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Enzymatic dyeing and functional finishing of textile fibres with ferulic acid

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The catalyzed polymerization of ferulic acid (FA) by laccase from *Rhus vernicifera* has been studied, and its polymeric products are used for the dyeing and functional finishing of silk, wool, nylon, viscose and cotton fabrics by two methods, namely simultaneous enzymatic polymerization of FA and dyeing at 50 °C (one-step method), and enzymatic polymerization of FA at 50 °C followed by dyeing at 90 °C (two-step method). The analyses of UV-Visible and FTIR spectra show the formation of yellow poly(ferulic acid) (PFA) in which FA units are mainly linked together with C–C bonds. The colouration of PFA on fabrics occurs due to physical adsorption, and not because of interaction of covalent bond between PFA and fibres. The enzymatically dyed fabrics display yellow to orange colour hues, and pale to moderate colour depth, depending on fibre species and dyeing methods. The dyed fabrics show excellent rub fastness and staining fastness during washing, relatively weak light fastness and colour change fastness during washing; the two-step method shows better wash fastness ratings for colour change. The enzymatic dyeing of FA provides fabrics with multifunctional properties of antioxidant activity, UV-protection and deodorization.

Keywords: Colouration, Cotton, Dyeing, Ferulic acid, Finishing, Laccase, Nylon, Silk, Viscose, Wool

1 Introduction

In recent years, there has been increasing interest in the application of laccase for the colouration of textiles by means of the formation of coloured compounds, which has potential benefits in saving chemicals or energy, mitigation of pollution or process streamlining[1,2]. Among the categories of oxidoreductases, laccase is the most studied biocatalyst for industrial application. Laccase, a multi-copper-containing oxidoreductase enzyme, is able to catalyze the oxidation of various compounds with the characteristics similar to a *p*-diphenol to aryloxy-radical, which may undergo non-enzymatic reactions, resulting in the formation of dimeric, oligomeric or polymeric compounds. The coloured products formed via laccase-catalyzed oxidation and polymerization cause the colouration of fibres. Laccase has already been used for the enzymatic colouration of wool[3], cotton[4,5], denim[6], and flax[7] with some reaction substrates.

A lot of plant phenols and phenolic acids are typical laccase substrates. Among the phenolic acids, ferulic acid (abbreviated as FA), occurring widely in cereals, fruits, and vegetables, is the most abundant hydroxycinnamic acid in the plant world[8]. FA possesses many physiological functions, including antioxidant, antimicrobial, anti-inflammatory, anti-thrombosis, and anti-cancer activities[9]. In the literature, it has been reported that FA was oxidized in aqueous medium by the laccase from *Myceliophthora thermophila* and the oxidation product shows a yellow colour[10]. The same phenomenon was observed when the laccases from *Pyricularia oryzae*[11] and from *Trametes pubescens*[12] were used. Moreover, the FA-chitosan derivative obtained by the functionalization of chitosan with FA as a substrate, and *Myceliophtora thermophyla* laccase as a biocatalyst presented an intense yellow-orange colour[13].

In recent years, the probability of the application of coloured product from the laccase-catalyzed transformation of FA in hair[14] and flax dyeing[15] has been discussed. However, still much less is known about the application of FA in textile colouration and finishing with an enzymatic method. The aim of the present study is therefore to investigate the application of FA as a potential multifunctional colourant for the dyeing and functional finishing of textiles. The laccase-catalyzed colouration reaction of FA is first studied and then characterized by UV-Visible (UV-Vis) and Fourier transform infrared (FTIR) spectra. Subsequently, FA is used for

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the dyeing of wool, silk, nylon, viscose and cotton fabrics by two methods, namely simultaneous enzymatic polymerization of FA and dyeing at 50 °C (one-step method), and enzymatic polymerization of FA at 50 °C followed by dyeing at 90 °C (two-step method). The colour parameters and fastness as well as the UV-protection, antioxidant and deodorizing properties of the fabrics are tested.

