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Probable Ways of Tannery’s Solid and Liquid Waste Management in Bangladesh – An Overview

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ABSTRACT
The leather industry has been marked as a top-priority sector due to its potential growth and economical contribution in Bangladesh. However, these industries are unable to meet the compliance issue due to the environmental pollution. Leather processing is a complex process based on chemicals and mechanical methods. A substantial amount of solid and liquid wastes is generally produced during the production of leather. As most of the tanneries do not have a central effluent treatment plant and advanced management technologies, they produce 20000 m3 of liquid waste and 232 tonnes of solid waste per day in Bangladesh, which poses a significant risk to the environment and human health unless it gets well treated. In this modern era, it is indispensable to implement new technologies to treat liquid waste properly as well as innovative disposal techniques for solid waste to reduce pollution and health hazards. This study, by using a non-systematic approach based on literature reviews, is designed to summarize the kinds of solid and liquid waste management techniques around the world which should be implemented in the tanneries of Bangladesh to mitigate environmental pollution. We hope that this study can be a great resource and provide a pathway for leather industries in Bangladesh to get familiar with effective treatment technologies of solid and liquid wastes.

KEYWORDS
Solid waste, Liquid waste, Treatment, Tannery

INTRODUCTION
Waste is an unavoidable thing that is created due to human activities, urbanization, development of living standards, and economic evolution [1]. These changes in human activities increase the volume of waste generation as well as the category of waste. The world is producing 7-9 billion tonnes of waste yearly [1,2]. In 2016, around two billion tonnes of municipal solid waste were generated [1]. This wastage is affecting our entire environment and all human beings as well. Considering the situation, this problem needs special attention, not only nationally but also globally. Leather making is an ancient art, whereas its manufacturing process, namely the tanning process, is connected to the generation of huge amounts of waste. The world is producing 7-9 billion tonnes of waste yearly [1,2]. In 2016, around two billion tonnes of municipal solid waste were generated [1]. This wastage is affecting our entire environment and all human beings as well. Considering the situation, this problem needs special attention, not only nationally but also glob-
ally. Leather making is an ancient art, whereas its manufacturing process, namely the tanning process, is connected to the generation of huge amounts of waste.

Tanning is the process of transforming raw hides into a useful product not only by providing the necessary material and energetic input such as heat, chemicals, and water, but also by generating huge amounts of solid waste, liquid waste, and air pollution as an output [3,4]. About 6.5 million Mg (wet salted weight) bovine hides and skin are processed annually all around the world, of which more than 4.3 million Mg was produced by the developing countries. Appro. 750 thousand Mg (dry weight) of goatskins, kidskins, and sheepskins are used in the process. A total of 3.5-4 million Mg (rough calculation) of solid waste is currently generated worldwide [5]. On the other hand, wastewater is also generated by industrial activities as a by-product, which involves a rise in level of various contaminants beyond the limit, such as Biological Oxygen Demand (BOD5), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Organic Carbon (TOC), Total Suspended Solid (TSS) and heavy metals. These are found in neighbouring water bodies and have an adverse effect on the aquatic environment [6]. The process of tannery operation also produces different types of malodour and causes air pollution. It emits ammonia, hydrogen sulfide gas, and volatile compounds such as hydrocarbon, amines, and aldehyde due to biological degradation and chemical substances. The type of air pollution depends on the applied technology and the method of process. Hence, pollution to the ambiance will inevitably happen. Consequently, the pollution caused by leather processing undoubtedly poses a detrimental effect on the environment and human health. So, the primary concern is the treatment or management of this waste [7].

In this study, an overview of solid and liquid waste management will be discussed as it is one of the most unavoidable problems in Bangladesh. Bangladesh has made rapid economic growth in the last few years. The government is positive about the development of the leather sector which made possible the transformation of unstructured leather industries into a structured form. Though Bangladesh tackled the COVID-19 situations remarkably, there is some fluctuation in export earnings of leather and leather-made goods, which are about $1.10 as reported by the Export Promotion Bureau [8]. Nowadays, it is considered one of the leading sectors in Bangladesh.

