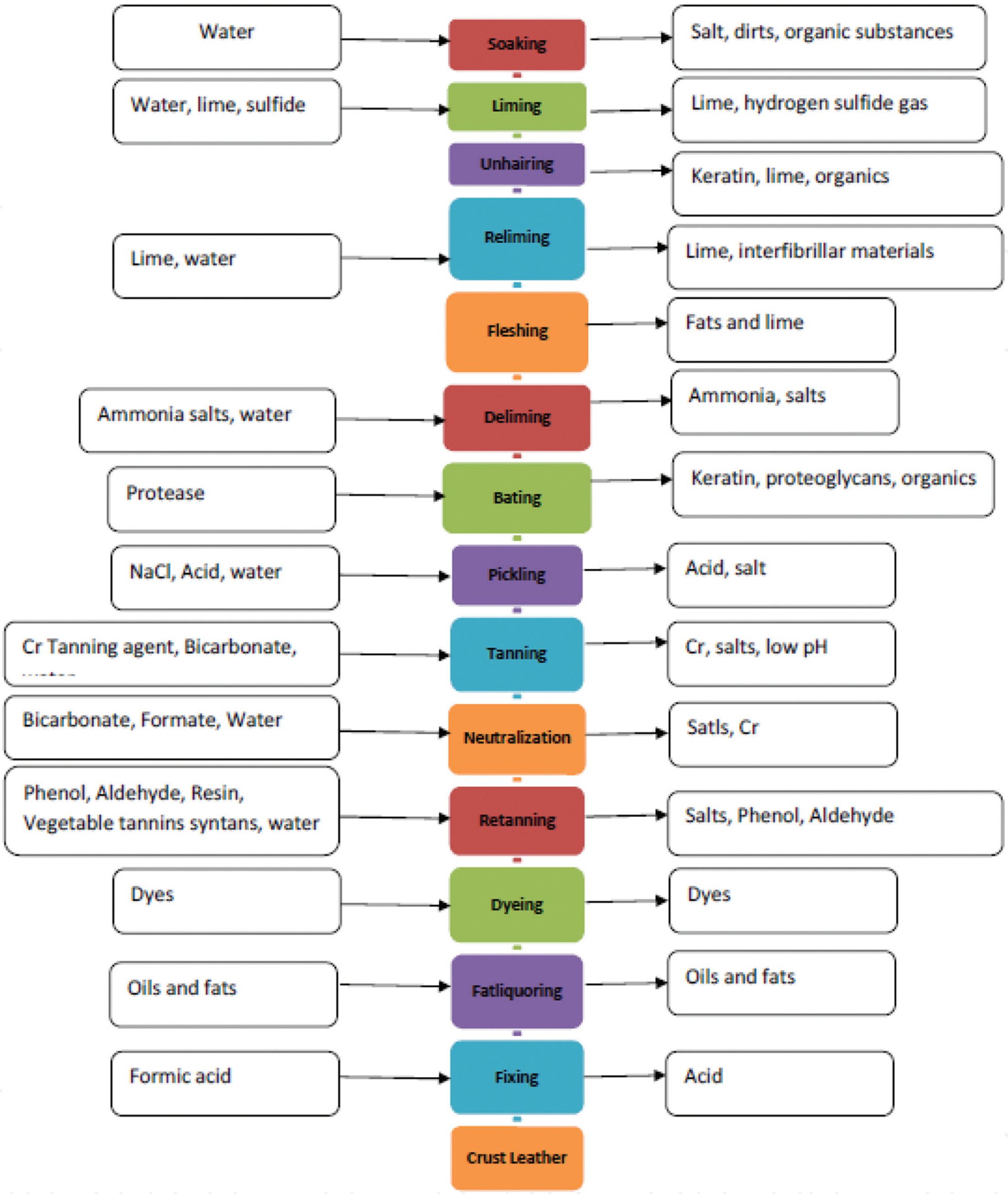

Figure 2. Schematic representation of leather unit processes.

Researchers also work to develop natural-derived materials from plants and microorganisms for tanning such as dialdehyde starch, dialdehyde cellulose, dialdehyde alginic acid, dialdehyde pectin, and scleraldehyde from fungal species (*Schizophyllum commune*). Post-tanning comprises retaining, dyeing, and fat liquoring to impart special properties to leathers as a functional requirement. The waste stream is composed of mixed wastes that make it more difficult during wastewater treatment. The composition of tannery wastewater is provided in **Table 1**.

