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APPLICATION OF THE DISCRETE LEAST SQUARES METHOD TO MEASUREMENTS OF CHEMICAL OXYGEN DEMAND IN TANNERY EFFLUENTS

APLICACIÓN DEL MÉTODO DE MÍNIMOS CUADRADOS DISCRETOS A MEDICIONES DE DEMANDA DE OXÍGENO QUÍMICO EN EFLUENTES DE CURTEMBRES

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Abstract

The tanning process is the process of treatment and transformation of animal skin into leather, where said process resides especially in the addition to the skins of a series of tanning products such as chrome salts, among others. In this sense, it can be said that, in the present investigation, the physicochemical and microbiological behavior of the reactor was studied during the leather process in the industries, which has been increasing this activity in the behavior of the wastewater produced by the producers. leather, taking into account that they need more efficient systems for the treatment of effluents generated in this sector. This is how, for the development of this research, a reactor was managed per load with a useful volume of 2 liters that worked in aerobic circumstances with 24-hour cycles. Likewise, for the development of this investigation, it was possible to progressively increase the concentration of the effluent from the tannery, taking into account the DQO and the count of heterotrophic microorganisms, which were the main variables studied during the investigation. Finally, biodegradable DQO removals achieved at the end of the acclimatization process were 57.9% for DQOt and 76.8% for DQOs, also presenting little significant amount of heterotrophic bacteria in the effluent.

Keywords: Reactor, acclimatization, tannery effluent, DQO

Resumen

El proceso de curtido es el proceso de tratamiento y transformación de la piel animal en cuero, donde dicho proceso reside especialmente en la adición a las pieles de una serie de productos curtientes como las sales de cromo, entre otros. En este sentido, se puede decir que, en la presente investigación, se estudió el comportamiento fisicoquímico y microbiológico del reactor durante el proceso del cuero en las industrias, lo que ha ido incrementando esta actividad en el comportamiento de las aguas residuales producidas por los productores cuero, teniendo en cuenta que necesitan sistemas más eficientes para el tratamiento de los efluentes generados en este sector. Es así como para el desarrollo de esta investigación se manejó un reactor por carga con un volumen útil de 2 litros que trabajó en circunstancias aeróbicas con ciclos de 24 horas. Asimismo, para el desarrollo de esta investigación se logró aumentar progresivamente la concentración del efluente de la curtiduría, teniendo en cuenta el DQO y el recuento de microorganismos heterótrofos, que fueron las principales variables estudiadas durante la investigación. Finalmente, las remociones de DQO biodegradables logradas al final del proceso de aclimatación fueron del 57,9% para DQOt y del 76,8% para DQOs, presentando además cantidades poco significativas de bacterias heterótrofas en el efluente.

Palabras Clave: Reactor, aclimatación, efluente de curtiembre, DQO

Introduction

The production process carried out in tanneries involves transforming animal hides into leather. This process is divided into four stages: cleaning, tanning, retanning, and finishing. The purpose of the tanning process is to seek the highest quality material that is not in a state of decomposition. These industries are characterized by consuming large volumes of water, leading to the generation of substantial and highly contaminated effluents that are challenging to treat. This is primarily due to the use of various chemical reagents such as surfactants, organometallic dyes, natural tanning agents, and chromium salts during leather production (Bhardwaj et al., 2023).

In these industries, water is used as a raw material and is considered a vital element in leather production. The water used traverses the production process and becomes laden with contaminants. Consequently, the quantity of wastewater originating from various industries, along with daily and hourly fluctuations, contributes to significant pollution (Kumar et al., 2023).

As a result, wastewater generated in the tanning industry is primarily characterized by a high organic load, elevated conductivity, and the presence of heavy metals, such as chromium. Studies conducted by various researchers demonstrate that the effluents generated during the production processes in tanneries generally exhibit high concentrations of Chemical Oxygen Demand (COD), ranging from 2,000 to 60,000 mg/L. Between 79% and 83% of this COD corresponds to the biodegradable fraction of the total COD, while the remainder is non-biodegradable. Additionally, these effluents contain high concentrations of Total Kjeldahl Nitrogen (TKN), NH4+, suspended solids (SS), and chromium (Oliveira et al., 2021).