2 Materials and Methods

2.1 Fabrics, Enzyme and Chemicals

Laccase (EC 1.10.3.2) from *Rhus vernicifera* was purchased from Sigma-Aldrich. Ferulic acid with purity above 99% was obtained from Wuhan Yuancheng Group, China. 2,2-Azino-bis(3-ethylbenzthiazoline- 6-sulfonic acid) (ABTS) was obtained from Becton, Dickinson and Company, USA. All other chemicals used were of analytical reagent grade.

The scoured, woven silk fabric of crepe de Chine and the scoured, woven semi-dull nylon fabric were purchased from Wujiang Zhiyuan Textile Co. Ltd., China. The scoured and bleached wool and viscose fabrics were up to the standards GB/T 7568.1-2002 and GB/T 7565-1987 respectively, and purchased from Shanghai Textile Industry Institute of Technical Supervision. The cotton fabric was obtained commercially from Suzhou Printing and Dyeing Co., Ltd., China. The specifications of these fabrics are given in Table 1.

2.2 Enzymatic Oxidation of FA

Since FA is not soluble in aqueous media, a 10 mM FA solution was prepared in 50 mM phosphate buffer (*p*H 7.4) containing 4% of ethanol in the presence of 2 U/mL (Sigma units) laccase. The reaction was carried out at a magnetic agitation speed of 60 rpm at 40 °C for 30 h. The reaction mixture was evaporated using a rotary evaporator, and the product was extracted with ethyl acetate followed by separation using a separation funnel and collected.

Table 1—Characterization parameters of fabrics used

Fabric	Count		Density threads/cm		Weight g/m^2
	Warp	Weft	Warp	Weft	
Silk	23.3 dtex/2	23.3 dtex/2	42	60	52
Wool	15.6 tex/2	15.6 tex/2	21	18	125
Nylon	55.6 dtex/48F	50.0 dtex/34F	75	50	59
Viscose	20 tex	30 tex	28	22	140
Cotton	14.8 tex	14.8 tex	43.3	35.4	120

2.3 Enzymatic Dyeing

FA was used to dye fabrics using two methods, namely simultaneous enzymatic polymerization of FA and dyeing (one-step method), and enzymatic polymerization of FA followed by dyeing (two-step method). All the experiments were undertaken using a 25:1 liquor ratio in a XW-ZDR oscillated dyeing machine. In the one-step method, the fabrics were dyed with 10 mM FA, 4% ethanol and 4 U/mL laccase in 50 mM phosphate buffer (*p*H 7.4) at 50 °C for 3 h. In the two-step method, the enzymatic polymerization of FA was first performed at 50 °C for 3h using the same recipe as ascribed above; afterwards, the fabrics were immersed into the above solutions, the temperature was increased up to 90 °C at a rate of 2 °C/min and this temperature was maintained for 2 h. In these two methods, a control dyeing experiment without laccase was also performed. At the end of dyeing, the dyed samples were removed, rinsed thoroughly with tap water, and allowed to dry in the open air. Besides, the enzymatically dyed fabrics were treated with N, N-dimethyl-formamide (DMF) under a heating condition in order to determine whether the covalent fixation of PFA onto fibre occurs.

2.4 Structural Characterization of FA and PFA

The UV-Vis spectra of FA and PFA were analyzed using a Shimadzu 1800 UV-Vis spectrophotometer. The FTIR spectra were recorded with a Nicolet 5700 FTIR spectrometer using the KBr pellet method.

2.5 Evaluation of Colour Characteristics and Fastness

The CIE L^*, a^* and b^* colour co-ordinates of fabrics were measured using a HunterLab UltraScan PRO reflectance spectrophotometer (illuminant D65; 10° standard observer). Each sample was fold twice so as to give a thickness of four layers. The colour difference (DE) was calculated using the following equation:

$$\mathrm{D}E=\left[\left(L^*_{tr}-L^*_{untr}\right)^2+\left(\mathrm{a}^*_{tr}-a^*_{untr}\right)^2+\left(b^*_{tr}-b^*_{untr}\right)^2\right]^{1/2} \quad \ldots(1)$$

where the subscripts '*tr*' and '*untr*' refer to the fabric treated with FA and the untreated white one respectively.

