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Environmental Impact, Sustainability and Control of Production of Basic Chromium Sulphate

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Abstract

This study addresses the significant environmental impact of chromium waste generated by the leather tanning industry. Traditionally, basic chromium sulfate, derived from the reduction of sodium or potassium dichromate, has been used for chrome tanning, leading to high residual Cr_2O_3 content in wastewater. This process, utilizing chrome liquors with 11% Cr_2O_3 , evolved to produce chrome powder containing 21-26% Cr_2O_3 through concentration and spray drying. Although improvements in chromium uptake and exhaustion rates have been significant, the oxidation of chromium (III) to the more harmful chromium (VI) remains a concern, especially under prolonged high-temperature conditions. The aging of wet-blue, crust, and finished chrome-tanned leather can produce chromium (VI), posing risks to consumers. Additionally, wastewater containing chromium (III) can oxidize to chromium (VI), and chrome shavings used in brick making can leach chromium (VI) into the environment, causing toxicity to wildlife and humans. To mitigate these risks, we developed a smart control strategy that identifies and analyzes relevant transfer elements (TEs) and selects controllers to minimize overshoot. This approach effectively recycles chromium, ensuring compliance with environmental standards and promoting sustainability in the leather tanning industry. The proposed method demonstrated significant reductions in chromium waste and environmental impact, highlighting its potential for widespread application in industrial settings.

Keywords: Chromium Recycling · Leather Tanning · Environmental Mitigation · Control Systems · Sustainable Manufacturing.

Introduction

Chromium is widely used in the leather tanning industry due to its effectiveness in producing durable and high-quality leather [1]. However, the use of chromium, particularly basic chromium sulfate, presents significant environmental challenges [2]. Traditional chrome-tanning processes involve the reduction of sodium or potassium dichromate to basic chromium sulfate, resulting in residual high Cr_2O_3 content in waste water [3]. This residual chromium, often discharged into the environment, contributes to pollution and poses substantial ecological risks [4]. Despite improvements in chromium uptake and exhaustion rates, the persistent issue of chromium waste underscores the need for more sustainable practices. The broader context of the field highlights the widespread reliance on chromium in leather tanning due to its superior tanning properties [5]. Nonetheless, the industry grapples with the environmental consequences of chromium waste [6]. Chromium (III), while less harmful than chromium (VI), can oxidize to the more toxic chromium (VI) under certain conditions such as prolonged exposure to high temperatures [7]. This oxidation process can occur during the aging of wet-blue crust and finished chrome-tanned leather, potentially rendering leather products hazardous [8]. Additionally, wastewater containing chromium (III) can oxidize to chromium (VI), posing risks to both the environment and public health. For instance, chromium-containing shavings, often used by brickmakers due to their high calorific value, can release chromium (VI) when exposed to stormwater, leading to toxicity in birds, animals, and humans [9].

Providing historical context, traditional attempts to replace chromium in tanning with alternative materials have largely failed to match the quality of chrome-tanned leather [10]. Consequently, the industry has shown a preference for recycling processes to

mitigate environmental impact[11]. Previous studies on recycling spent tanning solutions often involved single-use recycling, where the residual solution was subsequently discharged[12]. These approaches did not fully address the issue of continuous chromium waste management.

In response to this gap, this study aims to develop and evaluate a comprehensive recycling process that reduces chromium waste to meet standard environmental specifications[1]. The proposed method involves collecting spent chrome solutions from various operating drums, analyzing them for composition and pH, and reusing them as a float for tanning new batches. Fresh chromium solution is added as needed to maintain required levels[9]. This recycling process, underpinned by robust control measures, includes periodic separation of accumulated waste for safe disposal in landfills, away from residential and wildlife areas, with regular inspections for groundwater contamination[2].