Theoretical framework

Fundamentals of Leather Tanning Processes

The leather industry has been an integral part of human civilization for centuries, providing a versatile material with numerous applications. One of the crucial processes involved in transforming raw hides and skins into leather is tanning. Tanning is a complex chemical process that stabilizes the collagen structure of the hides, rendering them resistant to putrefaction and imparting desired properties such as flexibility, durability, and appearance.

The tanning process can be broadly categorized into two main types: chrome tanning and vegetable tanning. Chrome tanning, which involves the use of chromium salts, is the predominant method employed in modern leather production due to its efficiency and versatility (Hasan et al., 2021). Vegetable tanning, on the other hand, utilizes natural tannins derived from various plant sources, such as bark, leaves, and fruits, and is known for producing high-quality leathers with unique characteristics

The fundamental principles of leather tanning lie in the chemistry of collagen, the primary structural protein found in hides and skins. Collagen is a fibrous protein with a triple-helix structure, and its stabilization is essential for the production of leather. During the tanning process, tanning agents interact with the collagen fibers, forming cross-links that prevent the collagen from undergoing putrefaction and impart the desired properties to the leather (Rajan et al., 2023).

In chrome tanning, the chromium salts, typically basic chromium sulfate, react with the carboxyl groups of the collagen molecules, forming coordinative cross-links This cross-linking process results in improved thermal stability, resistance to biodegradation, and increased hydrothermal stability of the leather However, the environmental impact of chromium tanning has been a subject of concern, leading to the development of alternative tanning methods and strategies for chromium recovery and recycling (Xu et al., 2017).

Vegetable tanning, on the other hand, employs polyphenolic compounds known as tannins, which are extracted from various plant sources. These tannins form hydrogen bonds and hydrophobic interactions with the collagen fibers, resulting in a dense, rigid structure (Etuk and Ojekudo, 2015). Vegetable-tanned leathers are known for their unique characteristics, such as increased resistance to heat, water, and abrasion, as well as their distinctive color and aroma (Doulah, 2018).

Recent advancements in leather tanning have focused on the development of eco-friendly and sustainable practices. One such approach is the use of alternative tanning agents, such as aluminum, titanium, zirconium, and silica-based compounds. (Milenkovic and Bojovic, 2014). These tanning agents offer potential advantages in terms of reduced environmental impact and improved leather properties.

Furthermore, researchers have explored the incorporation of natural and renewable materials, such as plant extracts and biopolymers, into the tanning process. These materials can serve as tanning agents or auxiliaries, contributing to the development of more sustainable and environmentally friendly leather production methods (Devi et al., 2023).

Overall, the fundamentals of leather tanning processes lie in the understanding of collagen chemistry and the interactions between tanning agents and collagen fibers. As the industry continues to evolve, the pursuit of eco-friendly and sustainable practices, coupled with advancements in tanning technologies, holds promise for the future of leather production.

Overview of Leather Production Stages

The leather industry is a complex and multifaceted sector that involves various stages to transform raw hides and skins into finished leather products. Each stage plays a crucial role in determining the quality, properties, and characteristics of the final product. This theoretical framework aims to provide an overview of the primary stages involved in leather production, highlighting their significance and the latest advancements in the field.

The production of leather begins with the procurement of raw hides and skins, which are byproducts of the meat industry or obtained from animals specifically raised for their hides (Tian 2020). These raw materials undergo several preparatory stages, including trimming, curing, and soaking, to remove unwanted materials and prepare the hides for subsequent processes.

The next stage, known as liming, involves the immersion of the hides in a lime-based solution, which facilitates the removal of hair, epidermis, and other unwanted components (Zhang et al., 2022). This process also initiates the swelling and opening up of the collagen structure, preparing the hides for further processing.

Following liming, the deliming and bating stages are carried out to remove residual lime and facilitate the breakdown of non-fibrous proteins, respectively (Moeeni et al., 2017). These steps ensure proper preparation for the subsequent tanning process, which is the pivotal stage in leather production.

Tanning is the process of stabilizing the collagen structure of the hides, rendering them resistant to putrefaction and imparting desired properties (Fashae et al., 2019). Various tanning methods exist, with chrome tanning and vegetable tanning being the most prevalent. Chrome tanning involves the use of chromium salts, while vegetable tanning employs natural tannins derived from plant sources (Kramar and Alchakov, 2023).

After tanning, the leather undergoes a series of post-tanning operations, including slamming, setting, and dyeing, to improve its appearance, physical properties, and color (Kanagaraj et al., 2020) These processes are essential for achieving the desired aesthetic and functional characteristics of the leather.

