ECOFRIENDLY DYEING PROCESS WITH ENZYMES

SELIME MENTEŞ ÇOLAK, TUNÇ ORTAFIDAN

Ege University Engineering Faculty, Leather Engineering Department, 35100 Bornova-İzmir, TÜRKİYE, selime.mentes.colak@ege.edu.tr

Biological degradation of many dyes is difficult. Therefore dyeing baths give high pollution load to waste water. In this work, the use of enzyme in the dyeing of leather has been studied with the aim to improve the exhaustion of dye and to reduce pollution load of dyeing waste bath. For this purpose, chromium-tanned leather were treated with different ratio enzyme after the neutralization process. Then dyeing has been carried out. The effect of bacterial protease on colour properties of leathers was investigated. Also the change of the amount of COD load in the waste dye baths and leather physical properties were investigated. The obtained test and analysis results show that when the enzyme was used in the dyeing process, the COD load of waste dye baths was reduced.

Keywords: leather, ecofriendly dyeing, enzyme

INTRODUCTION

Tanning process involves conversion of putrefiable skin or hides to a nonputrescible material. Leather making involves operations like soaking (rehydration), liming, deliming, pickling, tanning, post-tanning and finishing processes (Kanagaraj *et al.*, 2015).

Dyeing is one of the inevitable steps of imparting color to the leather carried out in post-tanning operations. Synthetic dyes hold a major share in the dyeing of leather. In general, about 70% and 20% dyestuffs used today belong to acid and direct class (Hunger, 2002; Zengin *et al.*, 2012). These dyes have poor biodegradability due to higher biological and chemical oxygen demands. The conventional leather dyeing process is also very cumbersome and employs numerous chemicals and auxiliaries. Due to the number of pollutants involved in the wet processing of leather, this industry is striving to find natural and eco-friendly dyestuffs, auxiliaries and methods to reduce the environmental pollution (Dave, 2015). The total worldwide consumption of dye in several industries like textile, paper, pulp, leather, plastics is in excess of 104 tons/year. It is estimated that about 10% of unexhausted dyes are discharged into the waste streams irrespective of the substrate involved in dyeing. Hence, the generated effluent contributes to very high biological oxygen demand, chemical oxygen demand, color and suspended solids. The biotreatability of many of these synthetic dyes is normally poor and therefore, the treated waste water retains residual color, leading to the constant criticism from the civic community. In addition, the colored dye effluents become toxic to aquatic biota and thus affect the symbiotic process by disturbing the natural equilibrium thereby reducing the photosynthetic activity and primary production (Kanth *et al.*, 2009). In recent years, nearly 30% of the leather industries have been shut down due to environmental concern which urges the industries to adopt cleaner processing methods. Several greener approaches were proposed in this context, among them enzyme based processes for pre-tanning and pigment from natural sources (plants, microbes, insects/animals and minerals) for dyeing had been considered as effective, safer and a cleaner technology for making leather (Haddar *et al.*, 2014).

Different types of enzymes are commonly used in various stages of leather processing for modification of physical and chemical properties of leather. But the

information available on the use of enzymes in dyeing process of post-tanning operations in leather manufacture is scanty.

In this work, the influence of bacterial protease enzyme on leather properties and wastewater pollution load in dyeing process was investigated.

MATERIALS AND METHODS

Enzyme-aided Dyeing Process

The chrome tanned leather samples were neutralized, dyed and fatliquored according to the recipe given in Table 1. Enzyme concentrations 0,05 and 0,1% (based on weight of shaved chrome tanned leathers) have been used. The leathers have been further treated with fatliquors as per a standard leather processing recipe for garment leathers.

Control Dyeing Process

The control dyeing processes have been carried out without enzyme treatment. Fatliquoring and dyeing processes were done the same way in all leather groups (Table 1).

The process liquors from all the experimental and control trials have been analyzed for the uptake of dye and load of COD. The leathers have been washed, set, hooked to dry and stored at room temperature.

The unspent dyestuff in the exhausted process liquor was analyzed using a Shimadzu UV–Visible 1601 spectrophotometer. The percentage of dyestuff exhaustion (DE) was calculated using the following equation:

$$\% DE = [(C_r - C_t)/ C_r] \times 100 \quad (1)$$

where C_r and C_t represent the amount of dyes at the end of the dyeing procedure for the reference and treated samples respectively.