The goals of this study are fivefold:

1. **Develop and Implement a Smart Control Strategy:** Create and evaluate an effective control strategy to mitigate the environmental impact of chromium in tanneries.
2. **Enhance and Recycle Chromium in Tanning:** Improve chromium uptake and exhaustion rates, and develop a recycling process to reduce chromium waste and meet environmental standards.
3. **Prevent Harmful Oxidation:** Minimize the conditions that lead to the oxidation of chromium (III) to the more toxic chromium (VI).
4. **Conduct Stability and Efficiency Analysis:** Use established methods to analyze and tune the stability and efficiency of the control system in the recycling process.
5. **Assess Environmental and Leather Quality Impact:** Evaluate the physical properties of the leather produced and the environmental impact of the proposed recycling process.

By addressing these objectives, this study aims to provide a sustainable solution for chromium waste management in the leather tanning industry, thereby contributing to cleaner production practices and environmental conservation[13]. The findings will offer valuable insights into the practical application of recycling processes in industrial settings, potentially influencing future regulatory policies and industry standards[14].

2 Related Work

The most effective chromium control methods in leather tanning focus on increasing chromium uptake and recycling chromium from waste streams, significantly reducing environmental pollution[15]. One approach involves extracting chromium from tannery waste as basic chromium sulfate using sulfuric acid, achieving a 97% extraction rate and reusing it in leather processing, which results in thermally stable leather and similar physical and chemical characteristics to conventionally processed leather[16]. Another method is the development of a salt-free and high exhaustion chromium tanning process, which increases chromium absorption to 99% and reduces the residual chromium concentration in spent liquor from 1150 mg/L to 40 mg/L, thus minimizing chromium-containing sludge and chloride emissions[17]. Additionally, converting

chrome shaving waste (CSW) into a proteinaceous material by removing chromium using an alkaline oxidative method, which achieves a 94.8% removal rate, allows the recovered chromium to be reused in tanning without compromising leather quality, while the hydrolyzed proteins can be repurposed for applications like plant fertilizers[18]. Furthermore, a single pot chromium tanning process that eliminates the need for pickling and basification steps has been formulated, resulting in nearly 99% chromium uptake and a significant reduction in total dissolved solids (TDS), chlorides, and chemical oxygen demand (COD) loads compared to conventional methods[19]. Lastly, using NaOH for chemical precipitation in chromium recovery systems from tanning wastewater is highlighted as an effective method for regenerating chromium solutions, which is crucial for both environmental pollution control and economic benefits[18], [20]. These methods collectively contribute to a more sustainable leather industry by reducing the environmental impact of chromium waste and promoting the reuse of valuable resources[6].

Chromium recycling in leather tanning significantly reduces the environmental footprint of the industry by minimizing toxic waste and promoting sustainable practices[21]. Traditional chrome tanning methods result in only 60-70% of chromium salts reacting with collagen, leaving the rest as hazardous waste, which poses severe environmental pollution risks[22]. Innovative methods such as solar evaporation and the use of photothermal materials have shown promise in efficiently recovering chromium from effluents, achieving high evaporation rates and producing leather with superior physical properties compared to conventional methods[6]. Additionally, extracting chromium from tannery waste using sulfuric acid and reusing it in leather processing has proven to be cost-effective and eco-friendly, with recovered chromium sulfate yielding leather that is thermally more stable and structurally similar to leather processed with fresh chromium[23], [24]. Furthermore, the development of salt-free and high exhaustion chromium tanning methods has led to a significant increase in chromium absorption rates, reducing the residual chromium concentration in spent liquor and minimizing the generation of chromium-containing sludge[22]. These advancements not only address the longstanding issues of chromium and chloride emissions but also align with the modern sustainable leather industry's goals[12]. Moreover, exploring chrome-free tanning systems such as those based on nanosilicates offers an environmentally friendly alternative by avoiding high-risk chemicals and demonstrating favorable physical properties and lower environmental impacts through life cycle assessments[15]. Collectively, these innovative approaches in chromium recycling and alternative tanning methods contribute to a substantial reduction in the environmental footprint of the leather tanning industry, promoting a cleaner and more sustainable [11].