Chemical and Environmental Implications of Tanning

The tanning process, which is an essential component of leather production, has significant chemical and environmental implications that require careful consideration. Despite the importance of the leather industry, the use of hazardous chemicals and the generation of pollutants during tanning operations pose potential risks to human health and the environment. This

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theoretical framework aims to explore the chemical aspects of tanning and their associated environmental impacts, as well as the strategies and approaches being developed to mitigate these challenges.

One of the primary concerns in the tanning industry is the use of chromium salts, particularly basic chromium sulfate, in the chrome tanning process. Chromium (III) compounds are widely employed due to their effectiveness in stabilizing collagen fibers and imparting desirable properties to the leather (Nur et al., 2020). However, the potential conversion of chromium (III) to the more toxic and carcinogenic chromium (VI) form under certain conditions has raised concerns regarding its environmental impact and occupational exposure (Oruko et al., 2021).

The disposal of tanning effluents containing chromium and other pollutants poses a significant challenge. These effluents often contain high levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and suspended solids, which can have detrimental effects on aquatic ecosystems if not properly treated. Furthermore, the presence of toxic substances, such as sulfides, amines, and phenolic compounds, further exacerbates the environmental impact (Tisha et al., 2020).

To address these issues, various strategies have been explored to minimize the environmental footprint of tanning processes. One approach is the recovery and recycling of chromium from tanning effluents, which not only reduces the amount of chromium discharged into the environment but also facilitates the reuse of this valuable resource (Hira et al., 2022). Techniques such as membrane filtration, ion exchange, and chemical precipitation have been employed for chromium recovery, with ongoing research aimed at improving their efficiency and cost-effectiveness (Niamat et al., 2023).

Characterization of Organic and Inorganic Contaminants

The presence of organic and inorganic contaminants in various environmental matrices, such as water, soil, and air, poses significant challenges to human health and ecological systems. Accurate characterization of these contaminants is crucial for understanding their sources, behavior, and potential impacts, as well as developing effective mitigation strategies. This theoretical framework aims to explore the analytical techniques and methodologies employed in the characterization of organic and inorganic contaminants, highlighting the latest advancements and challenges in this field.

Organic contaminants encompass a diverse range of compounds, including persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), pesticides, pharmaceuticals, and personal care products (PPCPs), among others

(Yadav et al., 2020). These compounds can originate from various sources, such as industrial activities, agricultural practices, and domestic activities, and can have adverse effects on human health and the environment due to their persistence, bioaccumulation potential, and toxicity.

The characterization of organic contaminants often relies on advanced analytical techniques, such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). These hyphenated techniques provide high sensitivity, selectivity, and structural information, enabling the identification and quantification of trace levels of organic compounds in complex matrices. Additionally, sample preparation methods, such as solid-phase extraction (SPE) and QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe), play a crucial role in concentrating and isolating the target analytes from the sample matrix, improving analytical performance (Han et al., 2016).

Inorganic contaminants, on the other hand, encompass a wide range of elements and compounds, including heavy metals, metalloids, and radionuclides. These contaminants can originate from natural sources, such as geological formations and volcanic activities, as well as anthropogenic sources, including industrial processes, mining activities, and the use of fertilizers and pesticides. Exposure to inorganic contaminants can have detrimental effects on human health and the environment, as many of these substances are toxic, persistent, and can bioaccumulate in the food chain (Zhang et al., 2021).

The characterization of inorganic contaminants typically involves the use of advanced instrumental techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), and X-ray fluorescence (XRF). These techniques offer high sensitivity, multi-element analysis capabilities, and the ability to determine speciation and isotopic composition of inorganic contaminants. Sample preparation methods, such as acid digestion, extraction, and preconcentration, are often required to ensure accurate and reliable analysis of inorganic contaminants in various matrices (Al-Jabari et al., 2021).

Principles of Aerobic and Anaerobic Digestion

Waste management and resource recovery are critical challenges in modern societies, and biological processes such as aerobic and anaerobic digestion play a crucial role in addressing these issues. These processes involve the breakdown of organic matter by microbial communities, leading to the production of valuable products and the stabilization of waste materials. This theoretical framework aims to explore the fundamental principles governing aerobic and anaerobic digestion, highlighting their applications, benefits, and recent advancements in the field.