Pollutants	Values
pH	6.9
BOD_5	50 mg/mL
COD	250 mg/mL
Total suspended solids	50 mg/mL
Sulfide	1.0 mg/mL
Chromium(VI)	0.1 mg/mL
Total chromium	0.5 mg/mL
Chloride	1000 mg/mL
Sulfate	300 mg/mL
Ammonia	10 mg/mL
Oil and grease	10 mg/mL
Total nitrogen	10 mg/mL
Total phosphorous	2 mg/mL
Phenols	0.5 mg/mL
Total coliform bacteria	400 MPN/100 mL
Temperature increase	<3°C

Table 1. Effluent levels for tanning and leather finishing (ref. environmental health and safety guidelines, tanning and leather finishing).

Solvent-based post-tanning is carried out to reduce the pollution and maximize the chemicals exhaustion. Though several alternate cleaner leather processes exist, no holistic approach has been made till date. Furthermore, conventional leather processing methods have found an impeccable place among the tanners due to its unmatching physical and chemical properties to the leathers. Therefore, it would be highly appreciable if wastewater treatment becomes a relevant measure to combat the pollution load. Primary, secondary, and tertiary treatments are practiced to treat the wastes. Biological treatment methods are the fast-growing technology due to their eco-friendly and recycle method. In this chapter, a brief discussion about the various biological systems used in leather wastewater (otherwise known as tannery effluents) treatment is discussed.

2. Application of microorganisms in tannery wastewater treatment

The role of microorganisms is gaining importance in different applications due to their versatile abilities. Availability of single cell microorganism is largely found in the ecology system. These organisms are mainly found in the soil systems, water, and intestinal tract of living system. Microorganisms are classified based on the sources of energy and carbon. The major classifications are autotrophs and heterotrophs. Autotrophs are further classified into photoautotrophic and chemoautotrophic based on energy source as light and inorganic oxidation-reduction reaction, respectively. Heterotrophs are further classified into chemoheterotrophic and photoheterotrophic based on their energy source, organic oxidation-reduction reaction, and light, respectively. Researchers have focused to understand the importance and necessities of utilization of microorganisms of human well-being in the different technology fields. One of the unique aspects of their living organisms is their size, regular supplements of nutrition, water, and optimum physiological condition to grow and multiply the cells. During secondary treatment of leather wastes, microorganisms commonly used result in the generation of biomass sludge (see **Figure 3**).

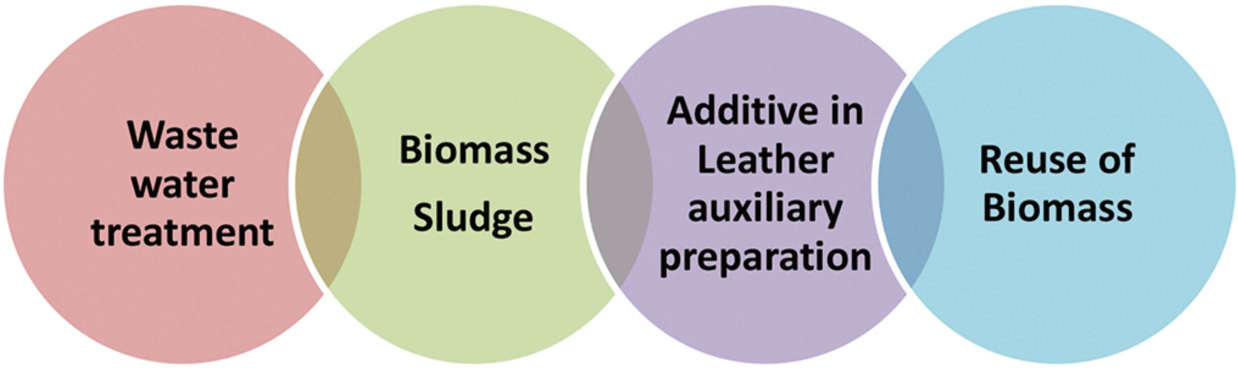

Figure 3. Schematic representation of role of microorganisms in leather wastewater treatment.

