Dyes and Pigments, Vol. 29, No. 3, pp. 203–209, 1995

0143-7208/95 $9.50 + 0.00

ELSEVIER

0143-7208(95)00044-5

Effect of Enzymatic Treatment on the Dyeing of Cotton and Wool Fibres with Natural Dyes

E. Tsatsaroni[a]* & M. Liakopoulou-Kyriakides[b]

[a] Faculty of Chemistry, [b] Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece

(Received 27 March 1995; accepted 10 May 1995)

ABSTRACT

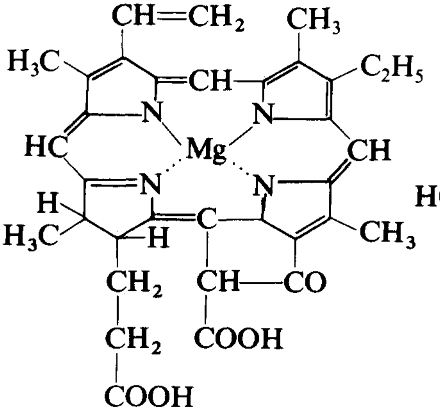
Cotton and wool fabrics were dyed with the natural dyes chlorophyll and carmine after treatment with the enzymes cellulase, α-amylase and trypsin. Wash and light fastnesses of the dyed samples were studied. Enzymatic pretreatment resulted in an increase in pigment uptake in all cases compared with the corresponding untreated samples, and did not affect fastness properties. Pretreatment with metallic salts and dyeing of pretreated samples was also carried out and the fastness properties of the dyed materials were studied. The effect of conventional mordanting with metallic salts was compared with that of enzymatic treatment on the dyeing properties of the dyes used.

INTRODUCTION

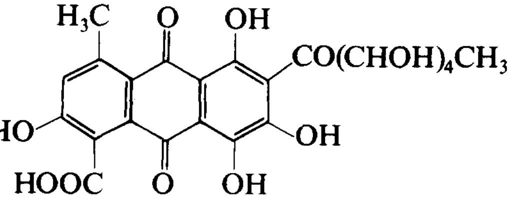
There is interest in the dyeing of textile fibres with natural dyes, on account of their high compatibility with the environment, and because of their lower toxicity and allergic reactions.

Problems in dyeing with natural dyes are related to the low exhaustion of the dyes and to the fastness of the dyed fabrics. Attempts to overcome these problems have been mainly focused on the use of metallic salts as mordants, which are traditionally used to improve fastness properties or exhaustion and to develop different shades with the same dye.[1–4] However, this method has lost much of its importance and other processes based on fibre modification (e.g. with resins) are used.

* To whom correspondence should be addressed.



1



2

Fig. 1. Dyes used in the study.

Enzymatic treatment has recently been applied to minimize wool shrinkage and to improve its dyeing properties.[5,6]

The aim of this work was to study the effect of the enzymatic treatment of cotton and wool (the preferred substrates for dyeing with natural dyes) on their dyeing properties using the water soluble dicarboxylic acid of chlorophyll **1** (CI Natural Green 5) and carmine **2** (CI Natural Red 4).[7] The results are compared with those obtained with the same dyes after treatment of the fibres with metallic salts.

The work is part of a larger project on the use of vegetable dyes in the dyeing of natural fibres.

EXPERIMENTAL

Materials

Commercial bleached cotton and wool fabrics, chlorophyll and carmine were used for the dyeings. Before dyeing, cotton fabrics were treated with the enzymes α-amylase and cellulase while wool fabrics were treated with trypsin. Aqueous solutions containing 20 g l^{-1} iron(II) sulphate heptahydrate (BDH), aluminium sulphate hexadecahydrate (Aldrich) and sodium potassium tartrate tetrahydrate (Merck) were used as mordants.

Apparatus

Dyeings and wash fastness tests were carried out in a Rotadyer apparatus (John Jeffreys Ltd). Spectrophotometric measurements were recorded in a Shimadzu UV-2101 PC spectrophotometer. An air-cooled Hahau Suntest

TABLE 1
Enzymatic Treatment Conditions used for Cotton and Wool

Enzyme	*Treatment duration (min)*	*Enzyme concentration ($g\ l^{-1}$)*	*pH*	*Temperature (°C)*
α-Amylase	10	2	7	25
Cellulase[a]	30	0·7	4·4	60
Trypsin	30	2	8	30

[a] Additional heating at 75°C for 30 min to inactivate the enzyme.

apparatus (Heraeus) with a Xenon lamp was used for the light fastness tests. Colour changes during the light fastness tests were evaluated in a Verivide colour assessment cabinet (Leslie Hubble) with an artificial daylight (D65) lamp. A Macbeth CE 3000 spectrophotometer (UV and specular component included, large area view 25·4 mm diameter) was used for colour measurements.

Enzymatic treatment

Treatment conditions for the enzymes used are given in Table 1. After treatment all samples were rinsed and squeezed.

