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Chapter- 27

Revolutionizing Leather Industry Wastewater Treatment: A Game-Changing Approach for Sustainable Environmental Management

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Abstract:

The substantial volume of wastewater generated by the leather industry, laden with high levels of pollutants, poses a significant environmental threat. Without proper treatment, the discharge of such wastewater could have severe and detrimental effects on the environment. The treatment of wastewater in the leather industry is pivotal for mitigating environmental impacts and represents a cornerstone of sustainable environmental management. The industry not only minimizes its environmental impact but also aligns with and contributes to various sustainable development goals (SDGs). The industry's commitment to responsible practices is demonstrated by employing diverse methods such as BOD, chlorides, COD, Cr (III), heavy metals, sulfates, and TDS. This includes adsorption, biochemical/biological treatment, chemical precipitation, Electro-coagulation, Fenton oxidation, hybrid processes, ozonation, electro-oxidation, photo-catalytic ozonation, and physical treatment. Moreover, a sustainable approach involves the recovery of valuable substances from the treated wastewater. The solid waste generated, particularly after chromium removal, contains minerals such as phosphorus (P) and potassium (K), which are categorized into 4R (reduce, reuse, recycle, and recover) dimensions. Integrating advanced wastewater treatment methods and resource recovery processes in the leather industry not only helps mitigate environmental impacts but also aligns with broader sustainability objectives, embodying a responsible and forward-thinking approach to wastewater management. Combining effective wastewater treatment in the leather industry is a cornerstone of sustainable environmental management. The emphasis on recovering valuable substances and repurposing solid waste underscores a holistic and responsible approach toward resource utilization. This comprehensive strategy indeed reflects a commitment to environmental stewardship and sustainability in the leather industry.

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Introduction:

The leather industry, though not one of the largest globally, holds significance in regional economies and has historical roots as one of the oldest industrial practices (Chen et al., 2023). Tanning, a key process within the industry, serves to transform raw animal hides into stable leather products and prevent decay (Dowlath et al., 2021). This process involves three main stages: collection and pre-treatment of raw hides, tanning with appropriate agents, and final drying and finishing before the end product reaches the manufacturers (Saxena et al., 2017; Mwondu, 2017). Mineral and vegetable tanning are the two main types, with chrome tanning, a form of mineral tanning, still predominating in the leather industry (Hu et al., 2011; Adiguzel-Zengin et al., 2017).

The leather-making process involves substantial water usage, as hides are transformed into leather in aqueous mediums containing various chemicals (Hansen et al., 2021). Approximately 40-45 liters of water are utilized per kilogram of rawhide processed into finished leather (Sundar et al., 2001). However, a significant environmental concern arises as about 90% of the total water used in the manufacturing process of pesticides is released into the environment as waste (Gruiz, 2015; Wang et al., 2016). This highlights the importance of addressing water consumption and implementing effective wastewater treatment measures in the leather industry for environmental sustainability (Karuppiah et al., 2021).

The significant amounts of waste generated from lethal manufacturing processes contain substantial chemical oxygen demand, biochemical oxygen demand, suspended and dissolved solids, chromium, surfactants, and other toxic materials (Azom et al., 2012; Jahan et al., 2014; Das et al., 2022). The complexity and wide-ranging nature of the leather industry, coupled with the extensive use of chemicals, make the treatment of tannery wastewater challenging (Wang et al., 2018). The need for isolation and separate treatment of each departmental flow necessitates considerable investments in terms of equipment and land, further emphasizing the intricate nature of addressing environmental concerns in the lethal processing sector (Ghulam & Abushammala, 2023).

Various methods exist for treating tannery wastewater (Droste & Gehr, 2018; Zhao & Chen, 2019). Physicochemical techniques commonly employed in wastewater treatment can be applied to tannery wastewater, either in the whole process or in specific steps (Elabbas et al., 2016). However, these processes may incur high costs. The selection of treatment operations is influenced by the contamination level in the water, which is directly involved in the production process, legal compliance for water discharge, and considerations such as a communal wastewater treatment plant sending water, the municipal collector, or the potential for reuse within the production process (Deghles & Kurt, 2016). The complexity of these factors underscores the need for a tailored and strategic approach to tannery wastewater treatment (Lofrano et al., 2013).