Aerobic digestion, also known as composting, is a process in which organic matter is decomposed by aerobic microorganisms in the presence of oxygen. This process involves a complex consortium of microorganisms, including bacteria, fungi, and actinomycetes, which work together to break down the organic matter through a series of metabolic pathways. The main stages of aerobic digestion include the mesophilic phase, where readily biodegradable compounds are consumed, and the thermophilic phase, where more recalcitrant materials are degraded at higher temperatures (Sharma and Vuppu, 2023).

The aerobic digestion process is influenced by various factors, such as the composition of the organic matter, moisture content, aeration rate, pH, temperature, and the presence of inhibitory compounds. Proper management of these factors is crucial for optimizing the process and ensuring efficient decomposition of the organic matter. The end products of aerobic digestion include a stabilized organic material called compost, which can be used as a soil amendment, and carbon dioxide, which is released into the atmosphere (Auad et al., 2020).

In contrast, anaerobic digestion is a process that occurs in the absence of oxygen, where organic matter is broken down by a consortium of anaerobic microorganisms, primarily bacteria and archaea. This process involves a series of complex biochemical reactions, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis, resulting in the production of biogas, a mixture of methane and carbon dioxide, as the primary end product (China et al., 2020).

Anaerobic digestion is widely used for the treatment of various organic waste streams, such as municipal solid waste, agricultural residues, industrial wastewater, and sewage sludge. The process offers several advantages, including the production of renewable energy in the form of biogas, reduction of waste volume and greenhouse gas emissions, and the generation of a nutrient-rich digestate that can be used as a fertilizer or soil amendment (Fraga et al., 2020).

Theoretical Basis of COD Measurement

The measurement of Chemical Oxygen Demand (COD) is a widely used analytical technique in various fields, including environmental monitoring, wastewater treatment, and industrial process control. COD serves as an important parameter for assessing the organic matter content and the degree of pollution in water and wastewater samples. This theoretical framework aims to explore the fundamental principles and methodologies underlying COD measurement, highlighting recent advancements and challenges in this area.

The COD value represents the amount of oxygen required to chemically oxidize the organic matter present in a sample under specific conditions. Traditionally, the COD measurement involves the use of a strong oxidizing agent, such as potassium dichromate, in an acidic environment, to oxidize the organic compounds in the sample (Naima et al., 2015). The reduction of the oxidizing agent is then measured, and the COD value is calculated based on the amount of oxidant consumed during the reaction.

The theoretical basis of the COD measurement lies in the principles of redox chemistry and the stoichiometry of the oxidation reactions. The choice of the oxidizing agent and the reaction conditions are crucial for ensuring accurate and reproducible results. Potassium dichromate is widely used as the oxidizing agent due to its strong oxidizing capability and its ability to oxidize a wide range of organic compounds, including those that are resistant to biological oxidation (Riguetto et al., 2020).

However, the traditional dichromate-based COD method has several limitations, including the use of hazardous chemicals, the generation of toxic waste, and the inability to oxidize certain organic compounds completely (Covington and Wise. 2020). To address these challenges, alternative methods for COD measurement have been developed, such as the manganese (III) oxidation method and the photocatalytic oxidation method (Khambhaty, 2020).

The manganese (III) oxidation method is based on the use of manganese (III) as the oxidizing agent, which is less hazardous than dichromate and can effectively oxidize a wide range of organic compounds (Sahu et al., 2022). This method has gained popularity due to its environmental friendliness and the potential for automation.

Methodology

This study employed a multifaceted approach to evaluate the efficiency of a discrete least squares method in assessing the treatment of tannery effluents, with a specific focus on the reduction of Chemical Oxygen Demand (COD). The methodology is structured into several key components as outlined below.

Reactor Setup and Operation

A cylindrical batch reactor constructed from transparent acrylic (polymethyl methacrylate) with a 3-liter capacity and a working volume of 2 liters was utilized. The reactor, measuring 50 cm in height and 10 cm in diameter, was equipped with three ports: an upper port for wastewater introduction, a middle port for effluent discharge, and a lower port for cleaning purposes.

The system was automated, utilizing digital timers to control the activation of electronic components within the treatment system.

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Wastewater loading was facilitated through a ¼" solenoid valve, enabling gravity-fed transfer from a feed container to the reactor. Effluent discharge was managed using a peristaltic pump, and aeration was provided by a fine bubble diffuser connected to a 3 PSI compressor, ensuring a minimum oxygen concentration of 2 mg/L within the reactor.