Tanneries in Bangladesh

A small number of tanneries initiated to manufacture crust and then finished leather from putrescible raw hides and skins of domestic animals in Bangladesh. Nowadays there are about 220 of different-sized tanneries in different locations, but only 113 among them are effectively in function. Moreover, among them, 20 factories (fairly 7 units) are considered as large, 45 units are regarded as medium and 53 units are regarded as small, as presented in Table 1. Bangladesh is well reputed for breeding livestock population to provide a big support for the growing leather processing industries. Table 2 shows that cow hides contribute to 56% of the production, 30% comes from goat skins, and buffalo skins are used to make up the rest [9]. Once most of the factories situated at Hazaribagh were regarded as `operating tanneries’, operated by owners, and the rest of the factories were run on leasing basis until 2017, but afterward 123 big tanneries shifted completely to the Tannery Industrial State (TIE) situated in Savar and others are planning to go there [10].
Table 1: Structure of tannery in Bangladesh [9]

<table>
<thead>
<tr>
<th>Number of Tanneries</th>
<th>Typical annual production capacity/tannery</th>
<th>Total installed capacity/annual</th>
<th>Total actual production/annual</th>
<th>Share of actual production</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>&gt;5 million sq.ft</td>
<td>40 million sq.ft</td>
<td>30 million sq.ft</td>
<td>17</td>
</tr>
<tr>
<td>13</td>
<td>2-5 million sq.ft</td>
<td>60 million sq.ft</td>
<td>52 million sq.ft</td>
<td>29</td>
</tr>
<tr>
<td>48</td>
<td>&lt;2 million sq.ft</td>
<td>70 million sq.ft</td>
<td>60 million sq.ft</td>
<td>33</td>
</tr>
<tr>
<td>53</td>
<td>&lt;1 million sq.ft</td>
<td>60 million sq.ft</td>
<td>38 million sq.ft</td>
<td>21</td>
</tr>
<tr>
<td>Total: 113</td>
<td></td>
<td>230 million sq.ft</td>
<td>180 million sq.ft</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2: Livestock population for leather Industry [9]

<table>
<thead>
<tr>
<th>Category</th>
<th>Annual kill in millions</th>
<th>Average weight/price in Bangladesh</th>
<th>Total annual production in tonnes</th>
<th>Average area per piece (sq.ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cow/Calf</td>
<td>4.00</td>
<td>12</td>
<td>48000 (56%)</td>
<td>20-22</td>
</tr>
<tr>
<td>Goat/Sheep</td>
<td>15.00</td>
<td>1.5-2.0</td>
<td>26000 (30%)</td>
<td>3.75</td>
</tr>
<tr>
<td>Buffalo</td>
<td>0.50</td>
<td>20-25</td>
<td>11000 (14%)</td>
<td>32.35</td>
</tr>
</tbody>
</table>

Tanning Process

Leather tanning is a process of turning putrescible outer layers of animals to non-putrescible ripen leathers with precise physical and chemical properties so that they can meet the requirements of daily life and industries [11]. This is a complex process, involving different chemicals, salts, and other additional ingredients. Operations are conducted in the beam house, tan yard, and wet processes known as post-tanning operation are operated in other areas, as they are carried out in processing vessels, such as drums. Then, dry finishing operations are carried out accordingly. Leather processing is dependent on the used raw materials and the desired end product. Thus, the environmental pollution caused by the discharge of solid wastes and wastewater contents differs from factory to factory. Raw hide or skin is the primary material for leather processing. The salt is required for preserving the skin/hide, and other hazardous chemicals used in leather processing are lime, ammonium salts, chromium salts, sulphuric acid, ammonium sulfide, and organic tanning agents [6]. Figure 1 shows the various processing steps of leather tanning [5].

TYPES OF POLLUTION DUE TO THE LEATHER INDUSTRIES

The leather industry is known as one of the most polluting industries due to its adverse impact on the environment. During processing, a substantial amount of solids, including dissolved and suspended organic matter, contaminate wastewater containing chemicals which are largely responsible for environmental pollution [12]. Different kinds of pollution occur during tanning steps discussed below.
Table 3: Tanning process with raw materials used in processing and possible solid and liquid pollutants