Wastewater treatment involves a range of methods, including physicochemical and biological processes, and often a combination of both. Conventional methods for wastewater treatment include physical techniques such as aerobic and anaerobic treatment, chemical processes such as precipitation, oxidation, ozonization, electrochemical methods, and mechanical treatment. The industry addresses pollutants such as COD, BOD, TDS, Cr(III), chloride, sulfate, and heavy metals. In tannery wastewater treatment, some facilities may opt for a comprehensive approach, employing various treatments on-site (Kowalik-Klimczak & Gierycz, 2014; Jahan et al., 2014: Thakur et al., 2021). This can involve separating different streams, chemically treating tanning yard wastewater to precipitate chromium, physically treating tanning yard wastewater to precipitate chromium, physically treating chloride-laden soaking wastewater, and employing biological treatment for the remaining effluent. Alternatively, tanneries may choose to conduct pre or partial treatment before sending the effluent to a central or municipal treatment plant (Stoller et al., 2013). Consequently, wastewater treatment becomes a pivotal aspect of mitigating impact and a cornerstone of sustainable environmental management (Yong et al., 2016).

The leather industry, although economically significant for many emerging countries, presents a substantial environmental challenge characterized by elevated pollution levels (Kanagaraj et al., 2020). The discharge of untreated water laden with diverse chemicals intensifies this environmental impact, generating a significant volume of effluent throughout the leather-making process (Ricky et al., 2022). Addressing this environmental concern requires the effective treatment and detoxification of tannery wastewater (Saxena et al., 2017). While conventional methods exhibit limitations, this paper explores the potential of membrane technologies as a promising solution (Obotey Ezugbe & Rathilal, 2020). The comprehensive review encompasses an examination of environmental pollution and toxicity aspects of tannery wastewater, a discussion of traditional treatment methods, and an in-depth exploration of membrane technologies. The evaluation extends to advancements in membrane treatment approaches, considering both laboratory and pilot/industrial scales. The paper underscores the potential role of membrane technologies in mitigating the environmental challenges associated with tannery wastewater. Furthermore, it explores integrating membrane treatments with physicochemical and biological methods, offering a nuanced perspective on sustainable solutions for the leather industry (Table 1). This commitment to responsible practices not only minimizes environmental impact but also aligns with various sustainable development goals (SDGs) (Zimon et al., 2020). Additionally, the industry’s focus on resource recovery, including valuable substances from treated wastewater and repurposing solid waste, further demonstrates a 4R (reduce, reuse, recycle, and recover) approach (Fan et al., 2020). Integrating advanced wastewater treatment methods underscores a forward-thinking approach to wastewater management, reflecting a dedication to environmental stewardship and sustainability in the leather industry (Hasan et al., 2023). The economic importance of the leather industry is clear, notably in countries like India where it significantly contributes to foreign exchange earnings. Nevertheless, the concentrated presence of tanneries necessitates continuous efforts to address potential environmental and health impacts. Regulatory measures and ongoing mitigation initiatives are essential for fostering sustainable development in the leather industry.

Table 1: Conventional waste treatment methods (Kowalik-Klimczak & Gieryoz, 2014; Gadlula et al., 2019).

Method	Advantages	Disadvantages
Precipitation	The precipitation of chromium (III) from wastewater is a common method used in water treatment to reduce its concentration to desired levels. The process involves introducing a precipitating agent that reacts with chromium (III) ions in the water, forming insoluble precipitates. These precipitates can then be separated from the water through processes such as sedimentation, filtration, or centrifugation.	The precipitation method for chromium (III) removal from wastewater, while effective in reducing chromium (III) concentrations, may not be selective enough. This lack of selectivity can lead to the co-precipitation of impurities or the inclusion of other metal ions along with chromium (III) in the precipitates. Such co-precipitation can result in a poor quality of the recovered chromium (III).
Activated Sludge	Activated sludge is a widely employed biological treatment process in wastewater treatment plants, offering several advantages and making it a popular choice for effectively removing pollutants from wastewater.	Activated sludge systems are sensitive to sudden increases in influent concentrations or flow rates, referred to as shock loads. The occurrence of foam and bulking sludge can transpire in activated sludge systems, especially when the microbial community is not well-balanced.
Biological methods	The reduction of chromium (III) in wastewater by approximately 94% indicates a substantial removal efficiency, suggesting that the treatment process is effective in lowering the concentration of chromium (III) to a significantly reduced level.	The pH of the effluent within the range of 6-9 is important for several reasons in the context of wastewater treatment, especially when dealing with chromium removal.
Ion exchange	The durability and ease of regeneration are important factors when considering the use of ion exchange beds in water treatment	The oxidation of chromium(III) to chromium(VI) before the process is probably driven by the desire to achieve a specific oxidation state