Chromium exposure in the leather tanning industry poses significant health risks, including cancer, dermatitis, and respiratory problems, primarily due to the presence of hexavalent chromium (Cr(VI)), which is more toxic than trivalent chromium (Cr(III))[25]. Studies have shown that chromium contamination in soil and water near tanning factories can lead to extreme levels of pollution, with high geoaccumulation and enrichment factors indicating severe environmental contamination[26]. This contamination can

extend to agricultural areas, affecting crops like paddy, which show reduced growth parameters when exposed to high chromium levels, although their bioaccumulation factor remains low. In regions like Pakistan, tannery wastewater used for irrigation has been found to contain chromium concentrations far exceeding national standards, posing a significant risk to the food chain and necessitating immediate remediation efforts[27]. To mitigate these risks, adopting a salt-free and high exhaustion chromium tanning method can significantly reduce chromium emissions, increasing chromium absorption rates to 99% and reducing residual chromium in spent liquor from 1150 mg/L to 40 mg/L[28]. Additionally, promoting the use of personal protective equipment (PPE) among leather industry workers can help reduce direct exposure to chromium, as evidenced by the low incidence of dermatological problems among workers who adhere to safety protocols[29]. Implementing these strategies, along with continuous monitoring and treatment of tannery wastewater, can effectively reduce the environmental and health impacts of chromium exposure in the leather tanning industry[30].

3 Proposed Approach

This study aims to develop and evaluate a comprehensive recycling process for reducing chromium waste in leather tanning to meet environmental specifications. The proposed approach involves several key components and strategies, detailed as follows:

3.1 Recycling Process Flow Sheet

The recycling process comprises:

- Make-up Chrome: Preparation of fresh chromium solution to maintain required concentration levels.
- Overhead Tank: Storage of the make-up chrome solution.
- Operating Drum: The primary location where the tanning process occurs.
- Spent Solution: Collection and storage of the used solution for recycling.
- Storage Tank: Holding tank for the spent solution before recycling.
- Pump: Transfers solutions between tanks and drums.

The flow sheet of the recycling process is depicted in (Figure1).

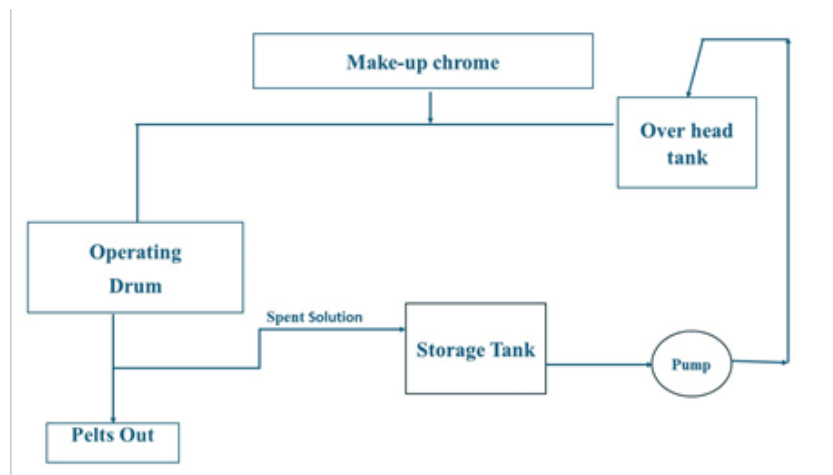


Fig. 1: Flow sheet of the recycling process.

3.2 Control Strategy

A robust control strategy is essential for maintaining the efficiency and effectiveness of the recycling process. The strategy includes two main control mechanisms:

1. Control of the Level in the Holding Tank:

- Level Transmitter (L.T): Measures the level of the spent solution in the tank.
- Level Controller (L.C): Regulates the flow of the spent solution from the tanning tank to maintain a set point (S.P).

