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Hydrolyzed collagen: A novel additive in cotton and leather dyeing

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ABSTRACT

The effect of hydrolyzed collagen in the dyeing of cotton and leather was investigated. First of all, the compatibility of direct and anionic dyes with hydrolyzed collagen was studied at different pHs. Dyeing of cotton and leather was then carried out using various fractions of hydrolyzed collagen. The pH plays a very important role and the results indicate that there is synergistic effect of hydrolyzed collagen in the dyeing of leather. Even though the results are not promising in the case of cotton, there is a possibility to avoid the use of salt and to reuse the residual bath.

1. Introduction

Both the textile and leather industries are faced with remarkable environmental problems, mainly in the wet processing sector. Conventional cotton and leather dyeing processes generate huge quantity of residual dye and salt in the effluents. This problem is mainly due to the low affinity of the dye to the substrates. Moreover, the lost quantity of dye and salt in the dyebath could imply economic losses in addition to environment problems.

Collagen is a natural byproduct of the leather industry with lots of applications in cosmetics and skincare. It can be obtained from the wastes generated at different steps of the leather manufacturing. It is noted for its extraordinary moisture retention capacity [1,2]. Collagen, once hydrolyzed, turns to a mixture of peptides. In order to obtain hydrolyzed collagen from tannery waste, a hydrolysis process is realized by means of acid, alkali or enzymes. In the industry, chemical and enzymatic methods are basically used to obtain protein hydrolysates. The alkaline treatment is softer than the acid one, and is more suitable to obtain industrial hydrolysates. The enzymatic hydrolysis in an alkaline environment at moderate temperatures is highly recommended because it allows control of the reaction in order to obtain products with different functional properties. The accessibility of peptide bonds to enzymatic hydrolysis is very important because these bonds may be inaccessible due to the proper structure of the protein. A denaturation pre-treatment may facilitate subsequent enzymatic attack [3].

Different processes are described in Ref. [4] to obtain protein hydrolysates from cattle hide waste, which are mainly chemical processes based on calcium hydroxide. Hide waste can also be hydrolyzed by means of enzymatic hydrolysis with alkaline protease [5,6]. Enzymatic process is preferred over chemical process as it is more environment friendly. Studies are also carried out on an aqueous extraction of animal skin tissue followed by an enzyme treatment at 40–70 °C at various pHs [7].

Hydrolyzed collagen is used in detergent formulations for providing a protective and finishing effect on textiles. But practically there are no references on the application of hydrolyzed collagen in the dyeing of textiles or leather. Cotton dyeing with the direct dyes involves the use of a large quantity of salt. In the mean time, it is difficult to obtain uniform shades in leather dyeing. These variations in shades and tones are due to the nature of the raw material, which has variations within the matrix [8–10]. In this context, it is interesting to know whether the efficiency of the cotton and leather dyeing process could be improved by incorporating hydrolyzed collagen.

2. Experimental

2.1. Materials

Plain weave cotton fabric, bleached without optical brightener, with a grammage value of 180 g/m^2 has been supplied by EMPA

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(referenced as 210). Chromed ovine leather was produced from sheepskin originating from Spain. The skins were processed using the standard chrome tanning techniques to produce leather in wet-blue state with 40–50% humidity. The direct dyes Sirius Yellow K-CF (C.I. Direct Yellow 86), Sirius Blue S-BRR (C.I. Direct Blue 71) and Sirius Red K-BE (C.I. Direct Red 243), were supplied by Dystar, Spain. The anionic leather dyes Sella Fast Yellow R (C.I. Direct Yellow 11), Sella Fast Red E (C.I. Direct Red 239) and Sella Fast Blue BBN (C.I. Acid Blue 83) were supplied by TFL Ledertechnik España S.L. Sodium chloride and hydrochloric acid were purchased from Sigma–Aldrich. Cowhide waste was used as feedstock for the production of hydrolyzed collagen. Commercial alkaline protease enzymes used were of bacterial origin.

2.2. Preparation of hydrolyzed collagen

Cowhide waste trimmings were first denatured by subjecting to a thermal treatment for enabling the enzymatic action. The enzymatic hydrolysis was carried out in a BIOSTAT®B bioreactor monitored by MFCS/win software (B. Braun Biotech International GmbH). The optimum conditions were found to be 0.1% o.w.f. alkaline protease enzyme at pH 9.5 and 50–60 °C for 2 h. On completion of the process, the enzyme was deactivated by raising the temperature to 90 °C for 20 min. Further the pH was adjusted to 4.5 to conserve the hydrolyzed protein. The obtained peptides were a mixture of various molecular weights and it was ultrafiltered through membranes of 15 and 5 kDa. The complete fraction as well as three different fractions (high, medium, low) based on their molecular weights were obtained.