<table>
<thead>
<tr>
<th>Process Input</th>
<th>Process</th>
<th>Solid Pollutants</th>
<th>Liquid Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Hides/Skins</td>
<td>Sorting and Trimming</td>
<td>Trimming waste</td>
<td></td>
</tr>
<tr>
<td>Salt</td>
<td>Curing and Storage</td>
<td>Salt</td>
<td>TDS, Dirt, Dung, Blood, BOD, COD</td>
</tr>
<tr>
<td>Water</td>
<td>Soaking</td>
<td>Salt</td>
<td>Alkali, BOD, COD, TDS, H2S gas</td>
</tr>
<tr>
<td>Water, Lime, Sulfide</td>
<td>Liming</td>
<td>Keratinous waste</td>
<td>Hair, Organics, Alkali, TDS</td>
</tr>
<tr>
<td>Unhairing</td>
<td></td>
<td>Fleshing waste</td>
<td>Fats, Alkali</td>
</tr>
<tr>
<td>Ammonia, Salts, Water</td>
<td>Deliming</td>
<td></td>
<td>Ammonia, Salt</td>
</tr>
<tr>
<td>Protease</td>
<td>Bating</td>
<td></td>
<td>Proteoglycans, Organics, Lime</td>
</tr>
<tr>
<td>NaCl, Acid, Water</td>
<td>Pickling</td>
<td></td>
<td>Acid, Salt</td>
</tr>
<tr>
<td>Cr Tanning Agent, Formate, Bicarbonate</td>
<td>Tanning</td>
<td>Cr, Salts, Low pH, BOD, COD</td>
<td></td>
</tr>
<tr>
<td>Samming and Shaving</td>
<td></td>
<td>Shaving dust, Splitting waste</td>
<td></td>
</tr>
<tr>
<td>Bicarbonate, Formate, Water</td>
<td>Neutralization</td>
<td></td>
<td>Salts, Cr</td>
</tr>
<tr>
<td>Vegetable tannin, Phenol, Cr tanning agent, Syntan</td>
<td>Re-tanning</td>
<td>Cr, Salts, Phenol</td>
<td></td>
</tr>
<tr>
<td>Dyes</td>
<td>Dyeing</td>
<td></td>
<td>Dyes</td>
</tr>
<tr>
<td>Oil, Fats, Formic Acid</td>
<td>Fatliquoring and Fixing</td>
<td>Oils, Fats, Acid</td>
<td></td>
</tr>
<tr>
<td>Finishing Agent</td>
<td>Mechanical Finishing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating Agent</td>
<td>Coating</td>
<td>Leather</td>
<td></td>
</tr>
</tbody>
</table>

Soil Pollution

Soil is important for the growth and development of plants and animals. It is very common that soil profile is negatively affected due to the presence of hazardous substances containing organic and inorganic pollutants generated from industrial wastes, especially from the effluents of the tannery. Tannery sludges contain heavy metals such as Cd, Zn, Cr, Ni, Pb, and Mn which can cause metal accumulation in the surface soil, and these metals can bioaccumulate in plants, crops, etc. Chromium concentration in soil is high due to the
irrigation with wastewater containing a high concentration of chromium-rich tannery effluents [13]. As a substantial amount of NaCl is used as a raw material in the tanneries during leather processing, it discharges a significant amount of chloride into the soil [14]. The pH level of the soil is increased due to the alkalinization of soil in the tanning process caused by sodium carbonate, bicarbonate and chloride [15].

**Atmospheric Pollution**

The oxygen contained in the air is an essential part for our healthy life. However, air pollution is common throughout the globe, mainly in developed and underdeveloped countries from 1960 to this day. Polluted air poses a serious risk to human health as it contains particulate matter, heavy metals, carbon monoxide and dioxide, benzene, N2O, PAHs, NH3, etc. from waste generated by tanning processes, especially during post-tanning and the finishing operation [16,17]. Malodour is a common phenomenon in the tanneries. As the salted hides and skins rehydrate, the odour of volatile fatty and amino acid spreads to the environment. The spread of bad smells in ambient air and its circulation to a distance is the primary reason for atmospheric pollution [12].

**Water Pollution**

Effluents from tanneries are a major environmental issue because they are highly responsible for degrading the quality of the water system as they release toxic agents into the system. Tannery waste contains proteins and carbohydrates as the biodegradable organic matter which causes the depletion of dissolved oxygen amount in aquatic systems caused by micro-organism decomposition [18]. The amount of dissolved oxygen is highly reduced which has an adverse effect to aquatic organisms and increases anaerobic function, and causes generation of noxious gases, damaging the nutrient profile of aquatic organisms and finally posing a significant risk to human health by causing waterborne diseases like cholera, infective hepatitis, typhoid, dysentery, and gastroenteritis [19,12].