	processes. Ion exchange is a widely used method for removing and recovering specific ions from water.	for chromium. This conversion is often necessary for certain tanning processes in the leather industry, where chromium(VI) facilitates better fixation of the metal onto the leather fibers.
Sequencing Batch Reactor (SBR)	SBRs offer operational flexibility, enabling the execution of various treatment phases (fill, react, settle, and decant) within the same tank. BRs can attain high levels of treatment efficiency, ensuring the outstanding removal of organic matter, nutrients (such as nitrogen and phosphorus), and suspended solids. In comparison to continuous flow systems, SBRs may have a smaller footprint due to the consolidation of multiple treatment steps within a single tank.	SBRs require sophisticated control systems to manage the sequencing of various phases (fill, react, settle, and decant). The initial capital costs for constructing SBRs can be relatively high compared to those of some other wastewater treatment technologies.
Carbon adsorption	Selectivity concerning anions, particularly in the context of solutions containing sulfate, chloride, or bicarbonate anions, implies the ability of a purification method or material to preferentially target and remove specific anions while leaving others relatively unaffected.	The low sorption capacity of activated carbon and the frequent need for regeneration can be influenced by several factors related to the properties of the activated carbon and the specific application.
Solvent extraction	High-efficiency solvent extraction is crucial for various industrial processes, including the separation and purification of valuable substances from complex mixtures. Solvent extraction, also known as liquid-liquid extraction, is a widely used technique for selectively extracting target compounds from liquid matrices.	The requirement for a significant quantity of extractable organic substances, particularly when handling toxic and flammable solvents in solvent extraction processes, poses both challenges and considerations for industrial applications. While solvent extraction is a potent technique for separating and purifying

		compounds, utilizing substantial amounts of potentially hazardous solvents necessitates careful management to guarantee safety, regulatory compliance, and environmental responsibility.

Distribution of leather industry:

The era of industrialization has indeed yielded substantial economic benefits for both developing and developed nations. Leather tanning has flourished worldwide, finding significant footholds in countries such as India, Bangladesh, China, Pakistan, Turkey, and Brazil. In India, the tannery, tannery products, tannery garments, and footwear industries play a substantial role in the economy, ranking among the country's top 10 foreign exchange earners (Rhys-Taylor, 2018; Leather Dictionary, 2021). India's global position in the leather industry is significant, ranking second in the world for exports of leather garments, third for saddles and harnesses (UNIDO, 2000), and fourth for leather goods. A total export value of $3.68 billion in 2020-2022 underlines its significant contribution to international trade. India's role as a major exporter of finished leather (Figure 1) (UN Com-trade database, 2022), India has more than 2,000 tanneries and an annual production of around 2 billion square feet of leather (Bhardwaj et al., 2023). India's position as one of the largest producers of leather in the world is evident, with a significant concentration of tanneries in various states. Tamil Nadu is followed by West Bengal, Uttar Pradesh, Punjab, Maharashtra, Andhra Pradesh, and other states, highlighting the wide distribution of this industry across the country (Bhardwaj et al., 2023) (Figure 2). This underscores its significant presence and impact in the global leather market.

Environmental Impact on the Leather Industry:

Leather waste poses environmental concerns due to its slow decomposition, releasing pollutants into soil and water (Kanagaraj et al., 2015). Improper disposal can contribute to land and water pollution, impacting ecosystems (Zahoor & Mushtaq, 2023). Additionally, leather production itself has environmental impacts, including deforestation for cattle farming and chemical use in tanning (Jones et al., 2021). The global water crisis, driven by factors like freshwater decline and water quality degradation, requires concerted efforts in sanitation, conservation, and industrial wastewater management. Sustainable practices and proper treatment of industrial effluents are crucial for safeguarding water resources and mitigating environmental contaminants.

