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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

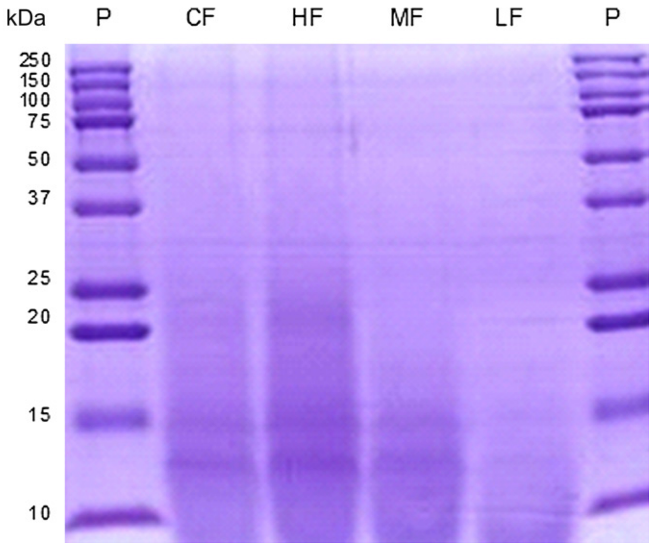

Fig. 1. SDS-PAGE analysis of various fractions of hydrolyzed collagen.

Fig. 1 shows the protein bands analyzed by SDS-PAGE analysis of the complete (CF), high (HF), medium (MF) and low (LF) fractions. Molecular weight marker for protein gels, “Kaleidoscope Prestained Standard” from Bio-Rad (P) was used for determining the exact molecular weight of the fractions. Specific bands of 13 and 15 kDa was observed for the complete fraction, 13, 15 and 20 kDa for the high fraction, 13 and 15 kDa for the medium fraction and no bands in this range for the low molecular fraction.

3.2. Compatibility study

It is necessary to know the compatibility of hydrolyzed collagen with various dyes at different pHs, in order to determine the best dyeing conditions. The 95:05 proportion of water:hydrolyzed collagen was selected in order to determine whether the fixation of the dyes is better with a very small concentration of hydrolyzed collagen. A blank study was also carried out without the hydrolyzed collagen, in order to compare the results. The samples of blank study are coded as shown in Table 2 and the samples containing hydrolyzed collagen in Table 3.

The solutions were analyzed visually to know the effect of hydrolyzed collagen on the dyes by observing whether there is any precipitation, sedimentation, agglomeration or phase separation. Further, the colour of the samples were referenced using the following scale: 0: transparent solution, but little lighter; 1: transparent solution, but little darker; 2: transparent solution, but darker; 3: turbid and 4: very turbid. Table 4 shows the results of the compatibility study based on visual observation of the direct and anionic dyes in water and hydrolyzed collagen solutions at different pHs.

Table 2
Samples description of the compatibility study of various dyes.

Without hydrolyzed collagen				
	pH 3	pH 5	pH 7	pH 9
Direct dye				
Yellow	A3	A5	A7	A9
Blue	B3	B5	B7	B9
Red	C3	C5	C7	C9
Anionic dye				
Yellow	G3	G5	G7	G9
Blue	H3	H5	H7	H9
Red	I3	I5	I7	I9

Table 3
Samples description of the compatibility study of various dyes.

With hydrolyzed collagen				
	pH 3	pH 5	pH 7	pH 9
Direct dye				
Yellow	A13	A15	A17	A19
Blue	B13	B15	B17	B19
Red	C13	C15	C17	C19
Anionic dye				
Yellow	G13	G15	G17	G19
Blue	H13	H15	H17	H19
Red	I13	I15	I17	I19

The results indicate that in general all the dyes are compatible with hydrolyzed collagen at all the pHs except the pH 3. The isoelectric point of hydrolyzed collagen is at 5.2 and so it becomes cationic at lower pHs and thus interacts with the anionic dyes electrostatically resulting in precipitation or sedimentation and colour change. In the case of yellow anionic dye, the solubility increased generally with the addition of hydrolyzed collagen. It also seems that hydrolyzed collagen may be acting as a surfactant by reducing the surface tension.