Acclimatization Process

The reactor was initially fed with synthetic water, mimicking the composition of tannery effluents, and granular biomass obtained from a laboratory-scale biological reactor. This phase aimed to acclimatize the microbial community to the specific contaminants present in tannery wastewater. Operational cycles of 1440 minutes (24 hours) were established, consisting of filling, oxic reaction, sedimentation, and discharge stages.

Analytical Procedures

The study's core analytical component focused on the measurement of COD to evaluate the organic matter concentration in the effluent before and after treatment. The discrete least squares method was applied to enhance the accuracy of COD measurements, allowing for the precise quantification of biodegradable and non-biodegradable fractions. Samples were taken at two-hour intervals, with additional measurements of temperature and pH conducted every 15 minutes to monitor the reactor's environmental conditions.

Wastewater Characterization

Tannery wastewater characterization involved assessing physical, chemical, and biological parameters, including pH, alkalinity, total and soluble COD, Total Kjeldahl Nitrogen (TKN), NH4+, and heavy metals content. This comprehensive analysis provided a baseline for evaluating the treatment process's efficiency.

Enhanced Acclimatization

Following the initial acclimatization with synthetic water, the reactor was gradually introduced to real tannery effluent, starting with a mixture of 80% synthetic water and 20% tannery effluent. This step aimed to adapt the microbial community to the more complex and variable composition of actual wastewater, thereby improving the treatment process's robustness and efficiency.

Data Analysis

Data collected throughout the study were analyzed using the discrete least squares method to determine the efficiency of COD removal and the overall performance of the treatment process. Statistical analysis was conducted to evaluate the significance of observed changes in COD levels, microbial activity, and other relevant parameters.

Results and discussion

Characteristics of the Biological Reactor

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In this study, a batch reactor with a cylindrical shape and a 3-liter capacity was used. The reactor was constructed from transparent acrylic (polymethyl methacrylate) with an effective volume of 2 liters. It had dimensions of 50 centimeters in height and 10 centimeters in diameter. The reactor featured three ports, which facilitated its operation. The upper port was located 34 cm from the bottom of the reactor and was used for the introduction of wastewater, while there were two lower ports. One of these was positioned 8 cm from the bottom and was used for discharging the treated effluent, and the other, located at the very bottom of the reactor, was used for cleaning.

The reactor operated in an automated fashion using digital timers to activate and deactivate the electronic components in the treatment system. The influent was introduced into the reactor by activating a ¼" solenoid valve, allowing gravity-fed loading from the feed container to the batch reactor. The discharge of treated wastewater was achieved using a peristaltic pump, enabling the effluent to exit the system and enter a receiving container. The aeration was provided through a fine bubble diffuser installed at the bottom of the reactor, connected to a 3 PSI compressor with a power rating of 2.5 watts/hour and a flow rate of 2,500 cc/min (Elite 801 model). During the aerobic phase, this system maintained a minimum oxygen concentration of 2 mg/L in the reactor (Figure 1).

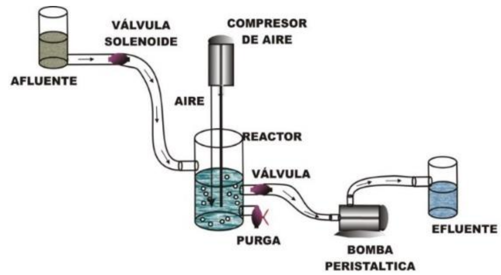

Figure 1. Sp Schematic of the batch reactor used in the research.

Characteristics of Granular Biomass

The reactor was fed with 2 liters of synthetic water (Table N. º 1) and 25 g/L of granular biomass. The biomass was obtained from another biological reactor used at the laboratory scale, which processed synthetic effluent with similar characteristics to that of the tannery (Zhu et al., 2020).

Table 1. Composition of Synthetic Water

Reagent	Quantity per 1 L
NH_4Cl	0,25 g
K_2HPO_4	0,045 g
$CaCO_3$	0,030 g
$MgSO_4.7H_2O$	0,025 g
$FeSO_4.7H_2O$	0.020 g
$NaCH_3COO$	4,5 g

In this context, to characterize the granular biomass at the beginning of the acclimatization process, biomass density was determined using the Archimedes' principle. Additionally, the average

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size of the granules was measured by randomly selecting 100 granules and determining their diameter with a graduated instrument. This process was conducted in triplicate to assess the physical characteristics of the biomass.