2.1. Bacteria

Microbial technology finds an immense application in technological industry owing to its size and handling conditions. Bacteria are single microorganisms and are in small size with different shapes. A list of bacteria involved in the remediation process is given in **Table 2**. Growth of the bacteria requires nutritional supplements like any other living organisms. *Pseudomonas* sp., *Bacillus* sp., and *Lactobacillus* sp. are commonly used bacterial strains. Nutritional requirements are obtained by decomposing organic material and aids in multiplying the cell. Hence, bacteria are efficiently used for decaying organic wastes present in the leather waste stream. Leather wastes during pre-tanning processes are chiefly made up of organic constituents such as collagen, elastin, reticulin, other proteoglycans, keratins, and other nutritional supplements. Aerobic and anaerobic systems are practiced in treating wastewater in the secondary treatment plant. Hydrogen sulfide gas release contributes to gas pollution during liming process. Chemolithotrophic bacteria are used to absorb the toxic gas. After primary treatment of wastewater, i.e., removal of floating materials and particles which can be filtered through screens is sent through biological treatment.

During this process, bacterial cells are purged to undergo biological oxidation. Bacteria tend to degrade the organic component in the waste stream and are used as nutritional supplement. This respiration process utilizes oxygen and exits the carbon dioxide. After the process the wastewater treatment plant will end up with a large amount of activated sludge (bacterial cell mass). Very often the activated sludge is condensed and treated in large-scale anaerobic digesters designed for further treatment via anaerobic bacteria. However, there should be very careful steps taken toward the disposal of bacterial sludge. Since, it is mainly composed of proteins and carbohydrates which were used as a raw material for preparing leather chemicals. Protein fillers and protein synthetic tanning agents are possible areas to venture for the recycling bacterial sludge.

Bacteria	Process	References
Bacillus subtilis	Biosorption of Cr	[2]
Arthrobacter sp.	Ultrafiltration/microfiltration Lead	[3]
Bacillus sp.	Livestock	[4]
Rhodococcus sp.	Heavy metal absorption	[5]
Escherichia coli	Removal of chlorophenol	[3]

Table 2. List of bacteria used in tannery wastewater treatment.

Mechanism: Biosorption is a process that utilizes the microbial biomass to accumulate the chromium metals. This is based on the process of adsorption. It is based on the nonspecific binding of chromium through addition of polysaccharides. Though, microbial process involves both enzymatic and nonenzymatic mode for the accumulation of microorganisms. During biosorption of chromium, the metal interacts with polysaccharides through nonenzymatic mode. This process is mainly dependent on the physical parameters such as pH and ionic strength. Charge of the polysaccharides is a critical factor that aids in the sorption of metal ions.

2.2. Algae

Algae are significant organisms for biological purification of wastewater because they can be able to accumulate plant nutrients, heavy metals, pesticides, and organic and inorganic toxic substances. **Table 3** lists out the algae species involved in the treatment process. The application of algae in biological wastewater treatment has gained a lot of importance in the recent years. Construction and energy costs are highly lower and the land requirement is not up to that of facultative pond in constructed wet lands. Algae are commonly used to absorb sectional waste from the composite waste liquors. They are chiefly used for the absorption of heavy metals due to their high tolerance and absorption. Moreover, the large surface area/volume ratio makes it as one of the important biological materials for wastewater treatment.

Mechanism: Algae are composed of polysaccharides that make convenient for the absorption of heavy metals. Their high tolerance to heavy metals and growth behavior of autotrophs and heterotrophs make them one of the best choices. Biosorption of chromium, cadmium, and copper ions by other blue green algae *Spirullina* sp. and *Chlorella* sp. is known well. Application

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of algae in absorption of chromium leads to the generation of sectional solid waste. It would be mere conversion of liquid into solid waste; hence, further intensive research needs to be carried out in order to effectively and efficiently reuse the solid waste. Since, solid waste is composed of carbohydrates and metals; it can be used as a raw material for preparing chrome-based retaining agents. It can be further investigated as one of the chemical components during post-tanning processes with chemical modifications.

Algae	Process	References
Phormidium bohneri	Removal of nitrogen and phosphorus	[6]
Spirulina (*Arthrospira*)	Removal of nitrogen and phosphorus	[7]
Spirogyra condensate	Biosorption of chromium	[8]
Scenedesmus sp.	Bioflocculation	[9]
Chlorella vulgaris	Immobilized to remove nutrients (P and N)	[10]

Table 3. List of algae used in tannery wastewater treatment.