The leather production process involves various batch processes, generating pollutants. Hazardous chemicals such as sodium hydroxide, pentachlorophenol, and sulfuric acid are utilized in over 175 different substances during tanning (Masood & Malik, 2014). The type of hides and tanning methods impact wastewater quality. The leather industry has created a negative impact causing environmental pollution. During leather processing, the process of tanning, liming, and soaking causes around 70 percent pollution of BOD, COD, and total dissolved solids (TDS) (Islam et al., 2014). Soaking, liming, and deliming processes generate large exposure of wastewater with high amounts of sulfide, lime, ammonium salt chloride sulfate, and proteins. The wastewater contains a high amount of BOD and COD loads. Wastewater treatment contributes to the emission of volatile organic compounds (Noyola et al., 2006). The solid waste generated, particularly after chromium removal, contains minerals such as phosphorus (P) and potassium (K). Chromium removal is important because exposure to Chromium (VII) and chromium (III) can lead to cancerous disease (Ashar et al., 2022; Saha et al., 2022).

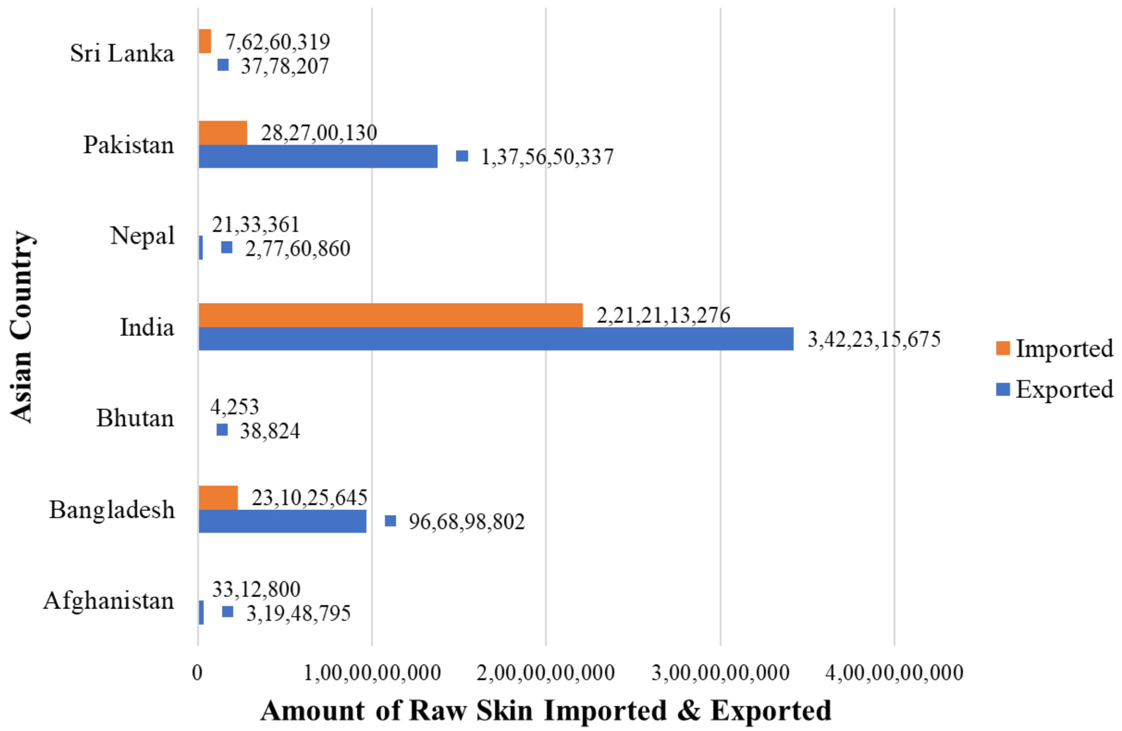

Figure 1. This diagram shows the import and export amount of raw skin in different countries of South Asia in 2000, 2005, 2010, 2015, 2019, and 2023. India is the highest importer as well as exporter of skin content throughout the world (UN Com-trade database, 2022).