3.3. Cotton dyeing process

The conventional direct dyeing of cotton is carried out with a high quantity of salt and in alkaline pH. In a preliminary study, we have carried out the treatment of cotton with hydrolyzed collagen at acidic pH followed by dyeing with salt at alkaline pH. The results from this dyeing process incorporating the hydrolyzed collagen were found to be much inferior to the conventional process. In order to interpret the results, the mechanism of action of hydrolyzed collagen in different pHs was elucidated and is shown in Table 5.

As mentioned before, the isoelectric point of hydrolyzed collagen is at 5.2. Cotton, once impregnated with water always shows anionic character [13], whereas the ionic charges of hydrolyzed collagen may change depending on the pH. At pHs below its isoelectric point it shows a cationic character and at higher pHs it shows anionic character. So we have thought that hydrolyzed collagen in acidic pH can do the same role of salt in the dyeing process, thus reducing the repulsion between the dye and cotton. But at higher pHs, the hydrolyzed collagen being anionic in nature will enhance the repulsion between the dye and cotton and thus has a detrimental effect in dyeing. The effect of pH on the ionic charges of hydrolyzed collagen is shown in Fig. 2.

Taking clues from the mechanism, we have modified the dyeing process and the dyeing was carried out at an acidic pH, but without the addition of salt. Some methods like cationisation with chemical pre-treatments have been proposed in order to avoid the use of salt in the cotton dyeing process [12]. We have tried to make cotton cationic by incorporating hydrolyzed collagen, which is a natural and ecological product. In order to determine the best dilution of hydrolyzed collagen in water, we have first studied the dyeing at different dilutions like 95:05, 90:10, 80:20 and found that the 90:10 was showing the best results. So the dilution was fixed at 90:10 and the samples are described in Table 6. Each fraction was different in the molecular weights and the complete fraction is a mixture of all. A conventional dyeing was also carried out for comparison.

3.4. Colour evaluation of dyed cotton

Fig. 3 shows the K/S values of the cotton samples dyed using various fractions of hydrolyzed collagen at λ_{max} 530 as compared to

Table 4
Visual analysis of the compatibility study.

	Sample															
	A3	A5	A7	A9	A13	A15	A17	A19	B3	B5	B7	B9	B13	B15	B17	B19
No change			x	x		x	x	x		x	x	x		x	x	x
Precipitation																
Sedimentation					x								x			
Agglomeration																
Phase separation																
Colour change	4	3			4				4							
	Sample															
	C3	C5	C7	C9	C13	C15	C17	C19	G3	G5	G7	G9	G13	G15	G17	G19
No change	x	x	x	x		x	x	x						x	x	
Precipitation									x	x	x	x	x			x
Sedimentation					x											
Agglomeration																
Phase separation																
Colour change													0	0	0	0
	Sample															
	H3	H5	H7	H9	H13	H15	H17	H19	I3	I5	I7	I9	I13	I15	I17	I19
No change	x	x	x	x		x	x	x	x	x	x	x		x	x	x
Precipitation					x								x			
Sedimentation																
Agglomeration																
Phase separation																
Colour change					0								0			

Table 5
Mechanism involved in the cotton dyeing process with hydrolyzed collagen.

	pH < 5	pH 5.0–7.0	pH > 7
Hydrolyzed collagen Isoelectric point 5.2	Cationic NH_3^+–R–COOH	Anionic NH_2–COO–	Anionic NH_2–COO–
Cotton	Anionic	Anionic	Anionic
	Coordination	Absorption	Repulsion of charges
Union of hydrolyzed collagen to cotton	The hydrolyzed collagen gets fixed electrostatically, reducing the negative charge of cotton	The hydrolyzed collagen is deposited physically over cotton. There is repulsion of charges, but something can be absorbed	

the conventional dyeing. As observed from the figure, the sample dyed by the conventional method developed the highest *K*/*S* values and the use of collagen has reduced the colour strength. Among all the samples dyed using hydrolyzed collagen, the low molecular fraction gave the best results. This similar trend continued even after 5 cycles of washing.