The wash and rub fastness were tested according to ISO 105-CO1 and ISO 105-X12 respectively. A multi-fibre fabric was attached to the treated sample so as to detect colour migration or staining. The light fastness was tested according to ISO 105-B02, and the fabrics were exposed to xenon arc lamp for 10 h under a standard testing condition.

2.6 Evaluation of Functional Properties

The ultraviolet protection factor (UPF) of fabric was determined in a Labsphere UV-1000F ultraviolet transmittance analyzer. Each sample was tested four times at different positions, and the average of the data was used.

The antioxidant activity of fabric was determined by the ABTS radical decolourization assay[16,17]. The ABTS radical ($ABTS^{\cdot+}$) was generated by mixing 7 mM ABTS in water and 2.45 mM potassium persulfate (final concentration) in the dark for 12 h, at room temperature. Before usage, the $ABTS^{\cdot+}$ solution was diluted to get an absorbance of 0.700 ± 0.020 at 734 nm with phosphate buffered saline at *p*H 7.4. Then, 10 mg of fabric was added to 10 mL of $ABTS^{\cdot+}$ solution, and the absorbance at 734 nm was recorded after 30 min. The inhibition or scavenging capability of $ABTS^{\cdot+}$ was calculated using the formula as given below:

$$\text{Inhibition or scavenging effect}(\%) = 100 \times \frac{A_{con} - A_{sam}}{A_{con}} \quad \ldots (2)$$

where A_{con} is the initial absorbance of the $ABTS^{\cdot+}$ (control sample); and A_{sam} , the absorbance of the remaining $ABTS^{\cdot+}$ in the presence of fabric.

The deodorizing ability of fabric was tested as follows. A proper amount of odor substrate (1000 mg/m^3 for ammonia) was injected into a 4 L airtight polyethylene vessel. The fabric (1g) was suspended in the vessel at 25°C and 40% RH for 1 h. The initial and residual gas concentrations of malodors were measured by corresponding gas detector tubes with GASTEC GV-100S gas sampling pump. The deodorizing ability described as deodorizing rate was calculated using the following equation:

$$\text{Deodorizing rate}(\%) = 100 \times \frac{C_{con} - C_{sam}}{C_{con}} \quad \ldots (3)$$

where C_{con} and C_{sam} are the concentrations of gases in the vessel in the absence and presence of fabric respectively.

3 Results and Discussion

3.1 Enzymatic Oxidation of FA

To determine laccase-catalyzed reaction of reactive *o*-quinone of FA followed by polymerization, the UV-Vis spectra of FA solution during the enzymatic reaction are monitored. The change in the colour of the reaction solution from colourless to bright yellow is observed. Moreover, an increase in the broad absorption in the visible region which could be explained by enzymatic polymerization reaction is detected although no remarkable absorption peak appears (Fig. 1, spectrum b). In addition, the control solution containing only FA shows no spectrum change after treatment under the similar condition for 30 h, suggesting that no substantial autoxidation occurs.

It is reported that the yellow FA dehydrodimers obtained by *Myceliophthora thermophila* laccase synthesis are not soluble in water but only soluble in the organic solvent[10]. In this study, the spectra of FA and PFA in ethyl acetate are observed and presented in Fig. 1 (spectra c and d). The PFA solution shows a yellow colour, and a peculiar absorption band at around 424 nm, indicating the occurrence of enzymatic oxidation.

