



## A REVIEW ON THE APPLICATIONS OF DEEP EUTECTIC SOLVENTS IN LEATHER MANUFACTURING PROCESSES

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### ABSTRACT

*Deep Eutectic Solvents (DESs) are new-generation solvents with excellent characteristics that make them preferable and potential substitutes for conventional and industrial reagents. They have found many industrial applications because of their superb tuneable characteristics. Due to these properties, they could serve as potential substitutes for conventional leather manufacturing chemicals. This work sought to review the possible applications of deep eutectic solvents in the various stages of the leather manufacturing process. From studies carried out, when DESs were used for tanning, the chromium content of the samples were 3.04, 2.27, 3.43, and 3.53 % for conventionally chrome-tanned,  $\text{ChCl} : \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Urea} : \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Urea} : \text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  respectively. Also, the shrinkage temperatures were 109, 71, 80, and 83 °C for conventionally chrome-tanned,  $\text{ChCl} : \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Urea} : \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Urea} : \text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  respectively. The use of DESs removed the tanning solvent from the process, increased the efficiency of chromium salt uptake into the hide, and minimised the treatment of aqueous effluent.*

### KEYWORDS

Chrome substitution, Deep Eutectic Solvents, Dyeing, Fatliquor, Leather, Leather processing, Tanning

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## INTRODUCTION

The tanning process requires a large amount of water, which can strain local water resources. The use of water also leads to wastewater and effluent that contains harmful chemicals and pollutants. Also, leather production involves the use of a variety of chemicals, including chromium, formaldehyde, and other hazardous substances. These chemicals can be toxic to humans, animals, and the environment. There is an increasing interest in eco-friendly chemicals due to the growing global environmental awareness. Conventional industrial processing methods involve the use of large quantities of molecular solvents, ionic liquids (ILs), and organic and inorganic chemicals. These conventional chemicals have the drawback of high vapour pressure (i.e. organic solvents), environmental pollution, toxicity, and recyclability when looked at from a sustainability point of view (Lange, 2002; Siddiqua *et al.*, 2022; Tchounwou *et al.*, 2012). Deep Eutectic Solvents (DESs) have recently emerged as green alternatives to these industrial reagents. Aside from their function as a substitute for conventional solvents (organic and ionic), they are ubiquitous in function. Of particular interest is DES's potential as a substitute and/or complementary reagent in the leather manufacturing industry (Abbott *et al.*, 2015; Covington and Wise, 2020; Wise *et al.*, 2023). The use of some DESs has been investigated in some operations in leather processing such as tanning, fatliquoring and dyeing and they have proven to be potential substitutes for conventional chemicals. This work sought to review studies on major leather processing steps in which DESs could be potential substitutes for conventional chemicals.