A natural selection process of the existing microorganisms was allowed through the system's operational cycles. This facilitated the growth and establishment of floc-forming microorganisms while eliminating filamentous bacteria that could cause delays in sedimentation times (Xu et al., 2022). The reactor operated with cycles of 1440 minutes (24 hours), each cycle divided into stages with specific durations as follows: filling for 15 minutes, oxic reaction for 1417 minutes, sedimentation for 2 minutes, and discharge for 6 minutes (Xu et al., 2022).

Chemical Oxygen Demand (COD) Profile vs Time

Chemical Oxygen Demand (COD) represents the amount of oxygen required to oxidize organic components in a specific type of water under specific conditions of oxidant, temperature, and time. In this context, COD is a measurement that quantifies the amount of readily oxidizable dissolved or suspended substances by chemical methods in a liquid sample. It is used to gauge the level of contamination emitted in milligrams of diatomic oxygen per liter (mgO2/L).

The COD (Chemical Oxygen Demand) method is often used to measure contaminants in natural and wastewater and to assess the strength of waste, such as municipal and industrial wastewater. The traditional method used to obtain the COD value is known as the Standard Method, in which potassium dichromate serves as the oxidizing agent. Essentially, this method involves subjecting the samples to heat treatment for about two hours in a Hach digester, following the addition of a known excess of the oxidant. The primary issue with this method lies in the low efficiency of the reaction mixture's heating method, resulting in excessively long reaction times (Zhang et al., 2016).

Although this method primarily aims to measure the concentration of organic matter, it is susceptible to interference from the presence of inorganic substances that can be oxidized (sulfides, sulfites, iodides), which also affect the measurements. This method is applicable to freshwater (rivers, lakes, or aquifers), wastewater, stormwater, or water from any other source that may contain a significant amount of organic matter (Ahmed et al., 2021).

In this context, it was necessary to conduct pH, temperature, COD total (total chemical oxygen demand), and COD soluble (soluble chemical oxygen demand) profiles over the duration of the cycle to initiate the enhanced acclimatization process, considering the use of synthetic water.

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These profiles were developed in three stages, or in other words, three repetitions, with the average of measurements obtained during the first stage of the research. Consequently, the process began by working with synthetic water in the reactor and 24-hour cycle durations. Subsequently, samples were taken for the COD study, with a sampling frequency of 2 hours, as well as every 15 minutes for temperature and pH measurements. After completing a 24-hour cycle in the reactor and conducting all the tests and analyses, the data is show in the Figure 2

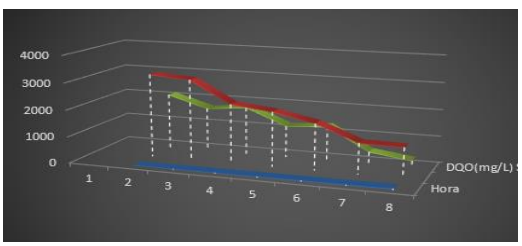

Figure 2. Chemical Oxygen Demand (COD) Profile vs Time

Based on the results shown in Figure 1 of the Chemical Oxygen Demand (COD) Profile vs Time, it can be observed that both COD values decreased gradually as the cycle progressed. This provides evidence that the microorganisms in this biomass analysis were absorbing the organic content of the synthetic water (Figure 3).

Relationship between the activity aM of a measurement ion in a solution and the potential measured between the reference electrode and the measurement electrode. Temperature influences the Nernst potential, often referred to as the slope in pH measurement. [30] In this regard, the pH value is probably the most commonly measured parameter in analytical chemistry.

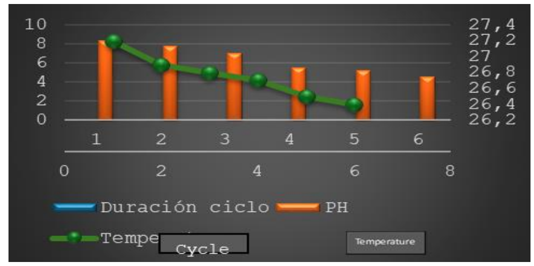

Figure 3. Temperature and pH Profile in the Reactor Using Synthetic Water During the Initial Hours of the Cycle

It affects product characteristics, chemical and biochemical reactions, and physiological processes, among other things. Constant environmental conditions are often required to obtain precise measurement results (Pradeep et al., 2021).