To characterize the structural properties of FA and PFA obtained by catalytic polymerization with laccase, the corresponding FTIR spectra are also determined (Fig. 2). The PFA spectrum exhibits

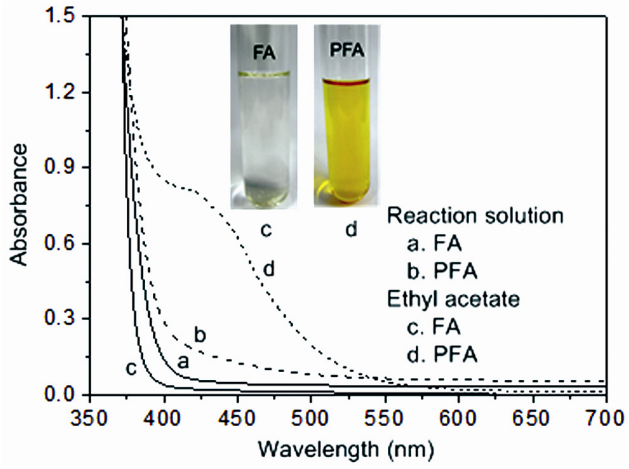

Fig. 1—UV-Vis spectra of FA and PFA in reaction solution and ethyl acetate

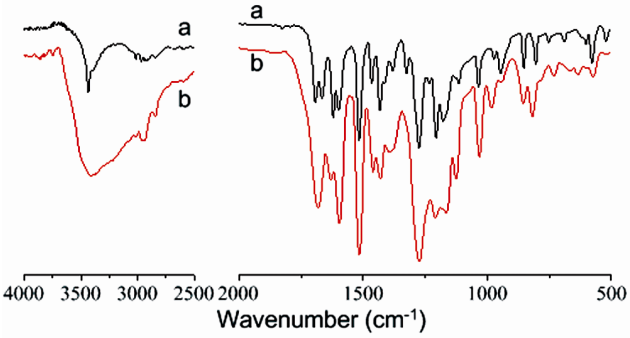

Fig. 2—FTIR spectra of (a) FA and (b) PFA

different profiles as compared to FA. The FA spectrum shows typical polyphenolic characteristics with the existence of O–H stretching of phenolic ring at 3436.2 cm^{-1} as a narrow and intensive band, propenoic acid' C–H stretching mode at 3016.4 cm^{-1}, in-plane bending at 1205.8 cm^{-1}, alkene C=C stretching at 1620.3 cm^{-1}, C=O stretching at 1691.8 cm^{-1}, and O–H in plane bending of COOH group at 1325.0 cm^{-1} (ref.18). The absorption peaks between 1450 and 1600 cm^{-1} are attributed to the aromatic ring C=C stretching which are characteristics for the benzene aromatic ring. The peaks within 1380.2-1465.0 cm^{-1} and at 2968.3 cm^{-1} are due to CH_3 vibrations. The C–H vibrations corresponding to in-plane bending modes of C2–H and C5–H for aromatic ring appear at the 1274.7 cm^{-1} and 1177.9 cm^{-1} respectively[18]. The C–O–C stretching of aromatic ether is also seen at 1205.8 cm^{-1} and 1034.7 cm^{-1}, and the two strong absorption bands are characteristics for aromatic ether and aliphatic ether.

As a consequence of enzymatic polymerization, the –OH band at 3386.7 cm^{-1} broadens while the propenoic acid' C-H band and alkene C=C band weaken. It can be proposed that the polymerization of FA occurs by nucleophilic addition reaction or nucleophilic substitution reaction involving the side-chain double-bond. The band at 1325.0 cm^{-1} attributing to the –OH in-plane bending of COOH group almost disappears, indicating the decrease in the number of COOH group. This may be due to the nucleophilic addition of hydroquinone double bond after quinone rearrangement to quinone methide, which leads to the disappearance of COOH group and the formation of β-β linked dimmer[12]. The decrease in the transmittance of the bands at 1274.7 and 1177.9 cm^{-1} can be discussed in relation to the Michael 1-4 type nucleophilic reaction, consisting in addition of a side-chain on an *o*-quinone, leading to C–C linkage in the polymerization products.