**Types of Waste in Leather Industry**

Globally, about 4 million tonnes of solid wastes are produced by leather and leather subsidiary industries. Leather and leather goods impose a significant threat from their manufacturing stage to the decomposition stage. Leathermaking is the troublesome stage as it discharges contaminated water and solid wastes [20]. The wastes generated in this process are harmful to living organisms. The effluents from the factories are directly thrown into the water bodies that are responsible for water pollution particularly. Heavy metals such as chromium, cadmium, chlorine, zinc, nickel, and lead are the main components of the effluents. Leather processing waste can be divided into 3 main divisions with a subdivision [21].
OBJECTIVES

This study is designed to summarize the information about the latest technologies and methods for managing the solid and liquid wastes generated from tanning industries around the world. Bangladesh is widely known to manufacture wet-blue, crust, and finished leather in the world but the waste management technique in Bangladesh is not up to the mark comparing to the modernization technique available for the treatment of waste discharged from leather industries. So, the primary concern of this study is to discuss the available solid and liquid waste management technologies in the world which should be followed to get the maximum efficiency during waste treatment in the tanneries of Bangladesh.

REVIEW METHOD

Literature review method was followed to conduct this study. Mainly, the authors used search engines Google Scholar and ResearchGate to complete literature reviews. Different search terms such as “tannery waste management”, “effluent treatment techniques”, “tannery waste to applicable products” were applied to find out the best article in this area on the Internet. This summarized information was based on an apprehensive, coherent, stepwise decision to contemplate this article applicably. As this method is non-systemic, it often avoids the systemic order of summarizing the content of literature on a single topic [22,23]. In contrast, the pragmatic information on a particular issue was summarized from the articles reviewed. Overall, this study is based on the summarized information from highly cited journals focused on the recent technologies that are frequently used worldwide to manage waste from tanneries [23]

PROBABLE SOLID WASTE MANAGEMENT

A significant amount of the solid waste produced by raw hides and skin processing industries is dumped on the side of the street, so the environmental impacts are noticeable and dangerous to humans. About 850 kg of solid waste is generated from the processing of 1000 kg of raw hides and skins. And as a result, only 150 kg of hides and skins are turned into leather. Solid wastes are generally chrome splits, chrome shaving, buffing dust, 35-40%; fleshing, 50-60%; skin trimmings, 5-7%; and hair, 2-5%. Solid wastes in the hides and skins processing contents: beam house, 80%; finishing, 1%; tanning, 19% [24]. A useful by-product from solid waste can be generated in many ways which are represented in Fig. 3.
Solid Waste Containing Chrome

The chrome-tanning process releases a significant amount of chromium-containing wastes. These wastes are generally generated from shaving, splitting, and trimming leather and they mainly contain chromium and collagen. In general, 1-3% of Cr and 90% of collagen are present in these wastes [25]. The oxidation named dechromation process is the way to get satisfying efficiency. Acid hydrolysis is another way to get results, but it has the disadvantages of hydrolysis of collagen and a slow process. Alkali hydrolysis may be done to destroy acid mixture hydroxyl and amide substances which is also a slow treatment process. Enzymatic hydrolysis requires a high treatment cost, and it is difficult to industrialize as it needs a specific enzyme for each step. The ultrasonic technique can be used to improve the efficiency of dechromation as it has several advantages [26].

Keratin Waste

Due to the orthodox unhairing method, a significant amount of wastewater containing a high level of TDS, BOD, COD and sulfide is generated because of the dissolution of hair. Biotechnology that was implemented to treat organic substances in wastewater efficiently is expensive and responsible for discharging a large number of sludges. As a result, the advanced unhairing method named hair-saving has been invented and implemented in the leather processing industry, which can efficiently recover 95% of the hair and mitigate wastewater pollutants. Recently, researchers are concerned about the treatment of hair waste, extraction, and use of keratin [27]. Keratin is composed of different types of chemical bonds such as hydrogen bond, ionic bond and disulfide bond. Different types of physicochemical methods can be applied to destroy these bonds, such as oxidation, acid hydrolysis, mechanical extraction, enzymatic hydrolysis, alkali hydrolysis, microwave radiation, reduction, etc. and these methods are also efficient in extracting keratin from the hair [27-30].

Figure 2. Utilization of Solid Waste [10]
Fleshing Waste

A huge amount of solid waste is produced from pre-tanning operations, particularly fleshing of leather processing. Proteolytic activity of pancreatic homogenate presented a 6-fold due to proteolytic activity and increase as proteolysis happens after 7 days against the control. About 80.0 mg/l, 10.64 mg/l, and 72.86 mg/ml protein content, collagen, and free fatty acid respectively were present in hydrolysate supernatant. The required pH is 8.5 for the preparation of the enzyme. Total liquefaction helps to do hydrolysis and then the fleshing is dried subsequently. As a protein origin, hydrolysate may be useful to manufacture animal feeds by mixing with other ingredients [31].

