

REVIEW ARTICLE

Enzymatic colouration with laccase and peroxidases: Recent progress

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Abstract

Enzymes have received significant attention as alternative catalysts to chemical auxiliaries in textile processing. For example, laccases and peroxidases are promising alternatives for bleaching and denim stone washing processes. Similarly, the ability to oxidise different phenolic substrates and dye precursors resulting in the formation of different coloured polymeric molecules is being exploited for developing green chemistry dyeing processes. The enzymatic process is simpler than conventional coloration processes, giving economic and environmental benefits. In this review, the applications of laccase and peroxidase enzymes in dyeing processes of various textile materials is discussed.

Keywords: Laccase, peroxidase, enzymatic colouration, polymerization, antioxidant

Introduction

Advances in enzymology and related areas of molecular biology and genetic engineering offer significant opportunities to develop novel enzyme-based processes (green chemistry technologies), representing a major step in environmentally friendly industrial development. The demand for application of enzymes in industry is increasing due to the need to overcome high consumption of energy and raw-materials as well as increased environmental concerns over the use and disposal of chemicals into landfills, water or the air during chemical processing. For this reason, enzyme applications have expanded to various fields, including the chemical, fuel, food, agricultural, paper, textile and cosmetic industrial sectors (Maciel et al. 2010).

This is particularly true in the textile industry. It is well known that conventional processes of dye production and colouration require high temperatures and pressure, have high consumption of alkali and unsafe chemical reagents, and release

effluents to the environment, which can cause severe environmental pollution, damage to coloured materials and instruments and harm human health. This has driven the search for environmentally acceptable alternatives to chemical synthesis of dyes and colouration. As stereospecific natural biological catalysts, enzymes greatly reduce the reaction activation energy and thus lower process energy consumption (Kim 2009). Enzyme application in textile treatment can minimize not only the COD (chemical oxygen demand) and BOD (biological oxygen demand) in effluents, but also the amount of effluent. Moreover, enzymes are biodegradable and therefore considered as non-pollutive and self-cleaning materials. This review focuses on the new concept of enzyme assisted textile colouration by introduction of various functional polymers through enzymatic catalysis using laccases and peroxidases. The physicochemical and biological properties of specific enzymes are also introduced.

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General biochemical properties and characteristics of oxidoreductase (laccase and peroxidase)

Laccase

Laccases (EC 1.10.3.2) are multi-copper containing oxidoreductases mainly obtained from bacteria and fungi (Alcalde 2007; Araújo et al. 2008; Baldrian 2006; Campos et al. 2001b; Desai & Nityanand 2011; Hoegger et al. 2006; Jeon et al. 2010; Kunamneni et al. 2008a; Mustafa et al. 2005; Pereira et al. 2005; Riva 2006; Zille 2005). Enzymes of this group were first described by Yoshida in 1883 based on the observation of rapid hardening of the latex from Japanese lacquer trees (*Rhus vernicifera*) in the presence of air (Call & Mücke 1997; Gianfreda et al. 1999; Yoshida 1883) and named laccase 10 years later, after isolation and purification (Bertrand 1894). Since then, laccase activity has been found in other plants species (e.g. mango, mung bean, peach), certain prokaryotes (e.g. *Azospirillum lipoferum*) and various insects, with the most biotechnologically useful laccases being predominantly of fungal origin (e.g. *Ascomycetes*, *Deuteromycetes*, *Basidiomycetes*) (Baldrian 2006; Benfield et al. 1964; Claus 2003, 2004; Desai & Nityanand 2011; Forte et al. 2010; Gianfreda et al. 1999; Kalmis et al. 2008; Kunamneni et al. 2008a). White-rot fungi from *Basidiomycetes* are the highest producers of laccases (Kunamneni et al. 2008a). Such widespread detection indicates that the laccase redox process is ubiquitous in nature.

Laccases are dimeric or tetrameric glycoproteins, containing four copper atoms per monomer bound to three redox sites T1 (blue copper centre), T2 and T3 Cu pair to coordinate at the active site of each enzyme molecule or functional unit (Dwivedi et al. 2011; Kunamneni et al. 2008b; Messerschmidt & Huber 1990; Solomon et al. 1992, 1996; Yaropolov et al. 1994). Copper atoms differ from each other in their characteristic electronic paramagnetic resonance (EPR) signals (Dwivedi et al. 2011; Gianfreda et al. 1999; Zille 2005). In the T1 copper site, the substrate is oxidised and shows an intense electronic absorbance around 610 nm (Burton 2003; Maciel et al. 2010; Zille 2005). The colourless T2 copper site shows no absorption in the visible spectrum but is EPR detectable (Dwivedi et al. 2011; Koroljova-Skorobogat'ko et al. 1998; Leontievsky et al. 1997; Solomon et al. 1996; Zille 2005;). The other two belong to the diamagnetic spin-coupled copper--copper pair at the T3 site with a weak UV absorbance at 330 nm (Dwivedi et al. 2011; Zille 2005). The T2 and T3 copper atoms cluster to form a trinuclear site responsible for oxygen binding and