Reduction/Recycling/Recovery/Reuse:

The leather industry can adopt sustainable practices for wastewater treatment through reduction, recycling, recovery, and reuse. Reducing water consumption is a crucial initial step in sustainable water management for the leather industry (Christopher et al., 2016). Precision in measurement and control, adopting technologies like low float processing and batch-type washing, and optimizing processes through compact recipes can significantly cut water usage by 30% or more (Liu et al., 2022). Recycling floats in specific processes, such as soaking, liming, unhairing, pickling, and chrome tanning liquors, holds great potential for substantial water savings in the leather industry (Liu et al., 2022). Implementing treatment installations for recycling can lead to a significant reduction in overall water consumption, ranging from 20-40% (Daigger, 2009). Biologically treated effluent presents an opportunity to substitute a portion of process floats, like those in the beam house process, with treated water (Lofrano et al., 2013). The effectiveness of this method depends on the type and efficiency of the treatment process. Membrane systems offer the potential for reusing treated effluents, given the effective removal of residual organic matter and the ability to manage the disposal of the concentrate. This technology enables a more advanced level of water treatment, allowing industries like leather production to recycle and reuse water in their processes. To maintain environmental sustainability in the overall wastewater treatment strategy.

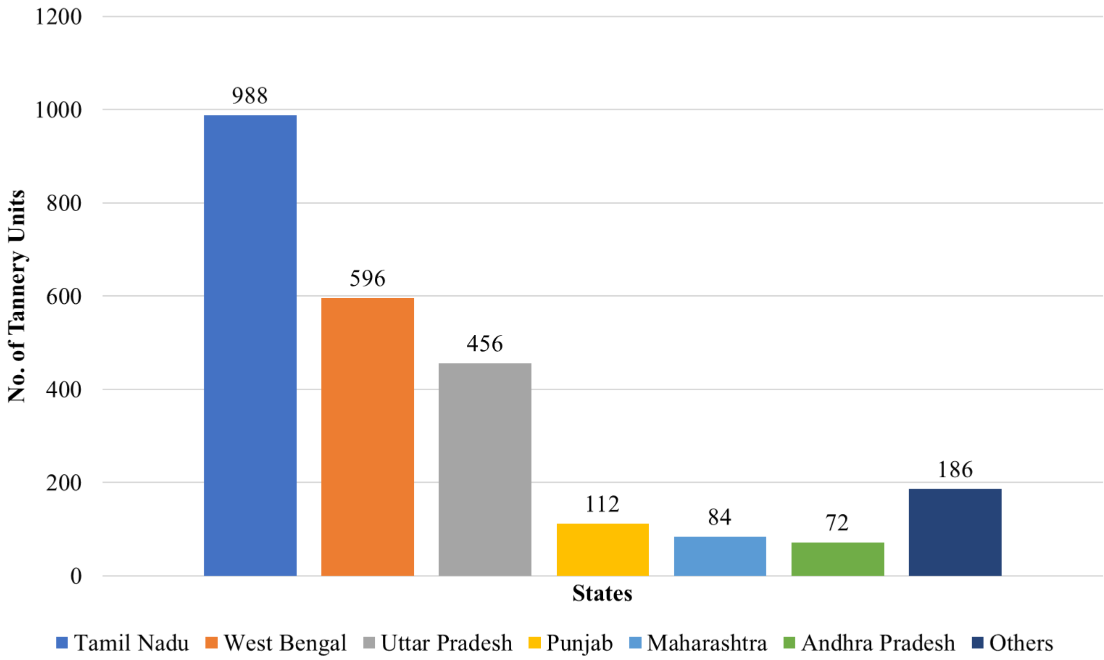

Figure 2. State-wise distribution of tanneries in India.