Even if we have achieved lower dye uptake values with hydrolyzed collagen than in the conventional process, we have achieved salt free dyeing. As depicted in Table 5, at pH <5 there is a coordination between hydrolyzed collagen and cotton. The hydrolyzed collagen gets fixed electrostatically, reducing the negative charge of cotton. Moreover, dyeing process with hydrolyzed collagen avoids the addition of salt in the dyebath. On the other hand, it is obvious that dye would not be fixed on cotton at pH >7 as there is a repulsion of charges among cotton, dye and the hydrolyzed collagen.

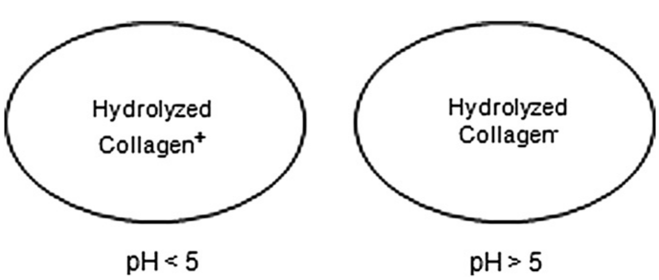

Fig. 2. Effect of pH on hydrolyzed collagen.

But it was interesting to note that it was possible to dye cotton with direct dyes at an acidic pH without using salt. So the hydrolyzed collagen can play the role of salt to reduce the repulsion of similar charges and helps in fixing the dye leading to salt free effluents. The hydrolyzed collagen being a natural product is biodegradable and do not raise any environmental concerns.

3.5. Fastness properties of cotton

Table 7 shows the washing and rubbing fastness of cotton samples dyed using various fractions of hydrolyzed collagen as compared to the conventional dyeing process.

As observed from the table, samples dyed with hydrolyzed collagen have shown similar washing fastness to the conventional samples. So it confirms that the addition of hydrolyzed collagen in the dyebath does not have any negative effect on the washing fastness of the samples. Moreover, dry and wet rubbing fastness tests have been realized on each sample. All the samples present good results at dry rubbing fastness and average results at wet rubbing fastness. So, hydrolyzed collagen does not affect the rubbing fastness of the samples.

Table 6
Description of dyed cotton samples.

Samples	Dyeing process
T	Conventional, with salt
TC1	Complete fraction, without salt
TC2	High fraction, without salt
TC3	Medium fraction, without salt
TC4	Low fraction, without salt

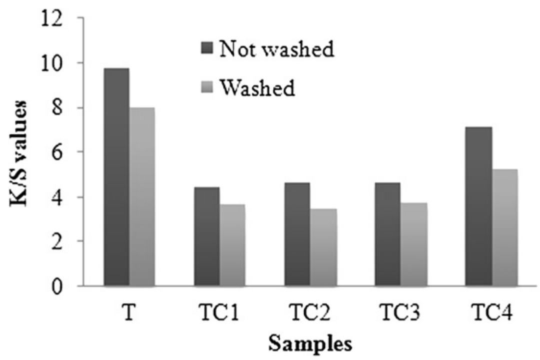

Fig. 3. *K*/*S* values of the dyed cotton samples, before and after washing.