Therefore, the results from Figure 3 confirm that the existing biomass was processing organic matter to grow, reproduce, and carry out metabolic processes. The biomass indicated that it was active at the beginning of the acclimatization process, under optimal conditions, initiating the feeding of the reactor with the synthetic water.

Tannery Wastewater

Wastewater consists of the effluents produced by human activities in their daily routines, which are collected in sewage systems or discharged directly into the environment (Hansen et al., 2021). Wastewater is characterized by its physical, chemical, and biological composition. Quantitative analysis methods are used for the precise determination of wastewater's chemical composition, while qualitative analyses provide insights into its physical and biological characteristics (Zhao et al., 2022).

Regarding physical characteristics, Odor is an important parameter for characterization, as it is a result of gases released during the decomposition of organic matter. Wastewater has a distinctive odor due to the presence of hydrogen sulfide, a product of the reduction of sulfates to sulfites by microorganisms (Fan et al., 2020).

Temperature is another distinguishing feature since wastewater typically has higher temperatures than uncontaminated water, primarily due to increased biochemical activity by microorganisms (Ji et al., 2021). Density is commonly defined as mass per unit volume, expressed in Kg/m3 and g/cm3. Alternatively, the specific weight of wastewater is obtained based on the known coefficient between the density of water and the density of wastewater (Min et al., 2021).

Turbidity measures the quality of water discharged by assessing the relationship between colloid and residual material in suspension (Mateo et al., 2021). Solid content is represented by visible and colloidal particles present in wastewater, including organic matter like carbohydrates, cellulose, fiber particles, chitin, and other elements (Eray et al., 2020). Total Solids (TS) are residues left after the sample has been evaporated and dried at around 105°C for a period of twenty-four hours under dry heat (Jasim, 2020). Color in wastewater is due to the presence of suspended solids, with a greenish color indicating the presence of colloidal and dissolved substances (Samsami et al., 2020).

Particle Size Distribution:

The size of wastewater particles varies in magnitude, including substances dissolved (< 0.08 µm), colloidal particles (0.08 to 1.0 µm), supracolloidal particles (1 to 100 µm), and settleable particles > 100 µm (Jiang et al., 2020). pH represents the acidity or alkalinity of water, depending on the proportion of hydrogen ions, with pH values ranging from 0 to 14, where pH = 7 is neutral. This parameter is significant because it indicates the level of acidification in wastewater.

Regarding chemical characteristics, Inorganic substances include

Nitrates, originating from the decomposition of plant and animal materials or nitrogen compounds, transformed into organic matter by microorganisms in the presence of oxygen (Hu et al., 2020). Sulfates are soluble and result from the bacterial oxidation of sulfides. Their concentration typically ranges from 20 to 50 mg/l in rivers (Xia et al., 2020).

Chromium occurs naturally but becomes a contaminating metal in wastewater. It forms aminated and cyanurated complexes in water, with stability complexes with other chemical compounds such as chlorides, sulfates, ammonium salts, cyanides, and nitrates. Chromium is highly toxic to organisms (Kerur et al., 2021).

Iron is present in wastewater due to steel and other material production, typically trivalent in surface waters. These chemicals cause serious health issues, such as dermatitis (Aragaw et al., 2021). Chlorides result from mineral deposits dissolution, originating from various industrial or domestic sources. They can also indicate unwanted microbiological contamination (Li et al., 2022).

Calcium, a metal, is present in wastewater as it forms soluble salts with bicarbonate, sulfate, fluoride, and chloride ions, associated with mineralization levels (Liu et al., 2023). Zinc is rare in surface and groundwater, existing in inorganic, ionic, and colloidal forms. In significant quantities, zinc causes water turbidity, indicating contamination from batteries and engine oils resulting from landfill leakage (Turkmen et al., 2021)

In light of the previously mentioned characteristics of wastewater, the tannery wastewater handled in the acclimatization process was represented by collecting a sample from the lagoon, where a significant amount of effluents from the organization's production process is stored. In this context, acclimatization, in a physiological sense, involves an organism adapting to changes in its environment. The duration of this period varies according to the species and the circumstances of the change (Tiwari et al., 2021).