Table 1. The dyeing recipes of study

Cr Retannage	150% Water 40 C
Neutralisation	3% Electrostable fatliquoring agent
	4% Basic chrome sulphate 45’
	1% Na -Formiate 30’
	1% $NaHCO_3$
	pH: 6.5
Enzyme treatment	100% Water 40 C
	X% Bacterial protease 30’
	(X= 0.05% and 0.1%)
Dyeing	100% Water 40C
	1 % Dyeing auxiliary agent 10’
	2 % Acid dye
	1 % formic acid 30’
Fatliquoring	150% Water 60 C
	12 % Combine fatliquoring agent
	2 % Electrostable fatliquoring agent
	2 % Syntetic fatliquoring agent 60’
	1% Formic acid 30’ pH: 3.8
	Washing

Chemical Oxygen Demand (COD) in the exhausted retanning process liquor was using Merck Cell Test kit Merck Spectroquant Move 100 spectrophotometer.

The leather samples were prepared in accordance with “sampling location” and conditioned according to “sample preparation and conditioning” standards TS EN ISO 2418 and TS EN ISO 2419 respectively prior to analysis (EN ISO 2419/2006).

In order to identify the color differences between research and control leathers , lab type spectrometer which has 4 mm width measuring range, Konica Minolta CM- 3600A brand was used. Measurements were performed according to CIELAB color coordination, under the conditions of CIE 100 standard observer angle and CIE standard D65 light source (Zengin *et al.*, 2012).

Wet and dry rub were carried out using standard procedures (EN ISO 11640/2001). Rubbing fastness was carried out by using the device "Otto Specht Bally Finish Tester". Significance of differences between fastness values were evaluated to a grey scale as shown in Table 2.

Determination of tensile strength and elongation was performed according to the ISO 3376:2011 standard method. The tensile strength of the dyed leathers were measured using a Shimadzu AG-IS Test Apparatus.

Scanning electron micrographs of the cross section of the leathers was taken used by HITACHI TM-1000 tabletop microscope with x250 magnification.

RESULTS AND DISCUSSION

Dyeing is an important process in the leather industry. Many dyes suffer from incomplete exhaustion and this causes concern, as the biotreatability of the unexhausted dyes in effluent is normally difficult. In the present study, an attempt has been made to improve the exhaustion of dyes by using enzymes. The effect on leather properties and waste dyeing baths of enzymatic treatment have been studied.

Table 2. Evaluation of fastness values with grey scale

Fastness value	Evaluation
1	Very poor
2	Poor
3	Average
4	Good
5	Very good

Table 3. The results of test and analyses of control and enzyme aided dyed leathers

	Exhaustion %	Tensile strength (N/mm^2)	Elongation (%)	COD (mg/l)
Control	36.7	12,68	72,57	5580
0.05% Enzyme	78.5	17.48	59,27	1064
0.1% Enzyme	85.5	15.08	62.73	638

The results of dyestuff exhaustion for control and enzyme-aided dyed leathers are given in Table 3. In the study, dye consumption value analyzed, in control group exhaustion of dye was found to be 36.7%. When the results are evaluated, enzyme treated groups have been found rather good than control group. 0,1% enzyme treated

group leather samples had the best consumption values when compared to other enzyme group in the study (Table 3).

The examination of Table 2 indicates that with the increasing ratio of the enzyme used from 0,05% to 0,1%, the exhaustion in the dye bath gradually increases from 78,5% to 88,5%. When the control group and enzyme aided leathers are compared to each other, it is clearly observed that the dyestuff exhaustion of the enzyme aided leathers are higher than that of the control groups. It was found that there was a significant increase in dye uptake after enzymatic treatment.

One of the most important rapid parameters in determining the pollution load of leather effluent is the COD test. The COD values of the dye liquors of leathers consumed in our study are shown in Table 2. When dyeing waste water's pollution load was examined in the study, it was seen that 0.1% enzyme treated group leather samples had the lowest COD values when compared to other trials. The COD values of 0.1% group were detected as 638 mg/l. COD value of the 0.05% enzyme treated group was found 1064mg/l. In order to identify the pollution load and leather properties, no enzyme was used in control group. The COD value of control group was obtained as 5580 mg/l. When control group and enzyme treated groups were compared, it was seen that dyeing process had substantially increasing effect on waste water pollution load. Waste dyebath COD values are seen in Table 3. The results show that there is a significant improvement in the pollution load of dye waste bath due to the presence of enzyme, when compared to dyeing in absence of enzyme.

