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Effect of enzymatic treatment on the dyeing of pineapple leaf fibres with natural dyes

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ABSTRACT: Naturally dyed garments are attracting increasing interest from environmentally-attentive consumers. While the lack of colour reproducibility is no longer of importance, issues regarding light fastness and dye uptake remain. While metal salts mordants may offer good results, they do not satisfactorily address environmental concerns. In this experimental work, pineapple leaf fibres, a by-product of the food industry, have been scoured with the naturally occurring enzymes pectinase and cellulase (separately) and dyed with a selection of 5 natural dyes. Morphological characterization, tensile tests, weight loss, dye uptake, colour measurements, and light fastness tests were conducted. Comparison of these results with those for fibres scoured in NaOH (with and without inorganic mordant) shows that enzymes lead to higher dye exhaustion, comparable or greater tensile strength, lighter shades, but similar light fastness. Enzyme-based scouring can therefore effectively prepare pineapple leaf fibres for dyeing with natural material without resorting to potentially toxic premordants.

KEYWORDS: mordant dye, scouring, light fastness, cellulase, pectinase, cellulosic fibres

INTRODUCTION

Enzymes have been increasingly employed in the textiles industry over the past decade. They have been used for desizing, scouring, polishing, washing, degumming, and bleaching, as well as for decolouring of dyehouse wastewater. As enzymes show a large variety of side chains of the outer amino acids and a large 3-d protein structure, it can be expected that an enzyme which can interact with virtually any chemical agent can always be found[1]. In general, the use of enzymes leads to a reduction in water and energy consumption. In addition, they can often replace toxic chemical agents and be recovered from the wastewater and reused, satisfying both environmental and economic requirements.

The scouring process represents the first step in the processing of natural fibres. It has the aim of removing dirt and impurities and preparing the fibres for further processing. It may also be performed again at a later stage, often with the aim of increasing fabric wettability. Traditionally, scouring is performed with inorganic compounds such as NaOH. However, several enzymes have also been used in the scouring process over the years. Cellulase and pectinase are among the most promising enzymes for scouring. They have been employed either together or separately and have proved effective for cotton scouring. Both enzymes improve cotton absorbency. They have been shown to impart adequate absorbency to the fibres with short treatment time[2]. Treatment with pectinase, lipase, and protease, applied individually, provide a slight improvement in the water wettability and strength retention properties of cotton[3]. The combination of pectinase and cellulase significantly improves the wetting outcome of the scouring process. Pectinase, however, improves the water absorbency more than either lipase or protease[4]. Cellulase, via a hydrolysis reaction, removes the readily accessible surface fibrils yielding a softer fabric hand[5]. The short duration of the treatment and the low concentration of cellulase, leave the tensile properties almost unaffected.

Up to the end of the nineteenth century, natural dyes were the main colourants used in textile dyeing. Most natural dyes come from plants, e.g. blue indigo from the leaves of *Indigofera tinctoria*, red madder from the roots of *Rubia tinctorum*, and yellow from the stigmas of the saffron plant. In the absence of sufficient scientific knowledge and clearly defined procedures, the colouring with natural dyes was a difficult art and obtaining the same shade twice was a difficult task. The development of synthetic dyes led to higher quality and more reproducible colours. As a result, the twentieth century has seen a progressive decline in the use of natural dyes. In the past decade, however, the use of natural dyes in the textile industry has been growing in popularity because many consumers have developed a new taste for natural colours. As for the colour reproducibility, most consumers are now ready to accept that thoroughly natural products can have variations. In fact, in many cases, this naturally occurring variation is marketed as guaranteeing the uniqueness of each product. In response to this new trend, research groups around the world have increasingly reported studies on natural dyes. Examples include the dyeing of cotton and jute with tea using alum, copper sulphate, or ferrous sulphate as mordants[6], and the dyeing of jute using selected natural dyes[7]. The properties of a selection of natural dyes on silk, cotton and cashmilon using alum or ferrous sulphate as mordants have also been reported[8]. Across these studies, the use of natural dyes is often linked to issues of "poor fastness", especially as regards the exposure to light (i.e. light fastness). Attempts to overcome these problems have focused on the use of metallic salts as mordants. e.g. alum, ferrous sulphate, stannous chloride, or tannic acid[9]. Most of the proposed dyeing procedures consist of a two-bath dyeing as they include a separate mordanting step. However, this extra bath is unusual and adds complications to a modern dyehouse.