The major products and possible structures of FA polymerization by thionyl chloride[19], lignin peroxidase[20], hydrogen peroxide/peroxidase[21], and FA dimerase[22] have already been reported. Also, the representative structures[11, 12] of FA dimers by enzyme catalysis using *fungal* laccase from different sources are shown in Fig. 3. In our study, FTIR analysis certifies the occurrence of polymerization of FA. Furthermore, it is presumed that all the three structures as shown in Fig. 3 may exist in PFA obtained by enzymatic catalysis using *Rhus vernicifera* laccase.

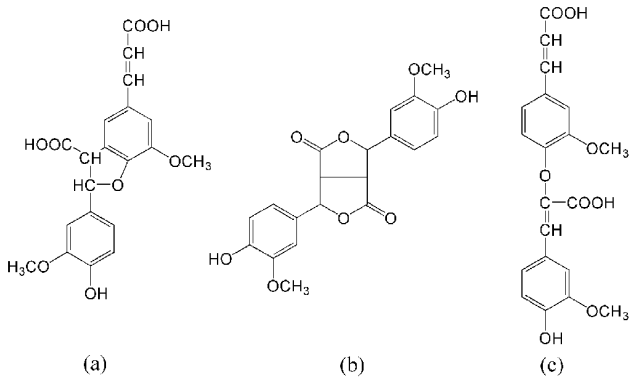

Fig. 3—Representative structures of laccase-catalyzed FA dimmers [(a) trans-5-[(E)-2-carboxyvinyl]-2-(4-hydroxy-3-methoxy -phenyl)-7-methoxy-2,3-dihydrobenzofuran- 3-carboxylic acid, (b) 4-cis,8-cis-bis(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo -[3.3.0]octane-2,6-dione, and (c) (Z)-β-{4-[(E)-2-carboxyvinyl]-2-methoxyphenoxy}-4-hydroxy-3-methoxy cinnamic acid][11, 12]

3.2 Colour Characteristics of Enzymatically Dyed Fabrics

The colour parameters of the fabrics dyed with FA in the presence and absence of laccase by the one-step and two-step methods are listed in Table 2. In most cases, very small redness-greenness (a^*) and yellowness-blueness (b^*) indexes and colour difference (DE) are observed between original samples and the fabrics treated with FA alone; two types of fabrics have similar colour parameters. These measurements clearly indicate that the fabrics treated with FA alone have almost no variation in colour as compared to original samples, and show white colour. In the two-step method, the silk and nylon fabrics treated with FA alone display relatively high b^* and DE values, which should be caused by the oxidation of FA at a high temperature (90 ^oC) and the uptake of the oxidation products by these two fibres.

In the case of enzymatically treated fabrics, the remarkable changes in colour parameters are found. This is especially true for silk and nylon. The reason for this phenomenon is the laccase-catalyzed polymerization of phenolic FA, the formation of an intensive yellow colour and the uptake of PFA by fibres. Indeed, the enzymatically dyed fabrics show obviously increased a^* and b^* indexes, and obviously decreased lightness (L^*), suggesting a yellow-orange appearance of fabrics, as described in Table 2. The colour shades of silk and nylon are found to be bright yellow, and much darker than those of other fabrics. Wool shows pale yellow colour, but viscose and cotton display pale orange colour. The differences among these fibres in colour hue and depth may be due to different types and nature of functional groups

Table 2—Colour parameters of the fabrics enzymatically treated using the one-step and two-step methods