2.3. Compatibility study

The compatibility of the complete fraction of hydrolyzed collagen with all the selected direct and anionic dyes was studied in detail. Study was carried out by preparing a solution of 95:05 proportion of water:hydrolyzed collagen at different pHs 3, 5, 7 and 9, and mixing with 1% o.w.f. of various dyes. The samples were kept for 24 h and the compatibility was observed visually. A blank study was also carried out without the hydrolyzed collagen, in order to compare the results.

2.4. Conventional cotton dyeing process

The cotton samples were dyed with the red direct dye, Sirius Red K-BE (1% o.w.f.). 20 g/L of sodium chloride was added to the dyebath at the beginning of the dyeing process [11,12]. The dyeing was carried out in an Ugolini dyeing machine at 80 °C for 30 min at a speed of 40 rpm and the material to liquor ratio was fixed at 1:20.

2.5. Hydrolyzed collagen based dyeing process

The preliminary screening test indicated that 90:10 proportion of water:collagen was the best in the case of direct dyes. So the cotton samples were dyed with Sirius Red K-BE (1% o.w.f.) using this proportion and the pH was adjusted to 4.7 using hydrochloric acid. The study was carried out using the complete, high, medium and low fractions of hydrolyzed collagen. The dyeing was carried out in an Ugolini dyeing machine at 80 °C for 30 min at a speed of 40 rpm and the material to liquor ratio was fixed at 1:20. In the dyeing with hydrolyzed collagen, no salt was added and was compared with the control sample dyed by the conventional method.

2.6. Reuse of residual bath

At the end of the conventional and hydrolyzed collagen based processes, the residual dyebath volume was adjusted with water and cotton samples were added. The dyeing was carried out by the same procedure as above.

2.7. Dyeing of leather with anionic dyes

Conventional dyeing (1% o.w.f.) was carried out on chromed leather using the red anionic dye, Sella Fast Red E. The dyeing was started at a pH 5.5 and later increased to pH 6.5 and finally ended at pH 3 in order to fix the colour. In parallel modified dyeing process incorporating hydrolyzed collagen was carried out. Based on the results of the preliminary studies, the weights of various fractions were adjusted so that the weight of the active content – hydrolyzed collagen – was 5% in the dyebath. Additionally the dye and hydrolyzed collagen were added in two lots as it was found to be better than the single addition.

2.8. Characterization

The various fractions of hydrolyzed collagen were analyzed with SDS-PAGE by electrophoresis in polyacrylamide gel under denatured conditions. In the compatibility study, the samples were analyzed visually in order to determine the effect of the hydrolyzed collagen on the dyes at various pHs. The samples were rated on a scale of 0–4. The dyed cotton samples were subjected to 5 cycles of domestic washing at 40 °C, following procedure 6A of the standard, EN ISO 6330, using detergent IEC-A* in a Wascator washing machine. The samples were then dried in a flat surface, according to procedure C of the standard. The leather samples were subjected to 5 cycles washing as per IUF 423, using sodium lauryl sulphate as detergent in BOMBO SIMPLEX-4 washing drums. The unwashed and washed samples were also analyzed spectrophotometrically to measure the *K/S* (colour intensity) values.

The dyed cotton samples were also subjected to wash fastness testing as per EN ISO 105-C06, using ECE phosphate detergent without optical brightener in a Gyrowash FOM 71 MP-Lab equipment. The wash fastness of leather samples were assessed in BOMBO SIMPLEX-4, as per IUF 423 and the grey scale evaluation was made according to IUF 131. Dry and wet rubbing fastness of dyed cotton and leather samples were measured as per UNE-EN ISO 105-X12 and IUF 450, respectively.

3. Results and discussion

3.1. Preparation of hydrolyzed collagen

The hydrolyzed collagen obtained was a mixture of various fractions of different molecular weights. This complete fraction was ultrafiltered to obtain the high, medium and low molecular weight fractions. The high fraction contains molecular weight higher than 15,000 Da, the medium contains molecular weight between 5000 and 15,000 Da and the low fraction had molecular weight lesser than 5000 Da. The chemical characteristics of these fractions are given in Table 1. As observed, there is a clear decrease in the dry material weight, organic or protein content from high to low fractions.

Table 1
Chemical characteristics of various fractions of hydrolyzed collagen.

	Complete fraction	High fraction	Medium fraction	Low fraction
Dry material weight (%)	16.3	20.9	12.2	5.6
Organic material (%)	15.1	19.8	11.0	4.5
Ash 500 °C (%)	1.2	1.1	1.2	1.1
Total nitrogen (mg/L)	25,576	33,745	18,811	7811
Ammoniacal nitrogen (mg/L)	829	1077	622	313
Protein (mg/L)	95,835	117,129	95,840	42,172