The use of enzymes in place of metal salts has yielded promising results and would resolve environmental issues, as the bio-compatibility of enzymes strikingly contrasts with the potential toxicity of many metal salts. When dyeing cotton and silk fabrics with enzymes in a simultaneous process, the addition of tannic acid, enzyme, and dye in the same bath improves the dye uptake[10]. Furthermore, when the enzymatic treatment is combined with ultrasonic dyeing with natural dyes, the dyeing rate accelerates. Enzymatic treatment on cotton and wool fibres combined with natural dyes showed similar results, with a notable improvement of dye uptake[11]. For some types of dyes, the fastness properties of samples treated with enzymes were the same as those of samples treated with conventional mordants.

Pineapple leaf fibres are a type of lignocellulose fibres readily available in tropical countries like Thailand. With the view of exploiting this by-product of the food industry, we have developed a decorticating machine to extract fibres from the leaves of the pineapple plant. These fibres have the proven potential to produce yarns and fabrics of a quality at least comparable to that of jute, ramie, or linen[12]. In the present study, the pineapple leaf fibres were treated with the enzymes pectinase and cellulase before being dyed with a selection of natural dyes. This treatment was compared with the traditional scouring method based on a NaOH solution. The investigation included tensile test measurements and a microscopic morphology characterization as well as tests on the light fastness of the dyed yarns. Dyeing efficiency and the range of colours achieved were assessed using CIELab.

MATERIALS AND METHODS

Materials

The fibres were extracted from pineapple leaves refuse. They were about 14 deniers fineness and were 13% moisture (as measured by the laboratories of the Textile Institute of Thailand according to standard AATCC 20A-2000). Since a detailed chemical analysis of the fibres is beyond the scope of this study, typical compositions together with references to the corresponding sources are shown in Table 1.

Scouring

For conventional scouring, the fibres were scoured for 30 min at 80 °C with a liquor ratio of 1:25 in a bath containing 1 ml/l of wetting agent (Laventin type) and 2% on weight fabric (owf) NaOH. Then the fibres were washed and dried.

In the case of enzymatic scouring, the fibres were scoured for 2 h in either pectinase (Pectinex Ultra SP-L) at 45 °C for 2 h at pH 4.5, or cellulase (Lava Cell NNM) at 55 °C at pH 7. A bath was prepared with the enzyme, 2% owf, and 1 ml/l wetting agent in a liquor ratio of 1:40. After the treatment, the fibres were boiled for 10 min to deactivate the enzyme, and then washed and dried.

Table 1 Chemical compositions of pineapple leaf fibres (% w/w) as reported in three published works.

α-cellulose	Hemicellulose	Lignin	Pectin	Ash	Fat and wax	Ref.
69.5–71.5	17.0–17.8	4.4–4.7	1.0–1.2	0.71–0.87	3.0–3.3	12
70–82	18	5–12	-	0.7–0.9	-	13
68.5	22.2	4.0	-	0.6	2.5	14

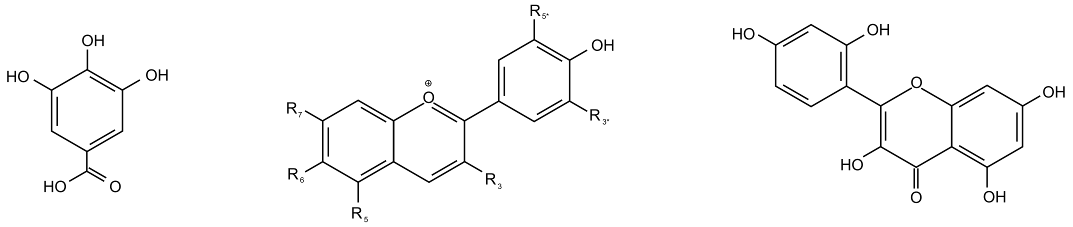

Fig. 1 Chemical structure of dyes used: Indian almond (*left*), *Schinopsis lorentzii* (*middle*), *Chlorophora tinctoria* (*right*). R_3, R_{5*}, R_7 = OH; R_{3*} R_5, R_6 = H.

Dyeing process

The treated pineapple leaf fibres were spun into yarns with a semi-automatic spinning machine. The yarns were dyed with in-house natural dyes and with commercial dyes. In the first case, the dyestuff was extracted from 4 kg of leaves of Indian almond and basts of Indica for each litre of water. The decoction was boiled for 1 h. The insoluble residue was separated by filtration before using the dye solution. Commercial natural dye powders were supplied by East Asiatic Ltd. (Thailand), a distribution company for Silva Chimica (Italy). The dyes originate from the wood of *Schinopsis lorentzii* (orange, CAS 1401-55-4) and *Chlorophora tinctoria* (yellow, CAS 480-16-0) and a mixture of *Chlorophora tinctoria*, sumac extract, sumac leaves, and indigo (green). The chemical structures of the dyes are shown in Fig. 1.