2.3. Fungi

Fungi are multicellular organisms unlike bacteria which are unicellular organisms and are abundantly present in wastewater stream. *Aspergillus*, *Penicillium*, *Fusarium*, and other types of fungi are reported to be found in the sectional waste stream. These fungi are found to be effectively used in the removal of nutrient source from the wastewater. It is also reported that certain fungi also have the ability to break down organic matter present in the waste. Critical role of Fungi in the tannery waste water, treatment at very high acidic pH. Though acid-resistance bacteria exist, there is still a challenge for the bacterial treatment at low pH. Hence, fungi can be used in the acidic medium to break down the organic constituents. Moreover, fungi have the ability to trap and absorb the material through their hyphae and aid in the metabolism. Enzymes are also secreted by some fungi that help in the biodegradation of organic compounds present in the waste. Apart from the species mentioned above, many other fungi could degrade the tannery effluent waste; however, their pathogenicity is a big question while it comes to the matter of large-scale applications.

3. Application of plants in bioremediation

3.1. Phytoremediation

Phytoremediation is a branch of bioremediation that deals with the utilization of plants for the wastewater treatment. Halophytes and aquatic plants are more commonly used for the tannery waste treatment. Many researchers have focused on developing phytoremediation technologies for treating the tannery effluent contaminated land sites into reusable lands. The major selections of plants are based on the availability and growth surrounding the tannery plants.

This is based on the hypothesis that plants are resistant to the environmental parameters and resistant to the pollutants discharged from the tanning industry.

Cristina et al., a research group, have investigated four different plants *Canna indica*, *Typha latifolia*, *Phragmites australis*, *Stenotaphrum secundatum*, and *Iris pseudacorus*. These plants are vegetated in wetlands for the treatment of tannery wastewater [11]. The plants are chosen based on the growth and availability surrounding the tannery effluent contaminated lands. Among the chosen five plants *P. australis* and *T. latifolia* are effectively involved in the waste treatment. It might be understood that there would be growth of plants surrounding tannery effluent–contaminated plants. However, it is not mandate that all plants have the ability to effectively participate for the effluent treatment.

Daniel et al. have carried out on water hyacinth (*Eichhornia crassipes*) for the removal of chromium from tannery effluent in constructed pond system. Water hyacinth is free-floating aquatic plants that originated from Amazon, South America. The samplings are collected in the Awash River, Ethiopia, for the treatment [12]. Many other plant species are also involved in the phytoremediation; however, the removal of heavy metals and nutrients should be considered for further applications.

3.2. Constructed wetland

A constructed wetland is an artificial wetland widely used for treatment of municipal and industrial wastewater. Constructed wetland system is a hybrid technology including phytoremediation, soil filtration, and microbial processes and has been reported to enhance overall biological performance by complex interactions inside the ecosystem [11]. In the past decade, researchers have attempted to study the potential of constructed wetland for the treatment of tannery effluent. Cristina et al. conducted the treatment of raw tannery wastewater by horizontal subsurface flow constructed wetlands (HSSFCW) with five different kinds of vegetation (mentioned in Section 3.1). During the one-year experiment, wastewater contained on average 2250 mg/L Chemical Oxygen Demand, 92 mg/L Total Suspended Solids, 188 mg/L Total Nitrogen, 1 mg/L Total Phosphorus, and 0.027 mg/L T-Cr, respectively [11]. All the six HSSFCW systems including control without plant showed significant removal of Chemical Oxygen Demand (833–913 mg/L in effluent), TSS (18–21 mg/L), and Cr (<0.001–0.012 mg/L) under a hydraulic loadings rates (HLR) of 6 cm/d. The *C. indica*-planted Constructed Wetlands showed the best performance in Cr removal (<0.001 mg/L throughout the experiment), while *P. australis*-planted Constructed Wetlands showed the best in Chemical Oxygen Demand removal (833 mg/L). However, all the N and P removal maintained low level.

