# Utilization of Waste Pickle Liquor for Sustainable Azo Dye Synthesis and Application in Leather Processing

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Utilization of Waste Pickle Liquor for Sustainable Azo Dye

Synthesis and Application in Leather Processing

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Abstract

The discharge of waste pickle liquor from the leather industry, characterized by high acidity and elevated sodium chloride content, poses serious environmental and health concerns. This study reports a novel and sustainable approach for the reuse of tannery pickle liquor as both a reaction medium and acid source for the synthesis of azo dyes, which are subsequently utilized within the same leather industry. The process follows green chemistry principles by valorizing waste, minimizing reagent consumption, and operating under energy-efficient, room-temperature conditions. The optimized one-pot process achieved high yields of up to 99.23%, producing 6.43 g of azo dye from skin pickle liquor and 7.7 g from hide pickle liquor at laboratory scale, demonstrating a viable alternative to conventional acid-intensive synthesis routes. The method exhibited strong sustainability metrics, including a high Eco-scale score of 84.19, low Efactor, high reaction mass efficiency, and reduced water intensity compared to traditional processes. Importantly, the sodium chloride–rich wastewater generated after dye synthesis was successfully reused in subsequent leather pickling after pH adjustment to 2.8, eliminating the need for fresh water and additional sodium chloride. The synthesized azo dyes were applied to zeolite-, vegetable-, and chrome-tanned

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leathers, showing good dye uptake, vibrant coloration, and lightfastness comparable to conventional dyes. Overall, this integrated waste-toresource strategy significantly reduces freshwater and chemical consumption, supports circular economy practices, and contributes to Sustainable Development Goals 6 and 12 by transforming hazardous tannery effluent into a valuable functional product.

Key words: Pickle liquor, Azo dyes, Circular economy, Waste valorization, Leather dyeing, Sustainable Development Goal.

## 1. Introduction

The leather industry is one of the major consumers of water and a significant generator of wastewater, among which pickled liquor is one of the most problematic effluents produced during the pre-tanning stage. During skin pickling (goat and sheep), approximately 1.0–1.1% sulfuric acid and 8% sodium chloride are applied, of which 0.1–0.15% acid remains unutilized and is discharged. Similarly, hide pickling (cow and buffalo) involves 1.5–1.6% sulfuric acid and 10% sodium chloride, leaving 0.15– 0.2% residual acid in the discharged liquor. This highly acidic and saline wastewater poses serious environmental concerns, including aquatic toxicity and ecological imbalance. Currently, only about 50% of pickle liquor is reused, mainly by blending with basic chromium sulfate

for tanning or by adjusting acid and salt levels for subsequent pickling cycles. However, its valorization under a true “waste-to-wealth” concept within the leather industry remains largely unexplored.

Azo dyes represent the most widely used class of dyes in leather coloration due to their high color strength, stability, and versatility1. However, conventional azo dye synthesis relies on concentrated mineral acids2, bases, and large volumes of water, generating significant saline wastewater and increasing environmental

burden. Globally, azo dye production is water-intensive, and wastewater treatment remains costly and energy demanding. Although limited greener approaches such as one-pot processes and solid acid catalysts have been reported, practical large-scale solutions that significantly reduce waste are still scarce2.

In this context, the present study introduces a sustainable approach that utilizes tannery waste pickle liquor as both the reaction medium and acid source for azo dye synthesis at room temperature. Furthermore, the NaCl-rich wastewater generated after dye synthesis is reused in subsequent leather pickling, and the synthesized dyes are successfully applied to chrome-tanned, zeolite-tanned, and vegetable-tanned leathers. This integrated strategy reduces fresh water and chemical consumption, converts hazardous waste into a value-added product, and promotes circular economy principles within the leather industry.

## 2. Experimental Methods

### 2.1 Source of Waste Pickled Liquor

The waste skin pickled liquor (SPL) and hide pickled liquor (HPL) were collected from tannery, CSIR-CLRI, Chennai, India. The collected pickled liquor was filtered through a Whatman no.1 filter paper and stored for further use. The acid and salt content in the spent pickle liquor was determined by standard chemical analysis methods.

### 2.2 General Procedure for Synthesis of Azo Dyes Using Waste Pickled Liquor

The azo dyes were synthesized according to previously reported procedure with slight modifications2. Typically,

1 mmol of arylamine, 1.05 mmol of sodium nitrate were added to 75 mL of skin pickled liquor, then 1 mmol of coupling agent was added and stirred at room temperature for 15 to 45 min3. The reaction was continued until all the reactants were consumed, as indicated by thin-layer chromatography (TLC). The obtained product was filtered, washed with water (2 mL) and taken for NMR studies.