The yarns were dyed with 2.5% owf. All natural dyes were applied to the yarn samples with a liquor ratio of 1:40 at 60 °C for 30 min. In the experiment with conventional premordant process, the yarns were immersed in 1% owf ferrous sulphate solution at 40 °C for 10 min before following the same dyeing procedure.

Testing method

The morphology of the fibres after the conventional and the enzyme scouring was investigated with a scanning electron microscope. The breaking force of the fibres was measured according to ISO 5079-1995, using an Instron universal testing machine (with constant rate of extension). The dye uptake was measured with a UV-visible spectrophotometer. The percentage of dye exhaustion was calculated from the absorbance of the dyebath at the wavelength of maximum absorption before and after the dyeing process. The CIELab values of the yarns were measured with a tristimulus colourimeter (Minolta CR-10, illuminant D65, 10° observer). The light fastness tests were carried out according to BS EN ISO 105-B02 and were related to the standard blue scale. The full range of the scale is from 1 to 8 (1 = poor, 8 = excellent), but as is customary with natural dyes, tests were focused on the lower range (1–4) only giving a 'greater than 4' result for better fastness (i.e., a 'Grade 4 below' test).

RESULTS AND DISCUSSION

Weight loss

The pineapple leaf fibres showed greater weight loss in the conventional NaOH scouring (21%) than in the enzymatic scouring (cellulase: 1.33%, pectinase: 1.74%). This meant that the NaOH treatment had removed more impurities from the surface. It is known that a NaOH solution at high temperature converts non-cellulosic material (pectins, hemicelluloses, and proteins) in the cuticle primary wall of the cell into water soluble forms. A hot NaOH solution will also melt some of the waxy materials and hydrolyse them into soaps and glycerol through a saponification reaction. The low weight loss observed in the enzymatic scouring was expected since the function of enzymes is very specific. For example, pectinase removes pectin and cellulase hydrolyses cellulose, leaving other substances unaffected.

Scanning electron microscopy

Bast and leaf fibres present elongated sclerenchyma cells that are assembled in bundles forming a part of the phloem[15]. These cells are surrounded by thin-walled tissues. Mechanical decorticating machines break the thin cell walls thereby releasing fibre bundles. Residual cell wall fragments remain on the surface of the fibre bundles as seen in Fig. 2a. Most of the waxy layer at the surface and other noncellulosic substances are removed by NaOH, as seen in Fig. 2b. This could be expected to yield fibres that are less tightly bound together when spun into a yarn. The hemicellulose, which is largely made of mixed polysaccharides, is converted into soluble soaps, while unsaponified oils are emulsified by these soaps. The pectinase enzyme comprises polygalacturonases, pectin esterases, pectin lyases, and pectate

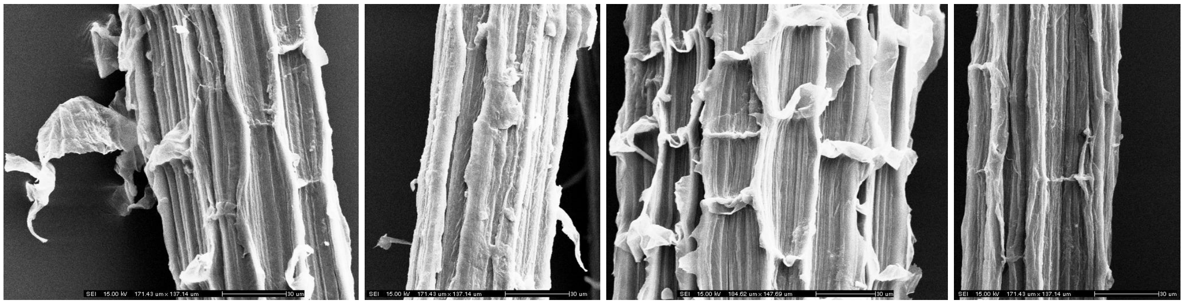

Fig. 2 Scanning electron micrographs of pineapple leaf fibres after scouring with (*left to right*): nothing (before scouring); NaOH solution; pectinase; cellulase.

lyases. Pectinase penetrates the cuticle through cracks or micropores and makes contact with the pectic substances in the fibre. The pectic substances are hydrolysed by pectinase, which results in the removal or partial removal of the cuticle or breakdown of the continuity of the cuticle (Fig. 2c). The breakage of the link between the cuticle and the cellulose can be assumed to be a direct effect of partial hydrolysis[2]. The cellulase enzyme penetrates the fibre in the same way as pectinase does. However, cellulase catalyses the hydrolysis of both the primary and secondary cell walls[15]. This effect is shown in Fig. 2d where the outside layer of the fibre is loosened and falls away.