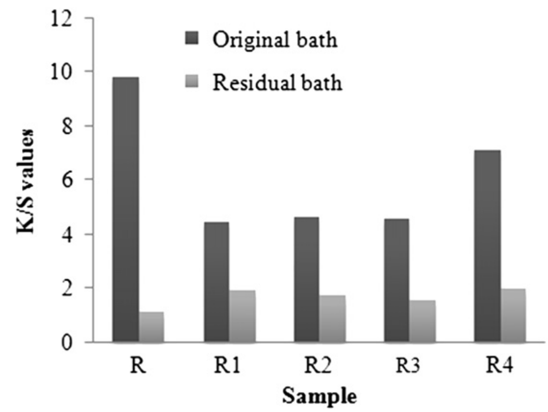

Fig. 4. *K*/*S* values of samples dyed with residual bath compared to the samples dyed using original bath.

Table 7
Washing and rubbing fastness of cotton samples.

Sample	Washing fastness	Rubbing fastness	
	Change in colour	Dry	Wet
T	4/5	4	3
TC1	4/5	4	3
TC2	4/5	4	3
TC3	4/5	4	3/4
TC4	4	4/5	2/3

3.6. *Reuse of residual bath*

As the dyebath effluents can cause major environmental problems, reusing the residual bath could be a solution [14–16]. One of the main issues in reuse is the high quantity of salt in the effluent bath, which can limit the number of reuses. As the dyeing with hydrolyzed collagen does not involve salt, the reuse should be easier. Samples dyed with residual bath are described in Table 8. The *K*/*S* values of the original dyeing are compared with the samples dyed using the residual baths as shown in Fig. 4.

As observed from the figure, the *K*/*S* values of the samples dyed with residual bath are much lower than *K*/*S* values of the samples dyed with the original bath. But it was interesting to note that the baths containing hydrolyzed collagen showed better results than the conventional one. The samples from reused bath showed good wash fastness properties also. Additionally, these baths could be used many times as they are free of salt precipitation problem. Also, residual bath dyeing could be a route for obtaining samples with different lighter shades. In addition, the residual baths may be used as standing baths by replenishing the dye in the residual bath to adjust the colour which may lead to samples of same colour strength as original baths.

3.7. *Leather dyeing mechanism*

In addition to the conventional dyeing, leather was dyed by incorporating hydrolyzed collagen in the dyebath. Based on the preliminary results, the weights of various fractions were adjusted so that the weight of the hydrolyzed collagen was 5% in the dyebath. Results show that all the samples dyed using hydrolyzed collagen result in uniform dyeing with higher colour strength than the conventional sample. Thus the hydrolyzed collagen exerts an important synergistic effect on the dyeing process, unlike in the case of cotton. The possible mechanism involved in the leather dyeing process containing hydrolyzed collagen has been elucidated and is shown in Table 9.

Chrome tanned leather shows a cationic nature in acidic pH [17,18] and during dyeing, the dye initially penetrates throughout the cross section of leather and is then fixed in leather fibres by electrostatic attraction. At the end of dyeing the dye is normally fixed by further reducing the pH. As observed from the table, when the pH is below the isoelectric point of hydrolyzed collagen, both hydrolyzed collagen and leather being cationic, there could be repulsion of charges. Still the hydrolyzed collagen may be deposited physically on the leather surface and something may be absorbed. But at the initial dyeing pH 5.5, the chromed leather being cationic and the hydrolyzed collagen being anionic, the hydrolyzed collagen gets fixed electrostatically onto the leather and reduces its positive

Table 8
Description of cotton samples dyed using residual bath.

Samples	Dyeing process
R	Conventional, with salt
R1	Complete fraction, without salt
R2	High fraction, without salt
R3	Medium fraction, without salt
R4	Low fraction, without salt

Table 9
Mechanism involved in the leather dyeing process with hydrolyzed collagen.

	pH < 5	pH 5.0–7.0	pH > 7
Hydrolyzed collagen Isoelectric point 5.2	Cationic NH_3^+–R–COOH	Anionic NH_2–COO–	Anionic NH_2–COO–
Chromed leather Isoelectric point 7.0	Cationic	Cationic	Anionic
	Absorption	Coordination	Repulsion of charges
Union of hydrolyzed collagen to leather	The hydrolyzed collagen is deposited physically over leather. There is repulsion of charges, but something can be absorbed	The hydrolyzed collagen gets fixed electrostatically, reducing the negative charge of cotton	

Table 10
Description of dyed leather samples.