### 2.3 Dyeing of Leather using Synthesized Azo dyes from Waste Pickle Liquor

To study the dye penetration and light fastness properties of synthesized azo dyes on leather, three leather types such as chrome-tanned, zeolite-tanned, and vegetabletanned were selected and maintained at pH ~6.5. The detailed leather process recipe is given in Table S5. The dyeing process was carried out in alkaline conditions for 1 h, the dyes were adjusted to pH 9 using sodium hydroxide for dye uptake. Post-dyeing, the CIE color coordinates of the dyed leathers were measured to assess color attributes, and their light fastness properties were evaluated according to ISO 105-B02 test standards.4

## 3. Results and Discussion

This study presents an integrated and sustainable approach that combines the synthesis of azo dyes (not in Restricted substance list5) using tannery waste pickle liquor with their practical application on different leather tanning systems. Waste skin pickle liquor (SPL) and hide pickle liquor (HPL), generated during the pickling stage of leather processing, were successfully employed as both the reaction medium and acid source for azo dye synthesis through a one-pot diazotization–coupling process. Five azo dyes were synthesized at room temperature within short reaction times (15–45 min), demonstrating that pickle liquor can effectively replace fresh mineral acids and water traditionally used in dye manufacture. The process showed good yields, scalability up to multi-millimole levels, and recyclability of the reaction medium, highlighting its feasibility for industrial adoption without requiring major process modifications.

Following synthesis, the dyes were applied to three representative leather tanning systems chrome-tanned, zeolite-tanned (chrome-free), and vegetable-tanned leathers to evaluate their dyeing performance6. Dyeing was carried out with a 2% dye offer at pH 9 in a drum for 60 minutes, conditions commonly employed in leather dyeing operations. The synthesized dyes exhibited good affinity toward all leather types, with dye absorption ranging from 60–66% for vegetable-tanned leather, 65– 73% for zeolite-tanned leather, and 75–81% for chrometanned leather. These uptake values are comparable to those obtained using conventionally synthesized azo dyes, confirming the suitability of the present dyes for leather coloration.

Distinct shade variations were observed depending on the tanning chemistry. Chrome-tanned leather produced lighter shades due to its inherent bluish tone and higher lightness (L*) values. Zeolite-tanned leather, which is white in appearance, yielded deeper and more intense redyellow shades with higher a* and b* values. Vegetabletanned leather produced warm red-to-yellow tones with moderate lightness, influenced by the natural brown color of the substrate. These variations demonstrate the versatility of the synthesized dyes across different tanning systems and their potential for generating a wide range of aesthetic effects.

Light fastness results showed moderate performance for chrome-tanned leather (Blue Wool rating 3–6), while zeolite- and vegetable-tanned leathers exhibited superior light fastness (ratings 6–8). The lower light fastness in

chrome-tanned leather is attributed to its compact fiber structure and possible interactions between chromium salts and dye molecules, which may reduce photostability. In contrast, the more open and porous structures of zeoliteand vegetable-tanned leathers facilitate better dye penetration and stronger dye–fiber interactions, resulting in improved resistance to light-induced fading. Wash fastness, assessed through dye leaching studies, showed low dye release (2–7%) across all leather types, indicating good fixation and durability.

SEM and EDAX analyses confirmed that dyeing did not alter the surface morphology or fiber compactness of the leathers. Overall, this work demonstrates that azo dyes synthesized using waste pickle liquor can be effectively applied to both conventional and chrome-free leathers, delivering satisfactory color strength and fastness while supporting circular economy principles and sustainable leather manufacturing.

4. Conclusions

This study establishes a sustainable closed-loop approach in which waste pickle liquor from leather processing is effectively recycled within the same industry through the synthesis of azo dyes. The green process achieved high dye yields (>97%), demonstrating efficiency, scalability, and cost-effectiveness while eliminating the need for fresh acids and brine due to the inherent sodium chloride content of the waste liquor. The synthesized dyes showed good dye uptake and color performance on chrome-, zeolite-, and vegetable-tanned leathers, with superior color vibrancy and lightfastness observed for zeolite- and vegetable-tanned leathers. Importantly, the sodium chloride–rich wastewater generated after dye synthesis was reused in subsequent pickling operations following simple pH adjustment, reducing freshwater and chemical consumption. Overall, this waste-toresource strategy supports circular economy principles and offers an environmentally sustainable pathway for leather manufacturing.

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