### Leather Manufacturing Process

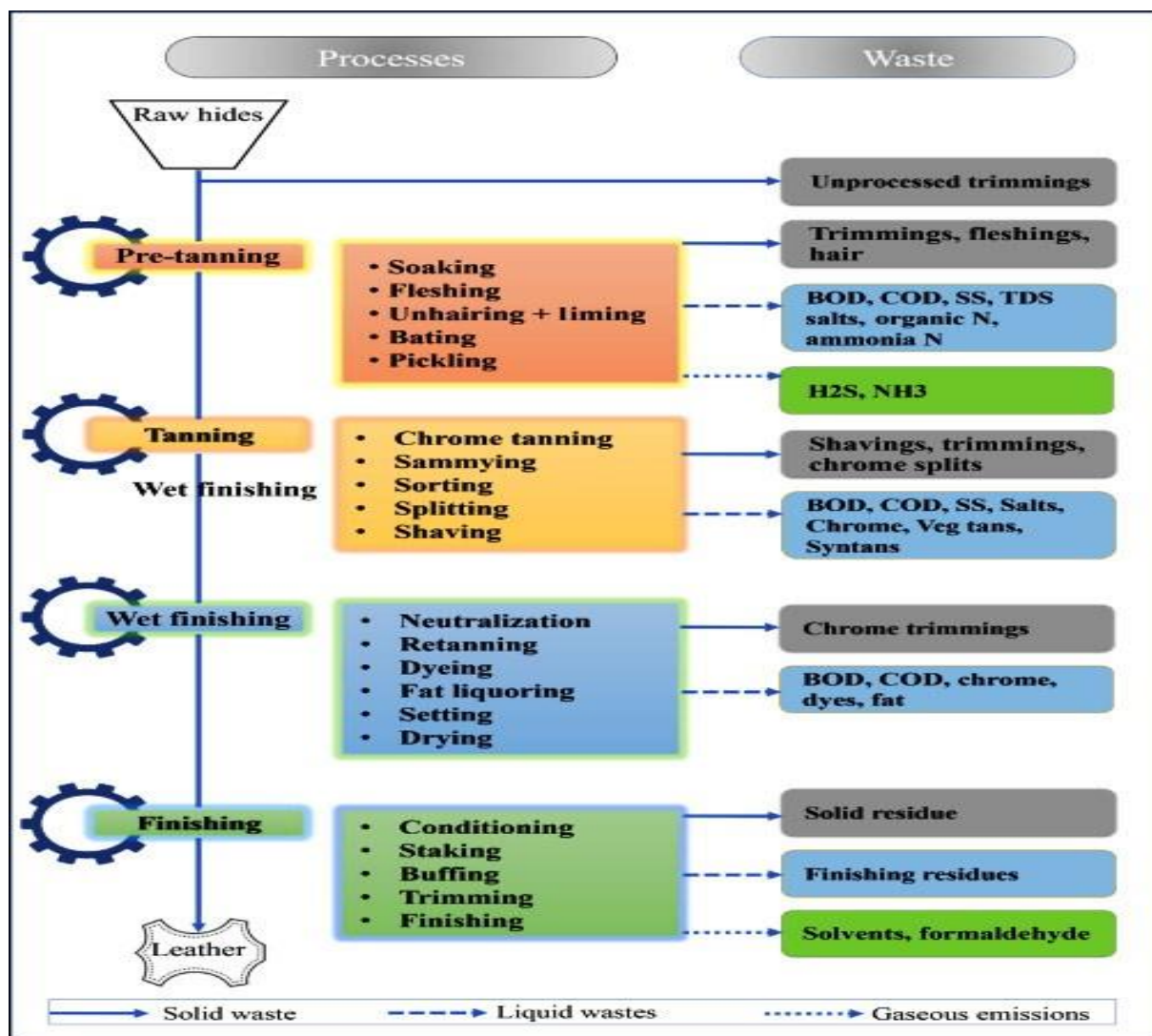
Tanning is an age-long art that has transcended generations. For centuries, skins of animals such as goats, rams, snakes, crocodiles etc. have been converted into useful end products which are used to manufacture fashion goods such as shoes, bags, caps, jackets etc., and other household products through the tanning process. The tanning industry has developed over the years to the point where chromium salt is used as a major tanning agent (Adeoye *et al.*, 2014; Dipu Ahmed *et al.*, 2021). Leather production is a chain of processes that can be categorised into three stages, namely: a pre-tanning operation which, includes flaying and curing; beam-house operations which include soaking, unhairing, liming, de-liming, bating and pickling; and tanning and post-tanning operations which include shaving, splitting, washing, neutralisation, dyeing, setting out, fatliquoring, drying and rolling. Tanning activities have been the major cause of some environmental pollution worldwide and the pollutant of most concern is chromium (China *et al.*, 2020; Oruko *et al.*, 2020).