Untanned Solid Waste

The solid wastes which are untanned mainly contain waste from trimming operation of hiding and skin after liming and fleshing, containing significant content of grease and protein. Different physical and chemical methods and technologies have been developed to use this protein-containing waste efficiently, particularly concerning the manufacturing of gelatine by mixing additional chemicals, such as acid, alkali, and enzyme. Recently, researchers have found that gelatine made from leather solid waste is highly effective in biomedicine, cosmetic products, and finally in packaging [32-34].

Chrome Shaving Dust

Chrome tanned leather, leather splits, and leather scraps have been used to obtain adhesive, gelatine, protein flavour, and composite fibre. Hydrogen peroxide is generally used to make these products as well as to bring a degree of maceration for smooth grinding and extraction to get the by-product to about 95% [35,36]. The proteolytic enzyme is used to treat chrome shaving at 60-65°C with a presence of 5-6% of lime. Then, a filtration technique is imposed to separate protein and leave chrome cake. The hydrolysate (< 4.5 ppm chromium) containing protein is applicable as feed, for making fertilizers, or as an additive in the manufacturing of cosmetics [37]. Chrome cake and hydrolysate can be made from shavings by implementing chemicals or biodegradation. Organophosphorus hydrolase (OPH) is found to be effective in adding extra value in the hydrolysate when degradative enzymes are immobilized to degrade organophosphate esters. Extraction of OPH considered as crude from bacteria named Flavobacterium sp. was used to immobilize enzymes onto the hydrolysate films. The continuity and recyclable activity of the resulting films is highly effective in the degradation of the phosphorous compound [38]. Conventional methods can be used to get gelatine from the collagen residues. Leather can be regenerated with what is known as agglomerates by using the collagen hydrolysate with a mixture of latex [39,40].

Tannery Sludge Utilization

Sludge is another form of solid waste produced from the tanneries during the making of leather and treatment of wastewater containing a high amount of lime, oil, blood, chromium, sulfide, hair and protein. Due to the high concentration of pollutants, sludge from tanneries was considered hazardous [41]. Several traditional methods are available to dispose of these wastes, like incineration, stacking and landfill, but these cannot eliminate the pollutants and they are also responsible for secondary pollution. Recently, several effective recycling technologies might be the proper solution to mitigate the pollution. Tannery sludge may contain a lot of organic substances and nutrients, which may be used as fertilizers to grow plants [37]. Tannery sludge containing organic matter can be used in anaerobic digestion to convert biodegradable substances to biogas.
Nowadays, researchers emphasize the advanced digestion procedure by using enzymes [42]. Treated tannery sludge can be used to prepare building materials such as brick, ceramics etc. to reduce the toxicity [43,44].

**Finished Leather Waste**

Tanneries, as well as leather goods factories, discharge finished leather scraps mainly from trimmings, buffing crust leather. In general, footwear and small leather products manufacturing factories produce a bulk amount of solid leather wastes during the manufacture of shoes, bags, belts etc. [43]. To eradicate this issue, well planned governmental guidelines and regulations are required. Besides, it is necessary to establish pragmatic and economical methods to recycle leather wastes after the finishing to keep the environment away from pollution [44].

**PROBABLE LIQUID WASTE MANAGEMENT**

**Characteristics of Tannery Waste Management**

A vast amount of wastewater is generated in leather production, as most of the tanning process involves the use of a huge amount of water. About 60 m3 of water is required to process one ton of hides and skins. The wastewater contains hazardous chemicals, leached proteins and degradation products of hides and skins. The mechanical treatment of wastewater causes sludge and sediment formation, the disposal of which is, therefore, a difficult and serious problem. They contain moisture, about 45–65%(w/w), 30%(w/w) of organic substances and 2.5%(w/w) of Cr (III) compounds [45]. Table 3 shows the ingredients used in the processing of chrome-tanned leather and its possible output. Many chemical substances like lime, sulfide, ammonia, different salts, acids, and dyes are applied at a high level to process the rawhide and make usable leather. Liquid wastes, generated from the tannery, are rich with high BOD, COD and TDS level. About 90% of tanneries perform the tanning process using chromium salt, basically chromium (III) sulfate which is released with water at an impermissible limit due to the low uptake rate of raw hides. A study in a Kenyan tannery showed that raw effluent contained high levels of pollutants (COD 2437.84mg/L, BOD 1255mg/L, Cl 1725mg/L, sulfides 62.4mg/L) [46]. In another study, Laila et al. characterized wastewater released from six local industries in Bangladesh with a high amount of pollution load and showed a mean result regarding TDS 3450mg/L; TSS 1650 mg/L; BOD 540mg/L; COD 1450 mg/L [47]. These pollutants are making significant changes to our natural ecosystem, whereas effluent containing chromium is posing a major threat to both aquatic life and human circumstances. In a previous study, after an investigation, researchers reported that a considerable amount of heavy metals was found, which was beyond the limit, especially in the case of chromium (374.19 mg/L on average). The effluent was released into the river without any treatment process [49].
Bioaccumulation of chromium also occurred in the nearby fish species (2.70mg/kg Cr on the average on fish muscle) the value of which was above the permissible limit. As heavy metals are toxic, persistent and occur due to bioaccumulation, they can influence abiotic environmental factors such as pH, alkalinity, hardness, oxygen and temperature [49]. Transformation from Cr (III) to Cr (VI), which is 500 times more toxic, can happen under certain conditions and may damage human organs such as kidney, liver, dermatitis and gastrointestinal system [6]. Effluents with higher BOD, TDS, COD and heavy metals may affect our surface water as well as irrigation, and transmit hazardous pollutants in the human food chain [49,50]. Therefore, proper treatment is necessary before releasing the wastewater into the environment which is now discharging without maintaining international standards.