Kaseva and Mbuligwe tested continuous treatment of tannery wastewater using two kinds of HSSFCW system: one was planted with macrophytes and the other without plant (control) at a hydraulic retention time of 1.6–1.8 days [13]. Although the wastewater contained more than 370 mg/L chromium, the HSSFCW system showed high Cr removing efficiency (99.83%), and even the control system recorded 92.53% removing efficiency. Turbidity was reduced from around 190 NTU to 29–79 NTU (HSSFCW) and 26–83 NTU (control). The study demonstrated

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the potential of constructed wetland systems to be used as an option for treating tannery wastewater with such a high Cr content, removing Cr and turbidity. However, the system was not suitable for reduction of TDS and EC. Saeed et al. tested three-stage hybrid CW system combining subsurface vertical flow (VF) wetland, followed by a horizontal flow (HF) and a VF wetland for tannery wastewater treatment, and demonstrated the high nutrient removal [14]. Although the wastewater contained high organic matter (11,500 mg/L COD, 111 mg NH_4^+, and 30 mg/L PO_4^{3-}), the overall system had 98%, 86%, and 87% of COD, NH_4^+-N, and PO_4^{3-}, respectively, removal efficiency on average.

4. Reuse and recycle of treated waste in tanning industry by-product utilization

Yearly, tannery industries generate more than 600,000 tonnes of waste, posing a major challenge to the environment [15]. It is reported that producing 150 kg of leather would require 1000 kg of raw hide and throw out 850 kg of solid waste to the environment [15]. With the high discharge amounts in leather processing, there is a critical need to treat and recycle the tanning industry by-product. The hierarchy of tanning waste treatment/management is suggested in **Figure 4**.

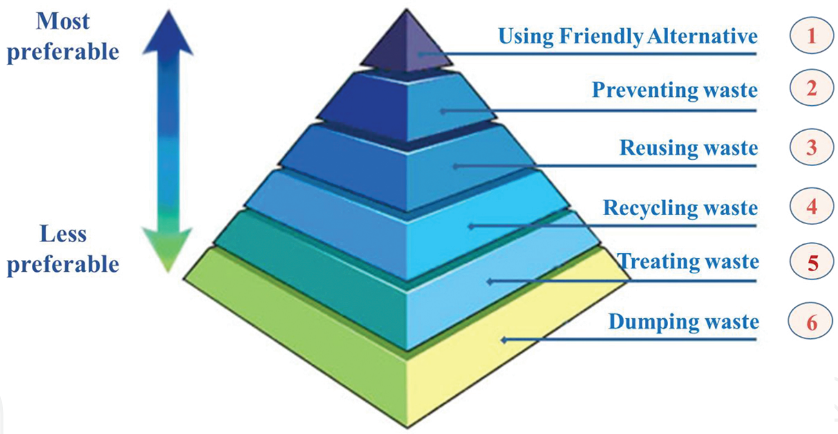

Figure 4. Hierarchy of tanning waste management.

The order of tanning waste management starts from the top of the hierarchy by friendlier option and finish at the bottom of the hierarchy in accordance with "using friendly alternative, preventing, reusing, recycling, treating and dumping waste".

1. *Using environmentally friendly alternatives*: Using biodegradable fat-liquoring alternatives, innovative compounds, which are based on natural materials such as palm oil, are the most preferable option, making them easier to treat wastewater from the tanning sector. Furthermore, the use of innovative technology for leather-tanning process with the goal of reducing hazardous waste should be chosen [16].

2. *Preventing*: Eliminating fat-liquoring agents such as chromium III, arsenic, cadmium, and lead is also recommended in tanning industry in order to prevent hazardous contaminants.
3. *Reusing*: The encouragement of reusing waste and residue for the reproduction or making new products is considered as the third option.
4. *Recycling*: Applying green technologies to treat waste by applying some energy conversion technologies such as biomethanation, bioenergy production, and other feasible technologies such as biosorption, bioaccumulation, biodegradation, and phytoremediation [12, 17].
5. *Treating*: The completed investment of wastewater treatment facility is preferred as end-of-pipe sector of tanning industry. Wastewater treatment standard must be critically followed up to the environmental friendly standards to prevent environmental affection from the untreated waste.
6. *Dumping*: At the bottom of hierarchy, dumpling is the less preferable option due to tanning wastes that cause high environmental pollution and further affect to human health. In fact, due to the costs of treating tanning waste, many tanning manufacturers deal tanning waste with illegal activities. Therefore, treating tanning waste by dumping should be banned in countries such as Bangladesh, Nepal, and Sri Lanka [18].

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