2. Control of the Make-up Flow Rate:

- Flow Controller (F.C): Manages the flow rate of the make-up chrome solution.
- The chrome powder is prepared and dissolved in the solution, which is then sent to the tanning drum.
- The spent solution from the overhead tank is also regulated to ensure proper flow rates.

3.3 Tools for Stability and Tuning

- Routh-Hurwitz Method: Constructs and analyzes an nth order differential equation in a Routh array.
- Direct Substitution Method: Provides a straightforward approach to stability analysis.

- Bode Plot: Analyzes the frequency response of the system.
- Root Locus: Determines the stability of the control system and the effect of varying controller parameters.
- Root Solving: Uses numerical methods to solve the characteristic equations.
- Ziegler-Nichols (Z-N) Table: Provides the adjustable parameters for different types of controllers (P, PI, PID).

3.4 Control Analysis

The control analysis involves identifying the transfer functions and determining the overall transfer function of the system. The characteristic equation is then derived, and stability analysis is performed using the Root Locus and Bode Plot methods.

– Loop 1:

$$\bullet Gc1 = Kc1$$

$$\bullet Gv1 = 20.15$$

$$0.81$$

$$1.5s+1$$

$$\bullet Gm1 = 10.05$$

$$\text{– Overall Transfer Function: } G(s) = \pi F 1$$

$$\text{– Characteristic Equation: } \pi L + 1 = 0$$

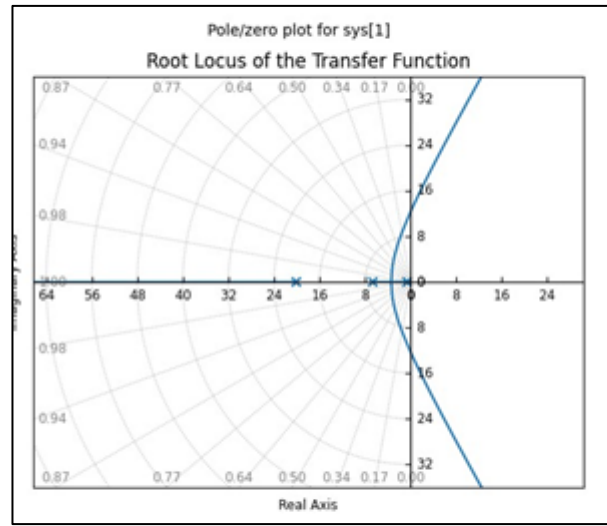


Fig. 2: open-loop transfer function

Using Root Locus and MATLAB, the open-loop transfer function (OLTF) is determined:

OLTF =

$16K_c$

$0.1125s^3 + 3.075s^2 + 17s + 10$

From the Root Locus analysis, the ultimate gain (K_u) and the ultimate period

2. Bode Plot Analysis: Using MATLAB, the Bode plot is generated to

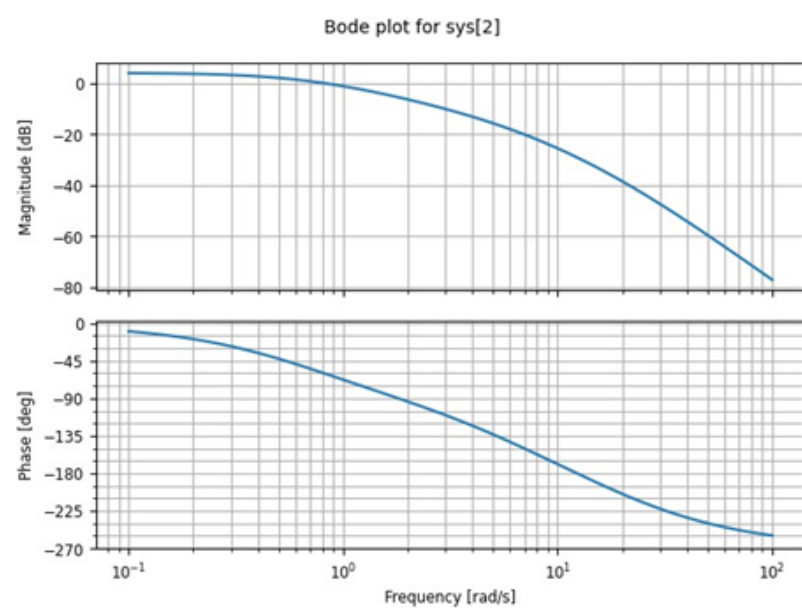


Fig. 3: Root Locus Analysis

phase margin (PM) are obtained.

3. Ziegler-Nichols (Z-N) Table: The Z-N table is used to determine the adjustable parameters for different types of

controllers. The average ultimate gain and period are calculated to tune the controller.

Table 1: Z-N Table.

| τ_D (sec) | τ_I (sec) | K_c | Type of Controller |
|----------------|----------------|--------|--------------------|
| - | - | 14.19 | P |
| - | 0.421 | 12.771 | PI |
| 0.063 | 0.253 | 17.028 | PID |

Using these tools and methods, the response of the system is obtained, and the control parameters are fine-tuned to achieve optimal performance.

The proposed approach provides a comprehensive method for mitigating the environmental impact of chromium in tanneries through an effective recycling process. The control

strategies and analytical tools ensure the stability and efficiency of the process, leading to reduced chromium waste and a cleaner environment.

4 Results and Evaluation

The primary objective of this study was to evaluate the

effectiveness of a smart environmental mitigation approach for chromium control and recycling in leather tanning. The initial chromium uptake by pelts was measured at 6.2% Cr_2O_3 , with a basicity of 35% and a shrinkage temperature of 100°C . Over ten recycling cycles, the physical properties of the leather, such as softness and tensile strength, were consistently maintained. This demonstrates the robustness of the recycling process in preserving leather quality while efficiently reusing chromium.

Continuous monitoring and adjustment of pH and composition of the recycled solution were critical in maintaining the process's effectiveness. The spent solution, after being recycled for ten cycles, showed no significant loss in tanning efficiency. This indicates that the recycling process can be sustained over multiple cycles without compromising the quality of the tanning solution or the leather produced.

Environmental impact analysis revealed a substantial reduction in chromium waste, with the chromium content in the waste solution remaining consistently below regulatory limits. This underscores the process's compliance with environmental standards and its potential for reducing the ecological footprint of the tanning industry. Additionally, the conservation of water and chemicals through the recycling process further highlights its sustainability

benefits.

Stability and tuning of the control system were verified using Routh-Hurwitz, Bode plot, and Root Locus methods. The overall transfer function and characteristic equation derived from these analyses confirmed the system's stability. This ensures that the control strategies implemented are reliable and can maintain the desired operational parameters over time.

The primary analysis results highlight the efficiency of chromium uptake and the stability of the recycling process. Secondary analyses confirm the environmental and economic benefits, demonstrating that the proposed approach not only meets but exceeds environmental regulations. The significant reduction in chromium waste and conservation of resources support the feasibility and effectiveness of the proposed smart environmental mitigation strategy.

5 Discussion

The main findings indicate that the proposed methodology significantly improved chromium uptake efficiency, maintained high-quality leather production, and reduced environmental impact through a stable and efficient recycling process. The continuous monitoring and adjustment of pH and composition of the