Treatment with mordants

Cotton fabrics were immersed in a 5% ammonia solution for 30 min and then in the mordant solutions for 45 min at 30°C. Wool fabrics were immersed directly in the mordant solution for 45 min at 30°C. All the mordanted fabrics were allowed to stand overnight[2–4] and then dyed. All treatments were carried out at a liquor ratio of 30:1.

Dyeing

The fabrics were dyed with 2% o.m.f. depth of dyeing at a liquor ratio 30:1. The temperature was raised to 90°C over 30 min and maintained at this level for 1 h. Sodium chloride (10% o.m.f.) or a few drops of 40% acetic acid solution were added to the dyeing liquors used for the cotton or wool fabrics respectively.

Determination of dye adsorbed on the fibre

This was done spectrophotometrically by extracting the pigment of the dye fabrics with pyridine (25% v/v in water) and measuring the absorbance of the extracts at 522 and 409 nm (λ_{max} of carmine and chlorophyll respectively).

Fastness determination

Wash fastness tests were carried out according to BS 1006: 1990 CO2[8] with a soap solution (5 g l^{-1}, liquor ratio 50:1) for 45 min at 50 ± 2°C. The samples were assessed against the standard grey scale for colour change.

Light fastness tests were carried out according to BS 1006: 1990 BO2.[9] Colour change of the samples was assessed against the grey scale and the blue wool standard.

Colour measurement

Dyed samples were prepared for colour measurement by folding the fabric three times to give a sample size of about 3 × 3 cm. Colour differences were evaluated by means of the modified CIE L^* C^* H^* (illuminant D65/10^0 observer systems). Reproducibility was checked by taking three measurements and recording the variation in percentage reflectance values over the range 400–800 nm; it was found to be very satisfactory in all cases.

RESULTS AND DISCUSSION

The dyeing results, percentage pigment exhaustion, wash and light fastness values for the dyed samples with and without enzymatic treatment are given in Table 2.

As can be seen, the amount of dye adsorbed on the fibre is higher for wool than for cotton. Chlorophyll has a higher percentage exhaustion than carmine in all cases, and especially in the case of wool dyeing where the uptake is significantly higher, similar to that of conventional synthetic dyes. Wash fastness values are also higher for chlorophyll than for carmine on the wool samples. This difference in dye uptake and wash fastness could be attributed to the structural features of the two dyes (Fig. 1) and the substrates. In the case of wool dyeing, hydrophobic interactions seem to be largely responsible for the affinity of the dyes and their wash fastness on wool, while ionic forces between the positively charged amine groups of the protein fibre and dye sites also play a role.[10] The large chlorophyll molecule seems to fulfil these requirements, while carmine, with many hydrophilic groups, does not. In addition, in

TABLE 2

Percentage Exhaustion and Wash and Light Fastnesses of Cotton and Wool Samples Dyed with Chlorophyll and Carmine With and Without Enzymatic Treatment

Pigment	*Enzyme*	*Pigment (g) per 100 g fibre*	*Percentage exhaustion*	*Colour change*	
				Wash fastness	*Light fastness*
Wool samples					
Chlorophyll	none	1·458	72·9	3	4–5
Chlorophyll	trypsin	1·818	90·9	3	4–5
Carmine	none	0·063	3·15	3	3–4
Carmine	trypsin	0·087	4·35	3	4
Cotton samples					
Chlorophyll	none	0·35	17·0	2–3	3
Chlorophyll	α-amylase	0·49	24·5	2–3	3
Chlorophyll	cellulase	0·40	20·0	2–3	3
Carmine	none	0·036	1·2	1	3
Carmine	α-amylase	0·055	2·0	1	3
Carmine	cellulase	0·090	3·0	1	3

cellulose dyeing hydrophobic interactions between the dye and —CH— groups of cellulose contribute, to dye stability,[11] apart from weak Van der Waals forces and hydrogen bonds.

Enzymatic treatment resulted in an improvement in dye uptake in all cases reported, which could be attributed to enhanced shrink-resistance properties of the fibre.[5,6] In all cases, wash and light fastness values of the treated samples remained the same as those for the reference samples, indicating that there is a real fixation of the pigment on the treated fibre.

The results obtained show low exhaustion for carmine from the dye liquor in all cases, and poor fastness properties especially in the case of cotton dyeings. Thus carmine would not be useful as a textile colorant even after enzymatic treatment of the fibre, which results in a considerable relative improvement in exhaustion (about 30 and 50% in the case of wool and cotton dyeing respectively). In contrast, chlorophyll showed high percentage exhaustion values and medium fastness properties, especially in the case of wool.

In order to compare these results with those obtained by dyeing after treatment of the cotton and wool with metallic salts (mordants), dyeings were repeated under the same conditions, as above, but after treatment of the cotton and wool with aluminium sulphate, sodium potassium tartrate and iron(II) sulphate, traditionally used as mordants for natural dyes. The fastness properties of the dyed samples are given in Table 3.