The production of leather is an industry that dates back over 6000 years, and elements of the process have not changed in about a century (Muthukrishnan, 2021). Around 6.5 million tonnes of wet salted hides are processed annually using an estimated 3.5 million tonnes of chemicals (Kanagaraj *et al.*, 2015). Leather processing typically involves several processing steps. Initially, the hide or skin is preserved with salt until required. Several processes are thus initiated and these are the soaking of the hide or skin to remove the salt as well as to rehydrate the material to return to or near its original state. This is followed by the removal of the hair from the hide using a reducing agent in a high-pH solution containing calcium hydroxide (liming). This process is subsequently followed by a reduction in pH (de-liming) to reduce swelling and prepare the hide for enzymatic treatment or bating (a crude mixture of proteolytic enzymes) to remove non-

structural proteins. The hide is further subjected to pickling (an acid treatment), followed by the tanning process using a metal salt or vegetable tannins. This is followed by dyeing, re-tanning and fatliquoring processes before finishing the leather with the application of a surface coating. Each batch of hides requires days of soaking or stirring in a series of concentrated aqueous solutions. It is estimated that over 600 kg of waste is generated and 30-35 m<sup>3</sup> of water is used for every tonne of wet-salted hide, which results in 200-300 kg of leather (Tian *et al.*, 2019).

A large volume of wastewater generated during leather production originates from the pre-tanning stage, while a significant amount of wastewater is produced from the post-tanning stages as well (Hutton and Shafahi, 2019; Bhardwaj *et al.*, 2023). The challenge of waste generated coupled with environmental pollution and the non-sustainability of some reagents used in leather processing has necessitated research into alternative and less pollution-producing reagents for this age-long process. To date, most approaches to improving the eco-friendliness of leather production had been either to neutralise waste or mechanical improvements that would decrease the volume of tanning solution needed. Numerous green alternatives have been proposed including biological and electrochemical wastewater treatment steps (Lofrano *et al.*, 2013; Tünay *et al.*, 2019). One of the biggest concerns is the release of heavy metals into the environment, particularly chromium. Approximately 80-85% of the total leathers produced industrially are processed using a chromium-based tanning process, principally as it allows the leather to be manipulated at high temperatures without visible shrinkage (Ahmed and Maraz, 2021; Zhang *et al.*, 2016).

The chrome tanning reaction occurs between partially hydrolysed chromium (III) sulphate species and ionised carboxyl groups on the collagen molecule forming covalent complexes within the pH range from 2.5 to 4.5 because of the solubility of the Cr (III) complex. This tanning reaction is influenced by pH, temperature and the presence of counter ions in solution. Much research has gone into substituting chromium, but none has been commercially viable to meet the industry's cost-efficiency demands. Basic chromium (III) sulphate is widely used as a tanning agent. A typical tanning solution contains approximately 1.5 to 2% Cr<sub>2</sub>O<sub>3</sub> by weight, and after tanning, the solution may contain up to 30% of its original chromium content (Abbott *et al.*, 2015). This equates to 4-6 g of Cr<sub>2</sub>O<sub>3</sub> per kg of hide. The chromium is usually precipitated and recovered from the solution by using alkalis. In developed countries, chrome recovery is very efficient, while others experience great environmental pollution majorly because of the cost of remediation (Kotas and Stasicka, 2000). In the current approach, transformative tanning, fatliquoring and dyeing stages for leather manufacture are proposed using a novel type of solvent known as Deep Eutectic Solvents (DESs). Figure 1 shows typical stages in leather production processes.



**Figure 1:** Stages in leather manufacturing process (Adapted from Dowlath *et al.*, 2020)

### Deep Eutectic Solvents

Deep Eutectic Solvents are a unique combination of two or more components that are capable of interacting through hydrogen bonding and other forms of bonding to give a eutectic mixture that is liquid at room temperature, which has a melting point that is lower than that of the individual components. DESs are usually prepared by a straightforward combination of two or more substances i.e. Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA). Abbott *et al* reported and deemed DESs as a new generation of ‘green’ solvents and has been recognized as a perfect alternative to organic solvents and ionic liquids (ILs) (Bansal *et al.*, 2016; Santana-Mayor *et al.*, 2021; Toledo Hijo *et al.*, 2022). DESs have gained great acceptance as a wonderful substitute for ILs due to their ready availability, thermal stability, biodegradability, non-toxicity, tuneability and very cheap production cost (Afonso *et al.*, 2023; Binnemans and Jones, 2023; Schuh *et al.*, 2023; Mohd Hatta and Abd Halim, 2024).