It's worth noting that acclimatization can apply to any environmental change, with one of the most studied being acclimatization to temperature changes. Animals take approximately 5 to 10 days to adjust their physiology to new conditions following a sudden temperature change (Ji et al., 2021). The results of wastewater characterization are shown in Table 2, with the maximum discharge limits to water bodies established by Ecuadorian legal regulations (MAATE, 2015) also reported.

Table 2. Characterization of the tannery's raw wastewater

Parameters	Reagent	Quantity per 1 L
pH	9,28-+0,28	6 a 9
Alkalinity	20.850 +-597,22	---
DQOt	5.584,74 +-680,36	350
DQOs	3900,7-942,85	---
NT	264,40+-39,10	40
$N\text{-}NH_4^+$	80,83+-13,22	---
$N\text{-}NH_3^-+N\text{-}NO_2^-$	4+-0	10

Within this context, it can be said that the comparison between the characterization and the limits set by legal regulations revealed that the industrial effluent requires treatment, given that the parameters were far from the maximum allowable values for discharge into bodies of water, especially pH, COD, and NT. Furthermore, to apply biological treatment, it is necessary to have a group of microorganisms capable of degrading organic matter and being tolerant to other typical contaminants in industrial effluent, such as chromium, sulfides, chlorides, refractory material, among others (Kapoor et al., 2021).

Among the characteristics of tannery effluent, it is important to note that the pH is at the upper limit set for a biological process to take place. Similarly, the effluent is characterized by high levels of organic matter and nitrogen. Thus, the study of the acclimatization process was justified, allowing for the treatment of microorganisms prepared to work under these conditions (Chan et al., 2022).

Enhanced Acclimatization Process

After observing the activity of microorganisms through COD profiles using synthetic water, the enhanced acclimatization process continued by feeding the reactor with a mixture of synthetic water and tannery effluent. In this regard, the laboratory-scale reactor was operated for approximately two months, which is the duration of the biomass acclimatization, ensuring a smooth process without any issues (Figure 4).

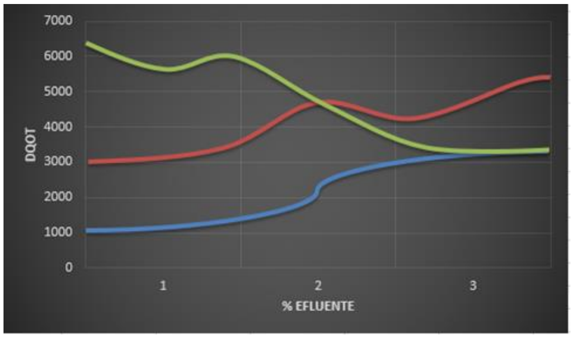

Figure 4. Behavior of CODtotal (Total Chemical Oxygen Demand) during the enhanced biomass acclimatization process

Conclusions

The leather tanning industry has traditionally been considered a polluting industry with a significant environmental impact. Often overlooked is the fact that it involves a process that utilizes a highly putrescible byproduct with slow biodegradation. The tanning process can be carried out in many ways, depending on the specific requirements for the final use of the leather, the animal source, and the specific characteristics imparted to the leather to enhance its properties and commercial value. Tanning is typically done in batch processes, with a high-water consumption, leading to the generation of polluting gases, contaminated wastewater, and solid waste, with wastewater being the most polluting component.

The success of wastewater treatment depends on the management of the organization, which can be regulated by authorities. This marks the beginning of a process where wastewater with residues must be processed and redistributed for disposal and utilization. Within this context, wastewater characterization uses quality parameters, considering physical, chemical, and biological aspects. These parameters allow for the quantification of the degree of contamination present in a wastewater sample. When the concentration of a particular parameter in wastewater is high, whether physical, chemical, or biological, it determines the appropriate treatment according to its intended use.

In summary, the protocol of enhanced acclimatization by feeding the reactor with a mixture of synthetic water and tannery effluent proved to be efficient, with a time frame of 60 days. During this period, a granular biomass was obtained, featuring a group of microorganisms suitable for their metabolic processes and sedimentation in less than two minutes, even with inhibitory compounds and refractory organic matter that characterize such effluents. Furthermore, biodegradable COD removal at the end of the acclimatization process reached 57.9% for CODtotal and 76.8% for CODs. There was also a limited presence of heterotrophic bacteria in the effluent. Environmental Impact Assessment indicated that the research conducted would not have specific negative impacts, thereby ensuring environmental viability and a positive impact on environmental quality.

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