TABLE 3
Wash and Light Fastness Values of Cotton and Wool Samples Dyed with Carmine and Chlorophyll With and Without Mordant

Pigment	*Mordant*	*Wash fastness*	*Light fastness*
Cotton samples			
Chlorophyll	none	2–3	3
Chlorophyll	$Al_2(SO_4)_3 . 16H_2O$	1	3
Chlorophyll	$FeSO_4 . 7H_2O$	1	4
Chlorophyll	$C_4H_4 KNaO_6 . 4H_2O$	4	3
Carmine	none	1	3
Carmine	$Al_2(SO_4)_3 . 16H_2O$	1	3
Carmine	$FeSO_4 . 7H_2O$	1	4
Carmine	$C_4H_4 KNaO_6 . 4H_2O$	1	2–3
Wool samples			
Chlorophyll	none	3	4–5
Chlorophyll	$Al_2(SO_4)_3 . 16H_2O$	2	4
Chlorophyll	$FeSO_4 . 7H_2O$	3	4–5
Chlorophyll	$C_4H_4 KNaO_6 . 4H_2O$	3	4
Carmine	none	3	3–4
Carmine	$Al_2(SO_4)_3 . 16H_2O$	2–3	3–4
Carmine	$FeSO_4 . 7H_2O$	2	5
Carmine	$C_4H_4 KNaO_6 . 4H_2O$	4–5	4

Table 3 indicates that mordanting of cotton and wool with metallic salts is not advantageous compared with the enzymatic treatment as regards the fastness properties of the materials dyed with chlorophyll and carmine. With the exception of the samples pretreated with sodium potassium tartrate, wash fastness was lower or equal to that of the reference samples and samples pretreated with enzymes, whereas light

TABLE 4
ΔL^*, ΔC^*, ΔH^* and ΔE Values for Fabrics Dyed after Mordanting with Iron Sulphate (Reference Sample: Fabric Dyed Without Mordant)

Dye	*Fibre*	ΔL^{*a}	ΔC^{*a}	ΔH^*	ΔE	*Visual colour description*
Carmine	cotton	−17·88	−12·45	0·98	21·81	darker, duller
Carmine	wool	−1·62	−27·84	4·22	28·20	darker, duller
Chlorophyll	cotton	−5·89	0·98	4·18	7·29	darker, brighter
Chlorophyll	wool	4·61	−3·94	5·49	8·18	darker, duller

[a] $\Delta C^* > 0$: sample brighter than reference; $\Delta C^* < 0$: sample duller than reference; $\Delta L^* > 0$: sample lighter than reference; $\Delta L^* < 0$: sample darker than reference.

fastness improvement was achieved only in the case of mordanting with iron sulphate for both fibres and dyes. It should be noted that dyeing after mordanting with iron sulphate yielded in all cases duller or darker colours, as is concluded from colour measurements (Table 4) for the corresponding dyed fabrics. The fabrics dyed without mordant were used as references. Particularly in the case of carmine, very high DE values were observed, mainly attributable to high DL and DC values, which are related to darkness and dullness of the colours (see footnote, Table 4). This colour differentiation is also visually confirmed.

ACKNOWLEDGEMENTS

Thanks are expressed to Dr N. Nikolaidis (C. Grivas S.A. Dyeing, Printing, Finishing) for providing the materials.

REFERENCES

1. Grierson, S., Duff, D. G. & Sinclair, R. S., *J. Soc. Dyers Colourists*, **101** (1985) 220.
2. Storey, J., in *Dyes and Fabrics*, 2nd edn, ed. W. S. Taylor. Thames and Hudson Ltd, London, 1985.
3. King, J. & Stewart, R. A., in *Dyes and Dyeing*. Griffin and George Ltd, 1970.
4. Tsatsaroni, E. G. & Eleftheriadis, I. C., *J. Soc. Dyes Colourists*, **110** (1994) 313.
5. Riva, A., Cegarra Sanchez, J. & Prieto, R., *Melliand Textilberichte*, **11** (1991) 934.
6. Riva, A., Cegarra, J. & Prieto, R., *J. Soc. Dyers Colourists*, **109** (1993) 210.
7. *Color Index*, 3rd edn. The Society of Dyers and Colourists, Bradford, 1971, Vol. 3.
8. *BS 1006: 1990 CO2 Colour Fastness to Washing: Test 2.* Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 5th edn. The Society of Dyers and Colourists, Bradford, 1990.
9. *BS 1006: 1990 BO2 Colour Fastness to Artificial Light: Xenon arc fading lamp test.* Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 5th edn. The Society of Dyers and Colourists, Bradford, 1990.
10. Pailthorpe, M. T., in *Wool Dyeing*, ed. D. M. Lewis. Society of Dyers and Colourists, Bradford, 1992.
11. Giles, C. H., in *The Theory of Coloration of Textiles*, ed. C. L. Bird & W. S. Boston. The Society of Dyers and Colourists, Bradford, 1975.