reduction to water (shown in Figure 1) (Cole et al. 1990; Solomon et al. 1992; Zille 2005). The redox potential of laccases depends on the structure and properties of the copper centres. Generally, laccases from *Basidiomycetes* (especially, white-rot fungi) have a high-redox potential (Gutiérrez et al. 2006), whereas, laccases from bacteria and plants have a low-redox potential (Mikolasch & Schauer 2009). Previous studies have indicated that the catalytic efficiency of laccases for some reducing substrates depends linearly on the redox potential of the T1 copper, showing the higher the redox potential of the T1 site is, the higher the catalytic efficiency of the laccase presents (Xu et al. 1996, 2000).

Laccases are able to catalyse monoelectronic oxidation with concomitant reduction of oxygen to water as the final by-product in a four-electron transfer process (Bourbonnais et al. 1997; Durán et al. 2002; Jeon et al. 2010; Kudanga et al. 2011; Kunamneni et al. 2008a; Morozova et al. 2007; Riva 2006; Robles et al. 2000; Thurston 1994; Xu 1996; Yaropolov et al. 1994). The mechanism of laccase catalysis involves the reduction of copper T1 by oxidising a substrate, internal electron transfer between the different copper types from copper T1 to the copper T2 and T3 trinuclear cluster, and the reduction of oxygen to water at the T2 and the T3 copper site (Messerschmidt 1994; Solomon et al. 1992; Thurston 1994; Yaropolov et al. 1994). Such

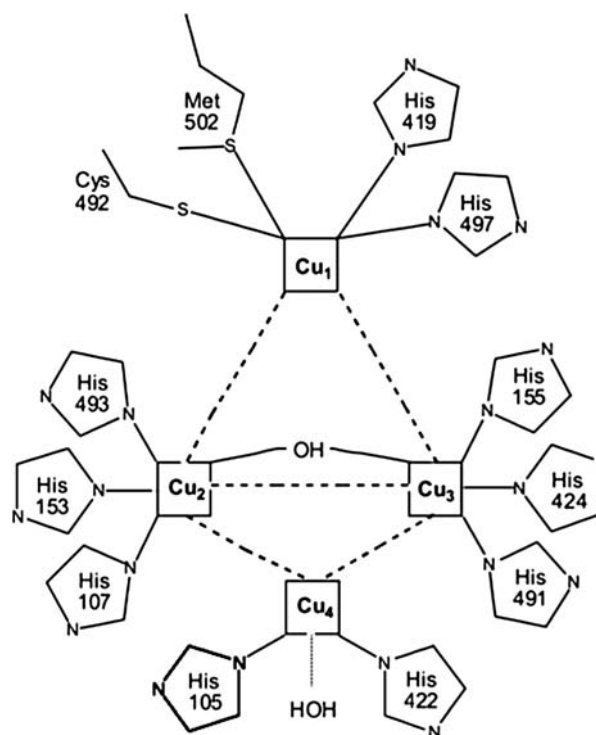


Figure 1. Copper centres of laccase (adapted from Claus 2004).

oxidation gives rise to radicals capable of spontaneously rearranging and undergoing further fission of C–C or C–O bonds of the alkyl side chains, or to cleavage of aromatic rings, resulting in depolymerization, repolymerization, demethylation or quinone formation (Thurston 1994; Yaropolov et al. 1994; Flickinger & Drew 1999; Kunamneni et al. 2008b). Thus, the main functions of laccases are briefly demonstrated as crosslinking of monomers (Claus 2004; Durán & Esposito 2000), degradation of polymers (Claus 2004; Claus et al. 2004; Durán & Esposito 2000) and ring cleavage of aromatics (Claus 2004; Kawai et al. 1999).