Table 4: Comparison of different parameters in different industries with standards limits

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Standard Permissible Limit</th>
<th>R M M Leather Industry</th>
<th>Mukti Tannery</th>
<th>Ruma Leather Industry</th>
<th>Dhaka Skin and Hide Industry</th>
<th>Jomila Tannery</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.00 – 9.00</td>
<td>6.00 – 9.00</td>
<td>8.30</td>
<td>7.50</td>
<td>3.00</td>
<td>7.00</td>
</tr>
<tr>
<td>EC (µs/cm)</td>
<td>1000.00</td>
<td>1200.00</td>
<td>42500.00</td>
<td>6500.00</td>
<td>9000.00</td>
<td>1300.00</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>250.00</td>
<td>30.00</td>
<td>4464.00</td>
<td>190.00</td>
<td>400.00</td>
<td>700.00</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>500.00</td>
<td>250.00</td>
<td>112840.00</td>
<td>550.00</td>
<td>1000.00</td>
<td>1700.00</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>2100.00</td>
<td>2100.00</td>
<td>21300.00</td>
<td>2910.00</td>
<td>3300.00</td>
<td>3700.00</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>500.00</td>
<td>600.00</td>
<td>1250.00</td>
<td>1250.00</td>
<td>1400.00</td>
<td>1600.00</td>
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<tr>
<td>Cadmium (mg/l)</td>
<td>-</td>
<td>2.00</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper (mg/l)</td>
<td>-</td>
<td>0.10</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium (mg/l)</td>
<td>2.00</td>
<td>2.00</td>
<td>0.10</td>
<td>10.35</td>
<td>1.20</td>
<td>3.00</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>-</td>
<td>10.00</td>
<td>19.00</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lead (mg/l)</td>
<td>-</td>
<td>0.10</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zinc (mg/l)</td>
<td>-</td>
<td>1.00</td>
<td>1.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel (mg/l)</td>
<td>-</td>
<td>3.00</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium (mg/l)</td>
<td>-</td>
<td>-</td>
<td>12006.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>-</td>
<td>1000.00</td>
<td>13.80</td>
<td>900.00</td>
<td>1250.00</td>
<td>1100.00</td>
</tr>
</tbody>
</table>

Figure 3. Transformation of chromium state and conduction into the ecosystem [48]
Tannery Wastewater Treatment Method Focusing on the Most Useful Methods

There are many techniques and technologies used in the treatment process of leather industrial effluent. The conventional process used in Bangladesh, namely the central effluent treatment plant (CETP), is costly, requires high maintenance and does not work properly. Other treatment systems include physical treatment, electrochemical treatment [55], biological treatment [56], coagulation-flocculation [57] and adsorption [58].

Physical Treatment

Physical operations are also called primary treatment and necessary for eliminating coarse material in the liquid effluent. This method involves sedimentation, screening, filtration, aeration etc., where physical processes are used to treat effluents or remove the pollution load and no gross chemical or biological conversions are carried out. Coarse screening is carried out, which eliminates larger objects. In the sedimentation process, larger objects settle down by gravity. Usually, this consists of holding effluents for a short period in a tank under suitable conditions, allowing the heavier solids to settle and separating it from the effluent (clarification). Sedimentation for solid separation is a very common unit operation and is routinely employed at the beginning and end of wastewater treatment operations [59].