No	Hydrolyzed collagen	Dye Sella Fast Red E
1		0.5% + 0.5%
2	5% Complete	0.5% + 0.5%
3	3.9% High	0.5% + 0.5%
4	6.7% Medium	0.5% + 0.5%
5	14.5% Low	0.5% + 0.5%

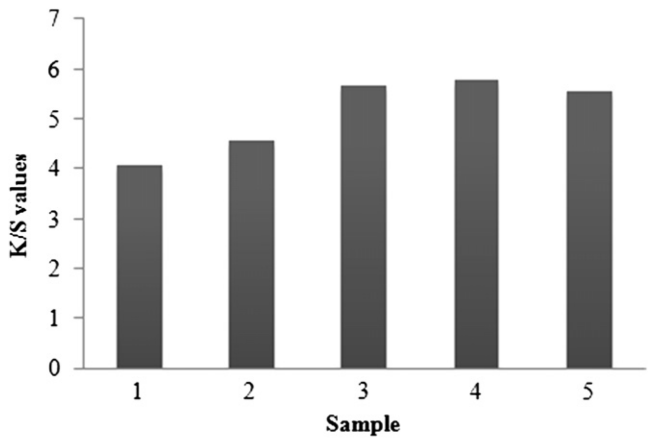

Fig. 5. *K/S* values of the dyed leather samples.

Table 11
Washing and rubbing fastness of leather samples.

Sample	Washing fastness	Rubbing fastness	
	Change in colour	Dry 10 cycles	Wet 5 cycles
1	4	4–5	4
2	4–5	4–5	4
3	4–5	4–5	4
4	4–5	4–5	4
5	4–5	4–5	4

charge. In this case there can be coordination between hydrolyzed collagen and leather which may lead to increased dye uptake and level dyeing.

3.8. Colour values of leather

In Table 10, the various leather samples dyed by the red anionic dye are described. The colour values of various dyed leather samples at λ_{max} 520 are given in Fig. 5.

As observed from the figure, better dyeing results were obtained for the dyeing of leather incorporating hydrolyzed collagen. In this case the synergistic effect of the hydrolyzed collagen was evident unlike in the case of cotton. The samples containing hydrolyzed collagen also developed uniformly dyed surfaces unlike in the case of the conventional sample. The results indicate that the medium fraction of hydrolyzed collagen was found to be the best followed by the high fraction.

3.9. Fastness properties

Table 11 shows the washing and rubbing fastness of leather samples dyed using various fractions of hydrolyzed collagen as compared to the conventional dyeing process.

As observed in the table, all the samples have shown good washing fastness properties. Moreover, samples dyed with hydrolyzed collagen presents slightly better results than the conventional sample. Results of dry and wet rubbing fastness show that all the samples have good dry and wet rubbing fastness. However, dry test showed better fastness than wet test. Moreover, results showed no difference between the conventional and the hydrolyzed collagen based process. So, we can conclude that that hydrolyzed collagen does not affect the rubbing fastness of leather.

4. Conclusions

The use of hydrolyzed collagen in the dyeing is a novel concept. Even though the results are not promising in the case of cotton, there is a possibility of dyeing without salt, where the hydrolyzed collagen plays the role of salt. Good results are obtained in the dyeing of leather where the synergistic effect of hydrolyzed collagen was evident. Both cotton and leather behave differently towards the hydrolyzed collagen at various pHs. Depending on the pH, the hydrolyzed collagen can improve or reduce the affinity of dyes onto the substrate. The residual bath dyeing process of cotton has not given good results, but it is easy to reuse unlike conventional baths containing salt. On the other hand, dyeing process with residual bath could be used for developing a range of lighter shades on the fabric.

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