The tensile strength and elongation test results of the leather samples in the study are given in Table 3. Table 3 shows that strength characteristics of leather dyed in presence of bacterial protease are comparable to those of control leathers, which implies that strength properties were increased use of enzyme during the dyeing process. The tensile strength test results show that the leathers treated with 0.1% and 0.05% enzyme demonstrated the best values of 17.48 N/mm and 15,08 N/mm respectively. The lowest values in the tear loading test were obtained in control groups leathers. According the research results, the strength properties are improved but the elongation of leather decreased by use of the bacterial protease.

All dyeing combinations of control and enzyme-aided leathers were analyzed spectrophotometrically and the color values of leathers are provided in Table 4.

Table 4. Values of the colors obtained with and without enzyme

	L*(D65)	a*(D65)	b*(D65)	ΔE(D65)
Control	28,60	6,02	4,57	70,77
0.05% Bacterial protease	33,45	6,74	5,64	66,10
0.1% Bacterial protease	33,87	7,27	5,99	65,77

When ΔE values are examined after enzyme implementations that have different concentrations, it has been observed that there is color difference between the leathers that are treated with enzyme-aided dyeing and control group's samples. When control group leather samples and enzyme group samples are compared, it has been detected that there is color difference. Colors that are closest to black are acquired from 0.1% enzyme applied leathers. It has been observed that black color of leather samples in enzyme-aided dyeing is lighter (brighter) than control group's leather. When enzyme implementations are compared among each other, it has been detected that closest color

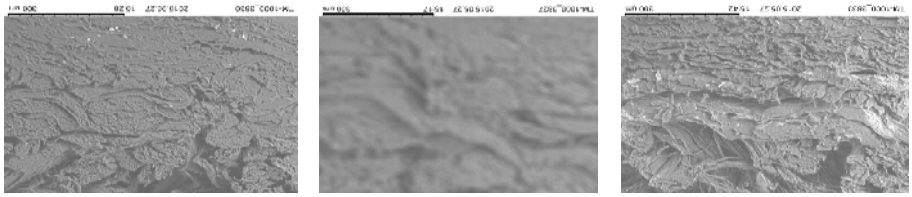
to black is acquired from 0.1% enzyme implementation and 0.1–0.05% enzyme implementations show very similar black color rates.

Besides, when a* rates are examined, it has been detected that color of control leather samples and leathers that were treated with enzyme implementations come from red. Also, there are differences in redness value of leathers that are acquired through control and enzyme implementation. Same effect is remarkable in enzyme implementations too. When "b*" rate, which shows yellowness and blueness values, is examined, it has been seen that same situation in "a*" rate is same for this rate too. It has been detected that control sample leathers that were processed with enzyme implementation has yellowness in their color. Also, in the yellowness rates of leathers that are acquired through control group and enzyme implementations has differences. It has been detected that same effect is also present in enzyme implementations.

Wet and dry color fastnesses of leathers analyzed on the grain sides to rubbing are comparatively shown in Table 2.

The colour fastness properties of dyed leathers were tested according to the standards and compared with the greyscale. The colour fastness properties of the enzyme treatment and control groups leather results are given in Table 4. The results of colouristic evaluation show that the wet fastness properties of control leathers and 0.1% enzyme treated leathers are not different, but dry fastness of control leathers were found lower than 0.1% enzyme treated leathers.

The Table shows that the dry and wet rubbing fastness of 0.1% enzyme treated leathers were better than the control leathers and 0.05% enzyme treated leathers. Although wet rubbing fastness of 0.5% enzyme treated leathers were lower than the control leathers and 0.1% enzyme treated leathers, dry rubbing fastness of 0.5% enzyme treated leathers were proved higher than control leathers. This implies that colour of the 0.1% enzyme treated leathers can withstand dry and wet conditions in a better way.



Control group 0.05% Enzyme 0.1% Enzyme

Figure 1. Scanning electron micrographs (250× magnification) showing the cross-section view of leathers

Scanning electron microscopy analysis showed a well opened-up fibre matrix for the enyzme treated leather.

CONCLUSION

This study showed that enzyme treatment improved the performance characteristics of leather that it provided some environmental protection. The best values of dyestuff consumption, wet-dry rubbing fastness, tensile strength and COD were found with the 0.1% bacterial protease treatment. The CF treated TTC leathers gave the best results in all the tests and analyses. The results suggest that bacterial protease can be used in

leather processing. It was found that there is a significant increase in dye uptake after enzymatic treatment. The results show that there is a significant improvement in the exhaustion of dye due to the presence of enzyme, when compared to dyeing without enzyme. From the ecological perspective, it could further be said that using bacterial protease is of extreme importance in terms of reducing the environmental pollution load and providing a sustainable solution to the leather industry.

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