The large size of laccase (MW~70 000) (Bourbonnais et al. 1997) makes it difficult to penetrate into substrates, meanwhile the relatively low redox potential limits laccase oxidation only for phenolic lignin fragments (Evans & Hedger 2001; Kersten et al. 1990). However, the discovery of new and efficient mediators extend the effect of laccase to non-phenolic lignin units and also overcome the accessibility problem (Bourbonnais & Paice 1990, 1992; Bourbonnais et al. 1997; Camarero et al. 2005; Crestini & Agryropoulos 1998; Eggert et al. 1996a; Galli & Gentili 2004; Hammel 1996; Hammel & Moen 1991; Kudanga et al. 2011; Kuhad et al. 1997; Van Aken & Agathos 2001, 2002). This is because a mediator is a small molecule that acts as a sort of ‘electron shuttle’ and is therefore able to penetrate to the inner part of polymers. In the laccase-mediator system (LMS), the mediator is first oxidised by laccase generating a strongly oxidising intermediate, the co-mediator (Med ox), and then diffuses away from the enzyme active site into the cell wall, and in turn oxidises any substrate inaccessible to laccase (shown in Figure 2) (Banci et al. 1999; Barreca et al. 2004).

An ideal redox mediator should be a good laccase substrate with cyclic redox conversion and its oxidised and reduced forms must be stable with no inhibition on enzymatic reaction (Johannes & Majcherczyk 2000). The addition of redox-mediators, such as ABTS (2,2'-azino-bis (3-ethylbenz- thiazoline-6-sulfonic acid), HBT (1-hydroxybenzo-triazole) or compounds secreted by lignolytic fungi, which transfer electrons between the enzymes and the substrates (Bourbonnais et al. 1995; Eggert et al. 1996b; Johannes & Majcherczyk 2000; Reyes et al. 1999;

Wong & Yu 1999) can further expand the substrate specificity of laccases, which is already broad, ranging from various organic substances (e.g. ortho- and para-diphenols, aminophenols, methoxy-substituted monophenols, polyphenols, polyamines, aromatic amines, alkyl- and alkoxy-substituted anilines, lignins, syringaldazine, aryl diamines) to some inorganic ions (Bourbonnais et al. 1997; Gianfreda et al. 1999; Hoff et al. 1985; Kobayashi et al. 2001; Kobayashi & Higashimura 2003; Li et al. 1999; Reinhammar 1984; Robles et al. 2000; Sakurai et al. 1992; Solomon et al. 1996; Thurston 1994; Yaropolov et al. 1994). Due to the high catalytic efficiency and broad oxidative capabilities, laccase has become attractive for many biotechnological and environmental applications, as compared to other conventional chemical or microbial catalysts (Desai & Nityanand 2011; Durán et al. 2002; Dwivedi et al. 2011; Widsten & Kandelbauer 2008). Additionally, substrate conversion using laccase coupled with small molecule redox shuttles is promising for the synthesis of new compounds (Pilz et al. 2003), offering new routes to colouration compounds for dyeing.

Peroxidase

Peroxidases (EC 1.11.1.7) are bifunctional oxidoreductase enzymes (Miranda et al. 2002; Mohamed et al. 2011) with molecular weights ranging from 35 000 to 100 000 (from 251 to 726 residues) (Banci 1997). They are able to catalyse the oxidation of a wide variety of organic and inorganic compounds in the presence of hydrogen peroxide but also produce reactive oxygen species (Dunford et al. 1976; Everse & Everse 1991; Nigel 2004; Mohamed et al. 2011).

Due to their wide distribution among living organisms, multiple physiological roles, multifunctional reactivities and broad substrate specificities, peroxidases have attained a prominent position in biotechnology and associated research areas such as enzymology, biochemistry, medicine, genetics, physiology and histo- and cytochemistry (Azevedo et al. 2003; de Montellano & Crab 1987; d'Ischia et al. 1991). Peroxidases have been found in plants, bacteria and fungi, and higher organisms (Battistuzzi et al. 2010; Reihmann & Ritter 2006), and can be divided into three superfamilies: plant peroxidases, animal peroxidases and catalases according to their source and mode of action. Most peroxidases are glycoproteins containing N-linked oligosaccharide chains (Dunford et al. 1976; Gray & Montgomery 1997) and protoporphyrin IX (heme) as prosthetic group (Conesa et al. 2002). The structure of the active site in different superfamilies is similar, and they all use a similar mechanism involving formation of a

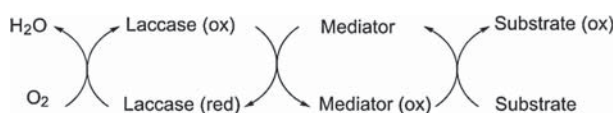


Figure 2. Catalytic cycle of a laccase-mediator oxidation system (adapted from Banci et al. 1999).

two-equivalent oxidised (Compound I) intermediate (Gumiero et al. 2010).