DESs are prepared using a simple one-pot sustainable method via the mixing of quaternary ammonium salt as HBA with HBD. Such fundamental investigations have been expanded enormously by researchers to explore and opt for a wide range of HBA (Choline chloride, Betain and Quaternary salts of phosphonium and HBD (Amide, Carboxylic acids, Esters and Polyols) thereby tuning the eutectic compositions and eutectic temperature (Scelsi *et al.*, 2021). Consequently, DESs have proven their promising significance due to their superior chemical properties and they hold wide applications in electrochemical deposition of metals, petrochemical engineering, organic synthesis process as catalyst cum solvent, gas separation and capturing, protein storage, polymer chemistry, formulation of smart nanomaterials, drug solubilization biopolymer dissolution and so on (Scelsi *et al.*, 2021; Afonso *et al.*, 2023; Schuh *et al.*, 2023). They present excellent characteristics such as a simple synthesis method without the need for purification and waste disposal, very cheap due to low cost of precursors, safe to be used, biodegradable and sustainable, environmental friendly, good biocompatibility since quaternary ammonium salts such as choline chloride were used as an additive in chicken feed, low Volatile Organic Compound (VOC), non-flammable and non-reactive to water (Scelsi *et al.*, 2021; Schuh *et al.*, 2023; Mohd Hatta and Abd Halim, 2024).

The study of DESs had been scarcely reported until the 21st century (Oyoun *et al.*, 2023). Before that time, some underground works had been carried out; the pioneer being its suitability as a reaction media for enzymatic reactions (Feng *et al.*, 2021; Nguyen *et al.*, 2021). As the years unfolded, DESs became ubiquitous in application due to their tuneable characteristics. Research studies undertaken by Abbott *et al.* have recently shown that eutectic mixtures of metal salts with amides, such as urea, also form useful liquids (Abbott *et al.*, 2007, 2014). They have properties comparable with ionic liquids and have been used for applications including metal processing, synthesis and control of phase transfer (Smith *et al.*, 2014).

### Types of Deep Eutectic Solvents

Deep eutectic solvents are typically grouped into four classes and this is as shown in Table 1.

**Table 1:** Classes of Deep Eutectic Solvents (Adapted from Smith *et al.*, 2014)

Type	General Formula	Terms	Combination
1	$Cat^+X^-zMCl_x$	M= Zn, Sn, Al, Ga, In	Metal salt + Organic salt
2	$Cat^+X^-zMCl_x \cdot YH_2O$	M=Cr, Co, Cu, Ni, Fe	Metal salt hydrate + organic salt
3	$Cat^+X^-zRZ$	Z= CONH <sub>2</sub> , COOH, OH	Organic salt + HDB
4	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x-1}^-$	M= Al, Zn and Z= CONH <sub>2</sub> , OH	Metal salt hydrate + HBD

Types 1 and 2 DESs are more suitable for application in leather processing. DESs have demonstrated the advantage of high solubility for polar compounds, such as vegetable tanning agents in leather processing. They can be formulated to contain metals such as chromium but also dissolve nonpolar compounds such as dyes. Previously, eutectic mixtures of Choline chloride: CrCl<sub>3</sub>·6H<sub>2</sub>O (1:2) and Urea: CrCl<sub>3</sub>·6H<sub>2</sub>O (2:1) have been used for the electro-deposition of chromium, circumventing the use of chromic acid. This is an effective way of making an extremely

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concentrated active ingredient. For example, the Choline chloride:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (1:2) had  $4.75 \text{ mol dm}^{-3}$  chromium salt. In water, a large excess of ancillary is used to allow the chromium to partition into the hide, using the DES solvent system, the aim is to ensure that all the active ingredients enter the hide and are fixed (Abbott *et al.*, 2015).

## DESs in Leather Processing

### *i. Tanning*

It is necessary to use excess ancillary in water for chromium to partition into the hide. While using DESs, the target is to ensure all active ingredients penetrate and fixate on the hide. Though Ionic liquids have been used to remove inter-fibrillary materials in the pre-tanning step and dilute aqueous solutions of choline thioglycolate have been used for hair removal, they have never been applied to leather tanning (Vijayaraghavan *et al.*, 2015). Interfacial processes influence the penetration of metal species into leather. Conventional tanning solutions operate under relatively concentrated conditions to make sure the species partition into a solid, largely ionic matrix.