Sustainable Development Goals in the Leather Industry:

The leather industry plays an economically important role for other businesses but hurts the environment. For this purpose, the leather industry started 17 sustainable developmental goals. The United Nations defined these sustainable developmental goals in 2015 (Mukherjee et al., 2022). Sustainable manufacturing in leather is important in the long term for the reduction of the effects of waste materials on the environment (Omoloso et al., 2021). These include an increase in competitiveness globally (Smith & Ball, 2012), product safety (Gupta et al., 2018), quality improvement, and reduced operational costs (Roberts, 2014), as well as an increment in the health profile and safety of employees. The 2030 Agenda for Sustainable Development Goals encompasses a comprehensive approach, addressing People, Planet, Prosperity, Peace, and Partnerships (Lim et al., 2018). The integration of these goals into the leather industry, particularly focusing on Clean Water, Decent Work, Responsible Consumption, and Partnerships, demonstrates the potential for a positive impact on economic, environmental, and social aspects. The leather industry not only helps mitigate environmental impacts but also aligns with broader and long-term sustainability goals (Lim et al., 2018). Sustainable Developmental Goals embody a responsible and forward-thinking approach to wastewater management, which leads to the reduction of the harmful effects of wastewater from the leather industry on the flora and fauna of the ecosystem and human beings. A holistic and responsible approach towards resource utilization is included in these goals. Environmental stewardship lies in every manufacturing industry. For the sustainability of the industry, wastewater management and solid waste management should be emphasized. SDGs drive the leather industry towards circularity by promoting sustainable production, waste reduction, and responsible consumption, aligning with goals such as responsible consumption and production (SDG 12) and sustainable cities and communities (SDG 11) (Saha, 2023).

Tannery Effluent Treatment Technologies:

Wastewater treatment techniques for managing post-treated effluents (PTEs) emphasize effectiveness, effluent types, main parameters, and study specifics. Common treatment methods mentioned include coagulation/flocculation, advanced oxidation processes, biological treatment, membrane separation processes, adsorption, and hybrid methods (Christopher et al., 2016).

Coagulation/flocculation:

The tanning industry is one of the oldest industries in the world. For sustainable development, wastewater is treated in various ways for detoxification. In the physical method, firstly, filtration and then electrocoagulation are done. In this process, wastewater is treated with $FeCl_3$ (coagulant) at a dose of 150 mg/L at neutral pH for detoxification (Chowdhury et al., 2013).

Adsorption:

In the leather industry, dye is used to achieve deep colors on leather. Due to the use of dye, wastewater becomes colored, creating complexity in wastewater management. Adsorption is an advanced treatment that can enhance wastewater quality. The Plackett–Burman factorial design eliminates certain factors, essentially focusing on important parameters for adsorption (Gomes et al., 2016).

Chemical precipitation:

The leather industry is not environmentally friendly (Yusuf & Agustina, 2023). Chromium is used in the processing of animal hides. Chemical precipitation is mainly done to recover heavy metals and inorganic substances, i.e., chromium, from wastewater (Kurniawan et al., 2006). Once the pH is adjusted, the metal ions that were dissolved in wastewater are converted into insoluble solids. This is done by a chemical reaction by adding alkali, which helps to precipitate the metal as hydroxide. For example, when chromium ions precipitate, they precipitate as chromium hydroxide (Mella et al., 2013).

Ozonation:

Ozonation is a wastewater treatment method that involves the use of ozone (O_3), a powerful oxidizing agent, to treat water or industrial effluents. In the context of the leather industry, ozonation can be applied to treat tannery effluents. Wastewater treatment plants are mainly used to reduce organic materials such as BOD. Ozone is primarily used for discoloration of wastewater that is colored through residual dyes (Srinivasan et al., 2009).

Electro oxidation:

The leather industry generates a large amount of wastewater. De-liming is a process in which 4.5 L of wastewater is generated per one kg pelt. Electro-oxidation is mainly used to remove organic material from wastewater. The treatment is evaluated for Biological Oxygen Demand, Chemical Oxygen Demand, and Kjeldahl Nitrogen. Electro-oxidation is considered the most effective process to prepare de-liming wastewater for reuse for various purposes such as soaking, etc. (Sundarapandiyan et al., 2018).