Tensile strength

The mechanical properties of natural fibres are influenced by the composition, structure, and number of defects in them. Biofibres like pineapple leaf fibres or banana fibres do not show the general relationship between crystallinity and strength observed in pure cellulose fibres such as cotton and rayon[13]. Their strength is rather determined by the presence of non-cellulosic materials, mainly lignin, and the dimensions of the cells in the tissue. Results on the tensile strength of pineapple fibres and the effect of the scouring methods investigated are collected in Table 2. With NaOH treatment, pineapple leaf fibres experienced a significant drop in strength. This drop is due to structural changes caused by alkali treatments. As shown by the SEM investigation, fibres treated with NaOH show degradation of non-cellulosic substances at the surface.

Pectin is one of the most complex non-cellulosic substances in the primary wall. It is responsible for holding other non-cellulosic substances together. It is clear that the removal of pectin can destabilize other substances. The structural changes induced by the pectinase treatment altered the mechanical properties of the fibres as indicated by an marked decrease in the tensile strength. This effect is primarily accounted for by the loosening of the pectin lamellae. Under stress, cracks propagate through the weakened bonding between cells, causing intercellular fracture[13]. Similar findings on the bioscouring of hemp have been reported[16]: pectinase smoothed the fibre surface, removed pectin, and increased the surface area as well as the pore size. However, it also appreciably decreased the tensile strength when the incubation time was more than 5 h. The cellulase-catalysed hydrolysis reaction removes readily accessible surface fibrils yielding yarns more compliant in bending[5]; the friction between fibres is altered due to the smoother fibre surface. For short treatment times, only the early stage of hydrolysis occurs and the tensile strength remains mostly unaffected.

Table 2 Tensile strength (N) of pineapple fibres treated.

none	NaOH	pectinase	cellulase
1.5 ± 0.6	0.96 ± 0.5	0.84 ± 0.4	1.55 ± 0.5

Dyeability

The dye exhaustion e was calculated from

$$e = \frac{A_0 - A_1}{A_0}$$

where A_0 and A_1 are, respectively, the absorbance of the dyebath before and after dyeing at the wavelength of maximum absorbance (λ_{max}) of the dye used. The dyeing results, in the form of dye exhaustion for the samples dyed with different types of scouring, are given in Table 3. We planned the investigation of the use of enzymes in the hope that they would offer an acceptable alternative to metal salts with the advantages of being biodegradable and effective at low temperatures and with small quantities of added chemicals. It was found that enzymatic treatments

Table 3 Dye exhaustion (e) and light fastness (LF) of the pineapple leaf fibres dyed with natural dyes.

Natural dye	$\lambda_{\max}$ (nm)	Treatment							
		NaOH		NaOH + PM[a]		Pectinase		Cellulase	
		e (%)	LF	e (%)	LF	e (%)	LF	e (%)	LF
Indian almond	270	39.7	>4	44.0	3–4	44.6	3–4	43.2	3–4
Basts of Indica	217	10.4	3–4	10.2	3	9.1	3	8.9	4
Natural Orange	229	13.5	4	14.8	>4	23.6	>4	26.9	>4
Natural Yellow	286	18.2	3	15.7	3	29.4	3	27.7	3
Natural Green	215	16.9	3–4	6.2	4	14.0	4	16.6	4

[a] premordant

actually improve the dye uptake in all cases reported, with the only exception being the dye from basts of Indica. This enhancement is particularly large for commercial natural dyes. This may result from other chemicals that are mixed with the powder with the aim of improving the dyeing outcome. Enzyme treatments effectively remove non-cellulosic substances. This results in a hydrophilic surface and improved wettability. Enzymatic treatment may have changed the dye-site availability[5], about which further investigation may shed some light.

Light fastness

Light fastness was very similar for all samples, irrespective of scouring method and use of mordants (Table 3). This indicates that there was a real fixation of the dye on both types of treated fibres. It is observed that almost all the treated fibres had moderate light fastness ranging from 3–4. The use of ferrous sulphate as a mordant in this experiment did not improve the light fastness property compared with the enzymatic treatment. In this case, the use of enzymes is therefore preferable on the basis of environmental considerations. However, ferrous sulphate may not be the best choice of mordant for all the natural dyes examined in this study, and better results may be obtained with an optimized selection of mordant. In practice, the choice of mordant is often dictated by the desired shade of colour rather than light fastness.