Abbott *et al.* (2015) used three types of DESs to tan hides. These were: Choline chloride ( $\text{ChCl}$ ): $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (1:2), Urea:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (2:1), and Urea:  $\text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  (1:1). The two components were mixed in the relevant ratios using a magnetic stirrer until no solid crystal was visible at  $50^\circ\text{C}$ . Samples of bovine hide were pre-treated and pickled according to the conventional leather manufacturing process to the final pH of approximately 4. The bulk water was removed from the hide and the final water content of the hide before tanning with DESs was determined gravimetrically to be 62 wt. %. Bovine hide samples weighing  $50 \pm 2 \text{ g}$  were tanned by contacting them with  $23 \pm 2 \text{ g}$  of DESs without mechanical action for 18 hours at room temperature. The control sample (chromium (III) reference) was tanned using the conventional aqueous formulation. After tanning, excess DESs were skimmed from the surface using a metal blade, and the hides were re-weighed. The control sample was washed in  $1 \text{ mol dm}^{-3}$  sodium sulphate solution and the deep eutectic solvent-tanned samples were washed in cold water and air-dried before analysis. Negligible leaching of the DESs from the hide into the water was observed during the washing stage. After the tanning process, the chromium content of the pelt (tanned hide) was determined.

Using DESs removed the solvent from the process and increased the efficiency of chromium salt uptake into the hide while minimizing the treatment of aqueous effluent. To demonstrate the fixation of chromium into the hide, the chrome content was determined for samples tanned with the DESs. The chromium content of the control sample and deep eutectic solvent-tanned leather samples were 3.04, 2.27, 3.43, and 3.53 % for conventionally chrome-tanned,  $\text{ChCl}:\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , Urea:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and Urea:  $\text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  respectively. The shrinkage temperature ( $T_s$ ) was determined using a Differential Scanning Calorimeter (DSC). Measuring the shrinkage temperature is vital to the determination of the efficacy of a tanning agent in stabilising the collagen fibres and this is usually measured in a wet state. Their shrinkage temperatures were 109, 71, 80, and  $83^\circ\text{C}$  for conventionally chrome-tanned,  $\text{ChCl}:\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , Urea:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and Urea:  $\text{KCr}(\text{SO}_4)_2 \cdot 10\text{H}_2\text{O}$  respectively. It is important to note that chromium salt fixation on hide is achieved by either raising the pH, increasing the temperature, and by the addition of complexing agents. Washing the sample tanned with  $\text{ChCl}:\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  with  $1 \text{ mol dm}^{-3}$  sodium sulphate solution at pH 4 increased the shrinkage temperature from  $71^\circ\text{C}$  to  $86^\circ\text{C}$  and this increased to  $96^\circ\text{C}$  when the pH was increased to 8. This shows that the chromium can be fixed to the collagen structure irrespective of the anion in the deep eutectic solvent.

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Ethaline 200 (a deep eutectic solvent which is a mixture of Ethylene glycol and Choline chloride (1:2)) was used for the vegetable tanning, dyeing, and fatliquoring experiments. Mimosa and chestnut vegetable tanning the eutectic mixture Ethaline 200 at a loading of 10 wt % of either ground mimosa bark or ground chestnut wood bark. The vegetable-deep eutectic solvent tanned leathers had shrinkage temperatures of 83 and 78 °C for Mimosa-Ethaline 200 and Chestnut-Ethaline respectively.

### **ii. Fatliquoring**

Plasticizing leather is the next stage after tanning, and this process is called fatliquoring. The oils used are mostly from plant or fish origins, and are poorly miscible with water and lead to turbid waste solutions which are difficult to treat. The experiment from vegetable tanning using Ethaline 200 showed that the leather was flexible and soft and this was concluded to originate from the DES trapped in the collagen structure. This suggested that the Ethaline 200 acted as an in-built fatliquor.