Fabric	Dyeing method	*L**	*a**	*b**	D*E*	Visual colour
Silk	Untreated	94.32	-0.71	5.81	—	White
	One-step					
	FA	93.17	0.06	7.55	2.22	White
	FA+laccase	88.50	2.36	40.96	35.76	Yellow
	Two-step					
	FA	90.19	0.30	25.03	19.69	Pale yellow
	FA+laccase	84.97	5.48	39.16	35.19	Yellow
Wool	Untreated	86.90	-0.23	13.27	—	White
	One-step					
	FA	87.87	-0.03	14.51	1.59	White
	FA+laccase	85.30	1.18	25.33	12.25	Pale yellow
	Two-step					
	FA	85.35	0.05	16.66	3.75	White
	FA+laccase	81.84	2.62	25.45	13.49	Pale yellow
Nylon	Untreated	94.87	-0.52	3.72	—	White
	One-step					
	FA	94.49	-0.27	6.39	2.71	White
	FA+laccase	90.03	4.05	38.76	35.67	Yellow
	Two-step					
	FA	91.71	1.41	27.10	23.68	Pale yellow
	FA+laccase	85.88	8.65	45.35	43.57	Yellow
Viscose	Untreated	93.98	-0.04	5.99	—	White
	One-step					
	FA	93.15	0.72	7.61	1.97	White
	FA+laccase	87.88	6.90	20.05	16.82	Pale orange
	Two-step					
	FA	91.36	2.04	12.02	6.89	White
	FA+laccase	88.30	4.49	15.56	12.01	Pale orange
Cotton	Untreated	94.35	-0.47	5.35	—	White
	One-step					
	FA	93.70	0.20	7.33	2.19	White
	FA+laccase	88.02	7.40	21.56	19.10	Pale orange
	Two-step					
	FA	91.22	2.57	13.38	9.13	Yellowish white
	FA+laccase	87.83	5.68	14.51	12.81	Pale orange

in these fibres, and the different affinity of PFA to these fibers. In comparison with the one-step method, the two-step method gives a higher D*E* value for nylon probably due to the greater diffusion of PFA into nylon interior at 90 ^{o}C, and lower D*E* values for viscose and cotton probably due to the reduced affinity of PFA to the two fibres.

A concept is presented that laccases catalyze the oxidation of flavonoids producing quinones which can be further polymerized and grafted with other phenolic compounds present in fibres by covalent bonds[23]. So, the enzymatically dyed fabrics are extracted by DMF under a heating condition. After extraction, the colour of these fabrics disappears. The observation suggests that no interaction of covalent bond occurs between PFA and fibres. Thus, the colouration of fabrics occurs due to physical adsorption of PFA caused by hydrogen bonds and van der Waals forces.

3.3 Colour Fastness Properties of Enzymatically Dyed Fabrics

Fabrics are subjected to frequent washing, rubbing and lighting during their usage. In practical applications, the textiles for different purposes have varied requirements for their resistance to these conditions. The colour fastness of the enzymatically dyed fabrics is evaluated, and the results are given in Table 3. All the fabrics show high wash fastness ratings for staining as well as high dry and wet rub fastness. The wash fastness ratings for colour change

Table 3—Colour fastnesses of the fabrics enzymatically dyed with FA using the one-step and two-step methods

[Rub fastness (dry and wet)—5/5/; and wash fastness (staining) for wool, acrylic, polyester and acetate—5/5]

Fabric	Light fastness	Wash fastness		
		Colour change	Staining	
			Nylon 6,6	Cotton
Silk	2/2	2/3	3-4/3-4	3-4/3-4
Wool	3/3	3/3	4-5/5	4-5/4-5
Nylon	2/2	4/4-5	4-5/5	4-5/4-5
Viscose	4/4	2/3	4/5	4/5
Cotton	3/3	2/3	4-5/5	4-5/5

The values before and after slash present the fastness of the fabrics dyed using the one-step and two-step methods respectively.

vary greatly according to fibre categories and dyeing methods, e.g. the dyed nylon and wool show higher ratings than other fabrics, and the two-step dyeing method gives higher ratings (≥3) than the one-step method because in this method PFA has the greater diffusion and penetration into fibre interior at a high temperature (90 °C). The light fastness depends greatly on fibres, which is poor (level 2) for silk, fair (level 3) for wool and cotton, and good (level 4) for viscose. On the whole, the light fastness is relatively poor in comparison with other fastness. The poor resistance of the dyed fabrics to light may be caused by the fact that the hydroxyl groups of the laccase-catalyzed FA dimmers are susceptible to photo-oxidation on exposure to light[24]. Thus, the fabrics enzymatically dyed with FA are not suitable for the applications having the requirements for the high colour fastness to light.