Heme peroxidases catalyse the oxidation of a variety of substrates, most commonly small organic substrates, and are widely distributed in biological systems (Gumiero et al. 2010) but share the same catalytic cycle (shown in Figure 3) due to their strikingly similar active site structure. The catalytic cycle is based on three consecutive and distinct redox steps, involving two high-valent intermediates (Compound I and Compound II) (Banci 1997; Dunford 1999; English 1994; English & Tsapralis 1995; Everse & Everse 1991; Nakayama & Amachi 1999; Smith & Veitch 1998; Veitch & Smith 2001). Initially, a molecule of hydrogen peroxide binds to the active site and undergoes a two-electron reduction to water and the formation of Compound I through oxidation of the enzyme. Compound I has an oxyferryl ($\text{Fe(IV)}=\text{O}$) centre and an organic cation radical located either on the heme or on a protein residue (Battistuzzi et al. 2010; Conesa et al. 2002). The cation radical then undergoes a one-electron reduction, oxidising one substrate molecule to give a substrate radical and forming Compound II. Finally, Compound II is reduced by a second substrate molecule to the resting ferric state (Banci 1997; Conesa et al. 2002; Dunford 1999; English 1994; English & Tsapralis 1995; Everse & Everse 1991; Nakayama & Amachi 1999; Smith & Veitch 1998; Veitch & Smith 2001).

Among all peroxidases, horseradish peroxidase (HRP), a classical plant heme-containing enzyme from *Armoracia rusticana* roots (Kay et al. 1967; Nigel 2004; Ryan et al. 2006), has received special attention (Azevedo et al. 2003) due to its practical and commercial applications (Nigel 2004). Although the term

'peroxidase' came into use towards the end of the nineteenth century, research on peroxidase from the horseradish root and other plant sources was initiated by the work of Robert Chodat (1865–1934) and Alexei Nikolaevich Bach (1857–1946) at the University of Geneva during the early years of the twentieth century (Bach & Chodat 1903). Horseradish peroxidases are most often used to catalyse an oxidative polymerization of electron-rich aromatic compounds like phenols, anilines and their derivative in the presence of peroxides like hydrogen peroxide, alkyl peroxides and benzyl peroxide (Reihmann & Ritter 2006; Uyama & Kobayashi 2006). HRP catalyses the one-electron oxidation of phenols by hydrogen peroxide as oxidising reagent to form the corresponding phenoxy radicals and two water molecules.

The phenoxy radicals go further to form polymers via subsequent recombination and radical transfer steps. The overall polymerization can therefore be written as shown in Figure 4 (Reihmann & Ritter 2006):

Applications of laccase/peroxidase in textile and other areas

Enhancement of whiteness (Bio-bleaching) in cellulosic materials. Bleaching is the process of removing naturally-occurring coloured substances in fibres like cotton wax, fatty acid, colouring matter, albuminoids and mineral matter, amounting in all to 5% of the weight of material. The flavonoids are the substances mainly responsible for the natural colour of cotton. The natural colour on the fabrics can affect further finishing and dyeing processes leading to unexpected colour shades (Ardon et al. 1996; Hedin et al. 1992). Hydrogen peroxide is commonly applied in conventional bleaching processes, under alkaline condition and temperatures close to boiling. However, the radical reactions by hydrogen peroxide on the fibres can not only affect impurities fabrics but also the cellulosic components. That can result in severe damage of fabrics. Specific processes only targeting coloured impurities offer a practical alternative to the traditional bleaching process. Laccase, due to its ability to oxidise flavonoids (Araújo et al. 2008), can be applied in the bleaching of cellulosic materials (Kim et al. 2007c). However, the mechanism of laccase oxidation of natural compounds in fabrics to improve their whiteness is not well studied. Tzanov et al. (2003a) initially reported enhancement of the bleaching effect on cotton fabric using a low dosage of laccase over a short-time, batchwise or in a pad-dry processes prior to conventional peroxide bleaching. Also, Pererira et al. (2005) reported that laccases from a newly isolated strain of *Trametes hirsuta* were responsible for oxidation of the flavonoids morin,

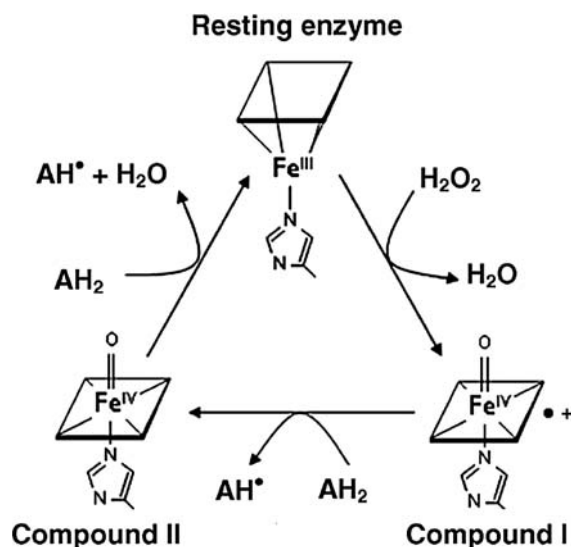


Figure 3. Catalytic cycle of peroxidase (adapted from Battistuzzi et al. 2010).