The fatliquoring experiments were carried out using air-dried conventionally chrome-tanned leather. The sample was soaked in Ethaline 200 at various temperatures and periods. Thereafter, they were washed for 15 minutes in de-ionized water, placed on absorbent paper and air-dried for a minimum of 24 hours at room temperature. The mass before and after treatment was determined using the weighing balance. At 70 °C for 24 hours, 73% by weight of Deep Eutectic Solvent (DES) was absorbed into the leather. The tensile strength of the chrome-tanned was observed to be approximately constant while the tensile strain doubled after fatliquoring. As expected, the amount of DES absorbed increased with time and temperature. However, the water content of the hide remained at about 12%, irrespective of the DES content compared to 18% in the un-fatliquored chrome-tanned leather. This shows that the DES does not act as a hydrophilic additive as might be expected, instead the ability of the anion to form hydrogen bonds with the collagen structure decreased its tendency to absorb moisture from the environment.

### **iii. Dyeing**

Acid dyes are commonly used in the leather industry because of their miscibility with water, and fixation to collagen under acidic conditions. The colours available are wide-ranging and they exhibit good colour-fastness. Their molecules are small, hydrophilic and generally anionic, binding electrostatically to protonated amino groups. These dyes also exhibit hydrogen bonding through autochrome groups. Basic dyes are charged with cations and are often more hydrophobic than the acid dyes with an affinity for anionic leather although interaction also occurs via hydrogen bonding. Although they can produce vivid, bright colours, they have poor colour fastness in comparison to acid dyes.

In Abbott *et al* (2015) dyeing experiments, 0.4 g of Sudan Black B was mixed with 200 mL of Ethaline 200 to make a  $4.38 \times 10^{-3}$  mol dm<sup>-3</sup> dye solution. Samples of dried wet-blue leather were fully submerged in the Ethaline 200 and Sudan Black B solution. The samples were left in the solution at 70 °C for 24 h. Once the required duration was completed, they were washed for

15 min in de-ionized water, placed on absorbent paper and air-dried for a minimum of 24 hours at room temperature.

The non-ionic, lysochromic dye Sudan Black B was found to be soluble in a Ethaline 200 and absorbed evenly throughout the leather. The dye produced an intense black shade, which showed no evidence of leaching when the sample was washed in water. The dye penetrated throughout the cross section of the leather showing that the deep eutectic solvent (ethaline 200) had transformed the collagen into a more hydrophobic environment. In principle, absorbing the dye and DES into the tanned leather as a gel should remove all wastewater treatment from the post-tanning process.

## **CONCLUSION**

The use of deep eutectic solvents in raw hides and skin processing, which includes mineral and vegetable tanning, dyeing and fatliquoring, has been proven. The use of these solvents offers some advantages, such as waste minimisation by the application of a liquid active ingredient directly to the surface of the pelt. If the bulk or all of the DES is absorbed within the tanned leather, little or no wastewater will be generated. Study (un-optimized) has shown that comparable chromium uptake may be achieved; however, there is significant scope to improve the fixing of the chromium to the collagen to increase the shrinkage temperature of the tanned leather by optimising the binding of chromium to the collagen by different crosslinking anions. Vegetable tanning agents were shown to penetrate rapidly into the hide using DESs. This is possibly due to their ability to dissolve rather than disperse the active ingredients and their ability to open up the hydrogen bond structure of collagen. DESs enabled the adsorption of non-ionic dyes, which do not bleed from the finished leather. The incorporation of DESs can also soften the leather considerably and decrease the loss of active ingredients during vegetable and chrome tanning. Also, it has been shown that dye emissions can be significantly reduced using DESs, and entrapment of the ionic component into the leather can act as an in-built plasticiser.

Therefore, the following studies are imperative for this technology to be fully embraced in leather processing:

1. Improvement of chrome fixation from DESs to collagen
2. Optimisation of chromium uptake from DESs

**CONFLICTS OF INTEREST:** The authors declare no conflict of interest.



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