3.4 UV-protection Properties of Enzymatically Dyed Fabrics

The presence of a broad absorption band in the spectral region between 250 nm and 350 nm makes FA a good protecting agent against the damages caused by UVA (380-315 nm) and UVB (315-280 nm) radiations. The UV-protection effect of FA on human skin has been documented[25]. In the present study, the UPF values of the fabrics treated with FA in the presence and absence of laccase using the one-step and two-step methods have been measured and are presented in Table 4. The fabrics treated with FA alone show an obvious increase in UPF, indicating the uptake of FA by fibres and supporting the use of FA as a UV protection agent. It is clearly observed that the UPF values of the fabrics enzymatically dyed using two methods are higher than those of the fabrics treated with FA alone (with the exceptions of the wool in the one-step method, and the wool and nylon in the two-step method), and much higher than those

Table 4—UPF values of the fabrics treated with FA in the presence and absence of laccase using the one-step and two-step methods

Fabric	Untreated	One-step method		Two-step method	
		FA	FA+laccase	FA	FA+laccase
Silk	6.65	11.43	20.30	13.61	16.66
Wool	20.75	47.12	42.15	56.87	50.07
Nylon	31.59	63.73	77.81	88.47	85.58
Viscose	5.75	50.44	52.86	32.51	47.11
Cotton	5.89	24.76	33.15	16.41	37.11

of original fabrics. It is obvious that by and large the addition of laccase is beneficial to enhance the UV-protection ability of the fabrics. This may be explained by the formation of yellow PFA, and the subsequent adsorption by fabrics.

The enzymatic dyeing with FA increases the UV-protection properties of the fabrics although the increment varies with fibres. This phenomenon is especially remarkable for viscose and cotton fabrics, whose UPF values are in the 'excellent' and 'very good' range respectively after the enzymatic dyeing according to AS/NZS 4399:1996 (the UPF values of less than 15, between 15 and 24, between 25 and 39, and above 40 are classified as bad, good, very good, and excellent protection against solar ultraviolet radiation respectively)[26]. In comparison, the UV-protection properties of the untreated viscose and cotton are both in the 'bad' range. The UPF of the enzymatically dyed silk is classified in the 'good' range. The wool and nylon fabrics treated with FA in the presence and absence of laccase exhibit 'excellent' UV-protection properties.

3.5 Antioxidant Activity of Enzymatically Dyed Fabrics

The antioxidant activity is one of the most important properties of bioactive fibres, which may be designed by conjugating bioactive compounds to fibres. The fibres with antioxidant activity may be used for medicinal purposes[16,27]. FA can serve an important antioxidant function in food and cosmetic products[28]. It is interesting to evaluate the antioxidant activity of the fabrics treated with FA in the presence and absence of laccase using the one-step method.

The antioxidant activity of the treated fabrics is determined by the ABTS radical decolourization assay (Table 5). Compared with the untreated samples, all the fabrics with treated FA in the presence and absence of laccase show the increased antioxidant properties. It is not surprising to obtain these results because FA is a good antioxidant agent whose phenolic hydroxyl groups have the ability of hydrogen donating primarily contributing to radical scavenging. In the process of enzymatic dyeing and finishing, both FA and PFA can

Table 5—Antioxidant activity of the fabrics treated with FA in the presence and absence of laccase using the one-step method