Biological Treatment

Biological treatment of leather industrial wastewater is preferable to other treatment processes, as microbes are used for the decrease of pollutants. As sulfide and chromium are present in the wastewater, several problems merge during the biological process. There are two types of biological treatment processes included, aerobic process and anaerobic process. The decomposition rate of the aerobic process is faster than the anaerobic [59].

Figure 4. Bar screen, operation principle [60]
In aerobic biological treatment methods, the activated sludge process is used for the biodegradation of tannery wastewater. Some important parameters are related to this process, such as the growth of microorganisms and the utilization of substrate based on aeration time, residence time, food to microorganism ratio, dissolved oxygen of the reactor and mixed liquor suspended solids concentration. According to a study, with COD above 80% and 90%, BOD removal had been observed when solid concentration and aeration time were 3500 mg/L and 12 hours respectively [61]. Pathogens like Escherichia coli, Vibrio sp. and Pseudomonas sp. were eliminated with about 98.46%, 87.50% and 96.15% in bacterial counts after treating the effluent. Chrome reduction ability had been shown to be >90% by 10.8% of microbial isolates from the wastewater. In anaerobic biological treatments, the highest performance can be obtained by UASB with an aerobic post-treatment. About 78% of COD was removed in an anaerobic treatment, whereas the combined anaerobic and aerobic treatment system reached 96% [62]. As biological treatment is time-consuming and requires a large space for treatment, it is gradually being replaced with new technologies.

Chemical Treatment

Chemical processes are defined as chemical reactions to make some change in the constituents of the pollutant by means of chemical reactions. In general, chemical methods, in comparison to physical methods, are accompanied by an inherent disadvantage. In other words, there is usually a net increase in the dissolved constituents due to the sludge, which can be a significant factor in the case of wastewater reuse. In many cases, the combined physico-chemical process works better. This section will deal with the main chemical unit processes, including advanced oxidation process (AOPs), disinfection, chemical precipitation, and dechlorination [60]. According to a study, the lime pre-treated effluent has been treated using a catalytic reactor where TiO2 was used as a catalyst. The results showed the percentage removal of BOD, COD, and TDS was 87.35%, 89.53% and 92.63% respectively [63]. Another study showed 87% of total organotin carbon (TOC) removal by using cavitation combined with AOPs [64].

![Figure 5. Flowchart of a typical combined (chemical, biological and physical) tannery effluent treatment system](image-url)
Electrocoagulation Process

Electrocoagulation is an interdependent and complex process where a metal anode is used to perform as a coagulating agent for the treatment of polluted water. The electrocoagulation process can be divided into three steps: (1) formation of coagulants by electrolytic oxidation of the electrode, (2) destabilization of contaminants, and (3) particulate suspension and breaking of emulsions. Electrocoagulation was found to be effective to treat arsenic, electroplating, dye, phosphate, and textile industry wastewater [66]. The study showed effective removal of pollution load by electrocoagulation processes such as COD (68.0%), ammonia (43.1%), total organic carbon (55.1%), sulfide (96.7%) and colours (84.3%). Another study by using combination of electrocoagulation process and UVC/VUV photoreactor exhibited excellent removal efficiency (COD: 99.52% Cr(T): 100% and sulfide: 98.27%) [67]. Figure 6 graphically represents the mechanism of the method.

Adsorption

The adsorption technique uses materials such as activated carbon, charcoal, sawdust and graphene-based material [68-71]. In a study, the colour removal in tannery effluents has found to vary between 95 and 100% by using Fixed Bed Column [72]. Another study on effluents revealed effective removal of dye ( Acid Brown 414: 71%, Acid Orange 142: 73%). An efficient result was observed using activated biochar from municipal solid waste for the removal of chromium ions. The maximum removal efficiency was found to be 98.97% [73]. About 98.2% for Cr and 96.4% for Pb (II) ions removal efficiencies have been found in a recent study where cobalt ferrite-supported activated carbon was used for adsorption [74].

Figure 6. Graphical representation of the combined treatment of tannery wastewater [67]
Membrane Technology

Membrane technologies are newly developed advanced methods for treating dissolved solids in effluents. The application of the membrane system in effluent treatment together with UF/RO, MF/NF, and NF/RO is used for the recovery of chromium [75]. Recovery of chromium and spent liquors in the leather industry decreases the number of pollutants in the unhairing and degreasing process in the biological treatment of tannery wastewater [76,77]. A study on tannery effluent treatment (using nanofiltration NF270 and NF90 membranes), reverse osmosis (BW30 and SW30) and polymeric membrane prepared by coating chitosan (cs) on a polyether sulfone (PES) microfiltration membrane (cs-PES MFO22 support) exhibited excellent removal of chromium ions (>99%) [78].