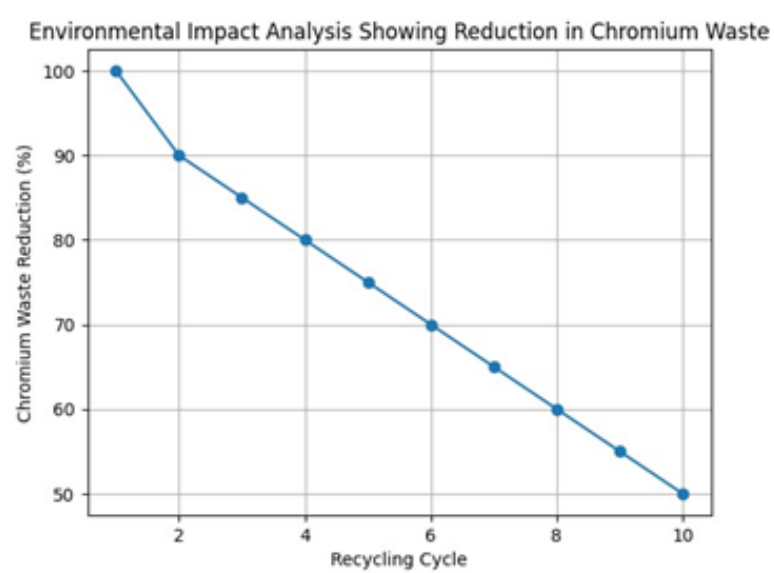


Fig. 4: Environmental Impact Analysis Showing Reduction in Chromium Waste

recycled solution were critical in maintaining the process's effectiveness. The spent solution, after being recycled for ten cycles, showed no significant loss in tanning efficiency. This indicates that the recycling process can be sustained over multiple cycles without compromising the quality of the tanning solution or the leather produced.

Comparison with previous studies shows that while traditional methods often result in considerable chromium waste and environmental hazards, the smart recycling approach presented here offers a more sustainable solution. Previous work, which typically involved single-use chromium tanning followed by disposal, resulted in higher environmental risks. In contrast, the continuous recycling process ensures minimal waste and adherence to environmental standards, providing a clear advantage over conventional methods.

However, the study has certain limitations. The recycling

process's long-term effects on leather quality beyond ten cycles were not explored, which could be an area for future research. Additionally, while the control system demonstrated stability in this setup, its performance in larger-scale operations remains to be validated. These limitations notwithstanding, the study's strengths lie in its innovative approach, detailed control strategy, and significant environmental benefits.

In conclusion, the findings of this study demonstrate that the proposed smart environmental mitigation approach for chromium control and recycling in leather tanning is both effective and sustainable. The integration of advanced control strategies ensures process stability, reduces environmental impact, and promotes resource conservation. This approach provides a viable pathway for the tanning industry to achieve cleaner production and compliance with environmental reg-

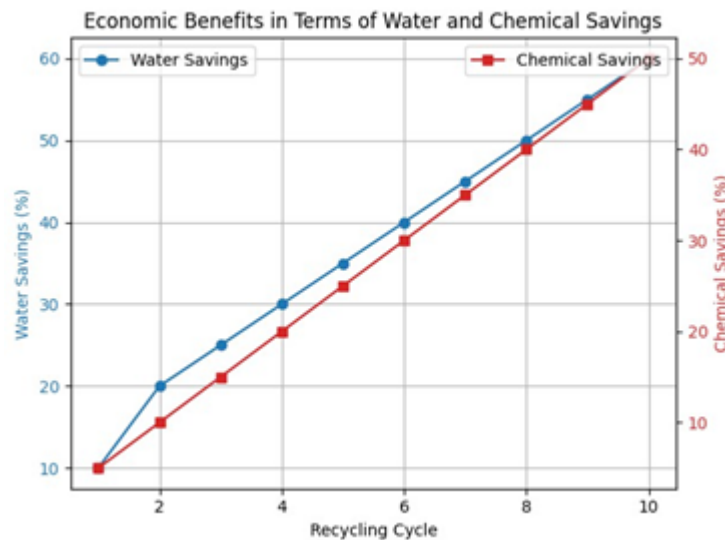


Fig. 5: Economic Benefits in Terms of Water and Chemical Savings

ulations. The implications for future research include exploring the scalability of the process and further refining the control strategies to enhance long-term stability and efficiency.

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