Colour measurements

The CIELab values are reported in Table 4. The pineapple leaf fibres yarns dyed without mordant were used as references to calculate ΔL^*, Δa^*, and Δb^*, where L^*, a^*, and b^* are the lightness, red-green coordinate, and yellow-blue coordinate, respectively. The colour difference (ΔE) is given by

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}.$$

It can be observed that dyeing the sample with ferrous sulphate as the premordant gave darker shades of colour (lower L^* values). Conversely, most of the fibres treated with enzymes showed L^* values close to those of the fibres without mordant. In general, the colour of enzyme-treated fibres was similar to that of untreated fibres, as shown by the colour difference, which was lower for the fibres treated with enzymes than for the samples dyed with a mordant. The only exception to this was encountered with the basts of Indica dye. This occurred because this dye shows a high value of L^* and b^*. Fig. 3 shows the colour scans of dyed yarns under different conditions.

Fig. 3 Dyed pineapple leaf fibre scans under different conditions.

Table 4 CIELab coordinates for the pineapple leaf fibre yarns treated under different conditions.

Samples	Treatment	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE
Indian Almond	NaOH	53.3 ± 0.3	4.8 ± 0.4	27.2 ± 0.4				
	NaOH + mordant	44.5 ± 0.4	5.8 ± 0.3	18.2 ± 0.3	−8.7	1.0	−9.0	12.6
	cellulase	57.5 ± 0.8	6.0 ± 0.2	28.1 ± 0.1	4.2	1.2	0.9	4.5
	pectinase	55.9 ± 1.5	6.9 ± 0.3	28.4 ± 0.6	2.7	2.1	1.2	3.6
Basts of Indica	NaOH	40.1 ± 0.6	17.5 ± 0.1	15.9 ± 0.4				
	NaOH + mordant	39.5 ± 0.8	18.8 ± 0.2	16.0 ± 0.3	−0.6	1.3	0.2	1.5
	cellulase	41.6 ± 1.3	18.6 ± 0.5	16.7 ± 0.3	1.5	1.1	0.8	2.0
	pectinase	44.6 ± 1.4	18.1 ± 1.6	19.3 ± 1.4	4.5	0.6	3.4	5.6
Natural orange	NaOH	34.8 ± 2.3	31.5 ± 3.7	32.1 ± 4.1				
	NaOH + mordant	27.6 ± 2.1	21.1 ± 2.2	21.9 ± 3.0	−7.2	−10.4	−10.1	16.2
	cellulase	32.3 ± 2.8	29.3 ± 5.0	28.7 ± 5.5	−2.5	−2.2	−3.4	4.8
	pectinase	34.9 ± 2.3	32.8 ± 1.6	33.3 ± 3.8	0.1	1.3	1.2	1.8
Natural yellow	NaOH	42.9 ± 1.1	14.4 ± 0.9	38.0 ± 1.0				
	NaOH + mordant	32.2 ± 1.9	6.9 ± 0.2	21.9 ± 1.7	−10.7	−7.5	−16.2	20.8
	cellulase	43.3 ± 0.6	15.6 ± 0.6	37.5 ± 0.5	0.4	1.2	−0.6	1.4
	pectinase	44.9 ± 0.8	14.5 ± 0.7	38.9 ± 1.4	2.0	0.1	0.9	2.2
Natural green	NaOH	43.9 ± 0.3	-11.6 ± 0.4	11.3 ± 0.3				
	NaOH + mordant	33.4 ± 1.5	-4.9 ± 0.4	9.9 ± 1.2	−10.4	6.7	−1.4	12.5
	cellulase	38.6 ± 0.6	-9.0 ± 0.5	9.5 ± 1.0	−5.3	2.6	−1.8	6.2
	pectinase	37.4 ± 0.6	-8.3 ± 1.1	9.1 ± 0.6	−6.5	3.2	−2.1	7.6

CONCLUSIONS

It can be concluded that enzymatic scouring of pineapple leaf fibres is a very interesting alternative to conventional scouring combined with the use of mordants. While nothing is lost in terms of light fastness, enzymatic scouring yields can improve the dyeing process, as suggested by the dye uptake results. Enzymes are biodegradable, can be reused, and are effective at lower process temperatures. All these factors make them extremely interesting from the point of view of an industry that strives to reduce its environmental impact and to appeal to the environmentally-conscious consumer.

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