Photo catalytic oxidation:

Wastewater from the leather industry contains various organic substances. The separation of this organic material is achieved through the solvent extraction process (Natarajan et al., 2013). In this process, two photocatalysts are employed: TiO_2 and ZnO_2. The experiment is conducted using UV radiation and follows the Box-Behnken design method. Three key parameters are essential in this method, namely the concentration of the catalyst, pH, and the use of hydrogen peroxide as a co-oxidant (Abdollahi et al., 2020).

Fenton oxidation:

Nowadays, biochemical processes are undergoing a trial process for detoxifying waste materials (Anastasi et al., 2011). Fenton's reagent (6g $FeSO_4$, 266g H_2O_2 in a liter of wastewater) is employed in the advanced oxidation process to degrade wastewater. In this treatment, a pH of 3.5 is required, and at 30^{o}C for 30 minutes under batch conditions, it leads to the reduction of BOD, COD, sulfide, and total chromium content (Mandal et al., 2010).

Biological treatment:

Biological wastewater treatment in the leather industry involves utilizing microorganisms to break down and eliminate organic pollutants from tannery effluents (Huang et al., 2015).

Hybrid treatments:

Advanced Oxidation and Nano-filtration are used together as a hybrid treatment for wastewater management. This treatment is employed to prepare wastewater for reuse.

Chromium (99.5%), COD (>99%), and TDS (>96%) are successfully removed by this process, but essential ions, i.e., Ca^{2+} and Mg^{2+}, are retained in the water (Pal et al., 2020).

Membrane Separation Process:

Membrane separation processes play a crucial role in removing dissolved compounds from tannery wastewater, employing methods such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration (Moreira et al., 2022). Scientific studies indicate that nanofiltration membranes effectively reduce the most pollution levels, followed by reverse osmosis membranes. Nanofiltration membranes can separate multivalent ions, while reverse osmosis membranes accumulate isolated monovalent ions. Ultrafiltration membranes eliminate solutes with molecular weights greater than 1,000 Da. Pore size alone does not determine pollutant elimination; membrane surface charge, influenced by pH, is also critical (Bhardwaj et al., 2023). However, membrane separation processes have drawbacks, including high energy consumption, leading to operational costs, and membrane fouling, reducing efficiency and increasing maintenance expenses. Chemical cleaning agents used for fouling removal may generate hazardous waste, requiring careful handling. Sensitivity to influent wastewater quality variations and the need for pre-treatment to prevent fouling are additional considerations (Gadlula et al., 2019).

Treated Effluent Reuse options:

The amount of pollutants allowed in treated tannery wastewater for reuse is governed by standards. These standards typically set thresholds for parameters such as total suspended solids (TSS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) (Sugasini & Rajagopal, 2015). Waste reuse is crucial to sustainable water management, as regulated by global environmental organizations. The standards set by these agencies ensure that reused wastewater meets certain quality criteria, preventing adverse environmental impacts. Examples of regulatory agencies include the Environmental Protection Agency (EPA) in the United States, the Urban Wastewater Treatment Directive in the European Union, the Central Pollution Control Board (CPCB) in India, and the Ministry of Environmental Protection (MEP) in China (UNESCO, 2021). Waste recycling is also emphasized (UNESCO, 2021).

Conclusion:

In conclusion, the revolutionization of leather industry wastewater treatment represents a monumental stride towards sustainable environmental management. Through innovative technologies and approaches, such as advanced filtration systems, enzymatic treatments, and bio-based remediation processes, significant progress has been made in mitigating the adverse impacts of leather production on water resources and ecosystems. This game-changing approach not only addresses the longstanding challenges of pollution associated with leather manufacturing but also underscores the industry's commitment to environmental stewardship and corporate responsibility. Furthermore, the adoption of sustainable wastewater treatment practices in the leather industry offers multifaceted benefits. Beyond environmental conservation, it enhances operational efficiency, reduces regulatory compliance burdens, and fosters positive relationships with stakeholders and communities. By prioritizing sustainability in wastewater management, leather manufacturers can position themselves as leaders in responsible production, thereby gaining a competitive edge in the global market. However, continued collaboration between industry stakeholders, governments, and research institutions is essential to further optimize wastewater treatment processes, scale up innovative technologies, and ensure widespread implementation across the sector. Together, we can build a more sustainable future where economic prosperity and environmental protection go hand in hand, setting a precedent for other industries to follow suit.

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