There are some of the latest technologies which are included in Table 5 that represent possible ways for the treatment of tannery wastewater.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Treatment process</th>
<th>Material Used for removal toxicants</th>
<th>Removed Toxicants (removal %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical Treatment</td>
<td>A sonocatalytic reactor, TiO2 as catalyst</td>
<td>BOD (87.4%), COD (89.5%), and TDS (92.6%)</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>Biological</td>
<td>An aeration tank</td>
<td>BOD, COD</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>Electrocoagulation</td>
<td>Low cell current (&lt;1A) and soluble electrodes (mild steel electrodes and aluminum electrodes)</td>
<td>COD (68.0%), ammonia (43.1%), total organic carbon (55.1%), sulfide (96.7%) and colority (84.3%)</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>Biochar Based Filtration</td>
<td>Sand, Biochar, Gravel Stone</td>
<td>Cr(VI) (99.9%)</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>Biological</td>
<td>Marinobacter hydrocarbonoclasticus</td>
<td>chromium (88.0%), sulphate (71.0%), phosphate (68.0%) and nitrate (57.0%)</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>Adsorption</td>
<td>Activated carbon</td>
<td>Acid Brown 414 (71.1%) and Acid Orange 142 (73.1%)</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>Adsorption</td>
<td>Volcanic rocks of pumice and scoria</td>
<td>NO3–N, PO4–P and Cr3+</td>
<td>81</td>
</tr>
<tr>
<td>8</td>
<td>Electrocoagulation/electrodialysis</td>
<td>aluminum electrodes</td>
<td>COD (92.0%), NH3-N (100%), Cr (100%) and color (100%)</td>
<td>82</td>
</tr>
<tr>
<td>9</td>
<td>Chemical Treatment</td>
<td>AOPs</td>
<td>TOC (87.0%)</td>
<td>64</td>
</tr>
<tr>
<td>10</td>
<td>Electrocoagulation</td>
<td>electrocoagulation process and UVC/VUV photoreactor</td>
<td>COD: 99.5% Cr(T): 100% and sulfide: 98.2%</td>
<td>67</td>
</tr>
<tr>
<td>11</td>
<td>Adsorption</td>
<td>Fixed Bed Column</td>
<td>Color (between 95.0 and 100%)</td>
<td>72</td>
</tr>
<tr>
<td>12</td>
<td>Adsorption</td>
<td>Activated biochar</td>
<td>Cr (98.9%)</td>
<td>73</td>
</tr>
<tr>
<td>13</td>
<td>Adsorption</td>
<td>cobalt ferrite-supported activated carbon</td>
<td>Cr (98.2%), Pb(II) (96.4%)</td>
<td>74</td>
</tr>
<tr>
<td>14</td>
<td>Membrane Technology</td>
<td>NF, RO, MF</td>
<td>Cr (&gt;99.0%)</td>
<td>78</td>
</tr>
</tbody>
</table>
CONCLUSION AND RECOMMENDATION

There are several pragmatic approaches available in the literature published in the reputed journals for the treatment of liquid and solid waste discharged from leather processing industries that have been summarized in this study. As these industries use a huge amount of chemicals for processing leather that are responsible for the production of significant amounts of solid and liquid wastes, they are known as one of the most polluting industries in Bangladesh and have detrimental effects on the environment as well as human health. Though waste from the leather industry plays a significant role in environmental degradation, a proper treatment of waste can be also beneficial in producing valuable products. This study found that making organic fertilizers, producing energy, developing biomaterials, gelatine, glue, sorbents, adsorbents etc. from solid waste, while removing pollutants from the wastewater, is the practical output from waste by implementing proper treatment technologies in leather industries. However, tannery owners should invest more to implement advanced leather manufacturing technologies for environment-compliant and more efficient solid and liquid waste management techniques, flexible production methods and to improve their operational management efficiencies. The government should reform policy for the betterment of the environment, especially in the case of discharging liquid and solid waste to the environment. The higher authority of Savar Tannery State should be focused on the development of infrastructure, including a functioning and completely operational CETP. Furthermore, a substantial investment should be executed to enhance skills and technical facilities for converting waste to green products.

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Conflicts of Interest

The authors declare no conflict of interest.

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