Fabric	Antioxidant activity, %		
	Untreated	FA	FA+laccase
Silk	2.24	42.55	67.25
Wool	24.02	30.21	34.50
Nylon	10.24	24.67	28.09
Viscose	2.40	80.90	92.72
Cotton	8.64	36.46	39.88

be adsorbed by fibres. But PFA has higher affinity to fibres than FA due to its larger conjugated system, and accordingly the higher extent of adsorption on fibres. Moreover, it has been reported that the β-5 dimmer (Fig. 3, dimer a) of FA obtained by laccase-catalyzed polymerization[12] and the 8-O-4 dimmer (Fig. 3, dimer c)[29] amplify the antioxidant activity. Thus, the enhancement of the antioxidant properties of the enzymatically dyed fabrics can be explained by the high adsorption ability and increasing antioxidant activity of PFA.

However, the different fabrics exhibit some variations in the enhancement of antioxidant activity. The highest increase is observed for viscose (2.4%–92.7% inhibition of $ABTS^{\cdot+}$) followed by silk (2.2%–67.3%). Cotton shows much lower enhancement in antioxidant activity than viscose. Wool shows an insignificant enhancement, which may be attributed to a low adsorption quantity of FA and PFA caused by the resistance of the epicuticle layer of wool at the temperature used.

3.6 Deodorizing Ability of Enzymatically Dyed Fabrics

Malodorous gases are widely produced in the environment by industrial factories and other commercial activities. Deodorizing aims to protect health and living environment. The deodorizing performance of textiles can enhance health and hygiene and improve living standards. In this study, the deodorization functionality of the enzymatically dyed fabrics is examined.

Table 6 shows the deodorizing properties of the enzymatically dyed fabrics towards ammonia. The deodorizing performance of untreated fabrics towards ammonia increases in the order of nylon < cotton < viscose < silk < wool, which is consistent with the previously reported results[30]. The deodorizing performance of different fabrics is related to the inherent surface characters of the fibres such as roughness or surface areas, polarity and reactivity of chemical groups, etc.

Table 6—Deodorizing ability of the fabrics treated with FA in the presence and absence of laccase using the one-step and two-step methods

Fabric	Untreated	One-step method		Two-step method	
		FA	FA+laccase	FA	FA+laccase
Silk	25	45	45	40	55
Wool	30	50	53	50	60
Nylon	10	10	10	10	20
Viscose	20	30	93	30	80
Cotton	15	30	30	33	35

As compared to the untreated samples, the deodorizing performance of the FA treated fabrics with and without laccase is enhanced. The chemical adsorption by virtue of neutralization operating between carboxyl groups in FA and PFA and ammonia is propitious to the improvement of deodorizing performance towards ammonia. It should be noted that the deodorization performance of viscose fabric towards ammonia is significantly modified when viscose is enzymatically dyed. Additionally, for the silk, wool, nylon and cotton fabrics, the enzymatic treatment of FA with the two-step method shows the highest deodorizing ability. According to the obtained results, it is predicted that PFA would have potential applications in odor treatment.

4 Conclusion

The study shows that FA would be used as a potential multifunctional colourant with biological enzymatic dyeing process in textile industry. The laccase-catalyzed polymerization of FA under mild conditions leads to the formation of yellow FA oligomers which are able to be physically adsorbed by fibres and show the colouration and functionalization effects. The fabrics enzymatically dyed with FA show varied colour parameters and fastness, depending on fibre categories and dyeing methods. All the dyed fabrics show high wash fastness ratings for staining as well as high dry and wet rub fastness. The poor wash fastness ratings for colour change are found in the one-step method, but they could be improved by the two-step method. The relatively poor ratings of light fastness indicate that the fabrics enzymatically dyed with FA are not suitable for the applications with high light fastness requirements. The enzymatically dyed fabrics exhibit significantly increased UV-protection performance, antioxidant activity and deodorizing ability. Thus, these fabrics can be utilized as functional textile materials.

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