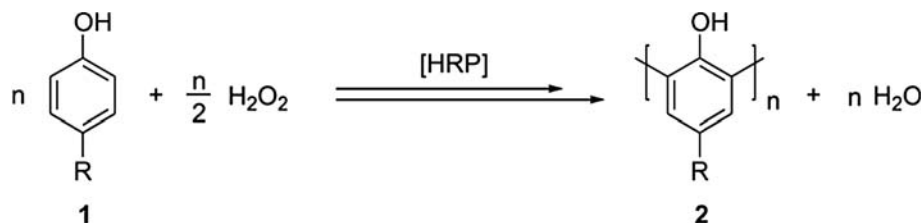


Figure 4. Polymerization of phenols catalyzed by horseradish peroxidase (HRP) (adapted from Reihmann & Ritter 2006).

luteolin, rutin and quercetin and resulted in an increase of whiteness of cotton. More recently, ultrasound was used in the work of Basto et al. (2007) as a trial to intensify the enzymatic process by sonication to improve final whiteness of the fabrics.

Stonewashing and denim over dyeing. Stonewashing is generally known as denim washing where excessive amounts of indigo are removed from the fabrics. Cellulases can partially replace the role of pumice stones in the traditional process with an abrasive effect on the fibre surface producing the stone-washed look (Cavaco-Paulo et al. 1998). In addition, laccases can bleach indigo dyed denim fabrics to lighter shades (Campos et al. 2001b; Kunamneni et al. 2008b; Pazarloglu et al. 2005). However, the re-deposition of removed indigo dye on white weft yarns of denim fabrics (high indigo 'back-staining' on denim fabrics) is a major problem when removing the indigo dye trapped inside the cellulose fibre by the cooperative action of cellulases and mechanical action, which is mainly due to the tendency of cellulases to re-adsorb on the fabrics and bind to indigo (Cavaco-Paulo et al. 1998; Montazer & Maryan 2008;). The degradation of indigo released during the stonewashing process could avoid the phenomenon of backstaining (Campos et al. 2001b). Laccases isolated from *Polyporus sp.* and *Sclerotium rolfsii* were found to degrade indigo on fabrics (Abadulla et al. 2000; Campos et al. 2001a). Those from *Trametes hirsute* and *Sclerotium rolfsii* in combination with redox-mediators caused various bleaching appearances in denim garments (Campos et al. 2001b), while the enzyme from batch cultures of *Trametes versicolor* can be used for denim washing without using a mediator, which is more effective than commercial laccase (obtained from recombinant *Aspergillus niger*, Novo Nordisk, Denmark) with a mediator (Pazarloglu et al. 2005). Recent investigations showed that laccases along with cellulases reduced the activity of neutral cellulases, and fibre damage was limited to the outer fibres with inner fibres remaining unaffected (Montazer & Maryan 2008). The co-application of laccase with cellulase increased the lightness and decreased the staining on both the back of the

garment and white pocket. Laccase decomposes the removed indigo during stone washing and in a concentration dependent manner, back-staining decreases (Maryan & Montazer 2009). There are already some successful industrial applications of laccases in denim finishing, for example, DeniLite™, DeniLiteII™, Zylite, ECOSTONE®LCC 10, PrimaGreen EcoFade LT100, etc. (AB Enzymes 2011; Couto & Toca-Herrera, 2006).

The over-dyeing of denim, achieved by a further dyeing step, primarily dyes the fill yarn of the desized denim but also imparts some degree of dyeing to the previously dyed warp yarn, which can bring in new shades on textiles. Polymers formed by enzymatic polymerization have drawn considerable attention for application as 'dyes' in the denim over dyeing process. US Pat. No.5925148 (Barfoed & Kirk 1999) claimed an enzymatic method for over dyeing warp dyed denim textiles, in which a hydrogen peroxide source or at least one enzyme exhibiting peroxidase activity and/or oxidase activity was employed for over dyeing fabrics and articles. Recently, Guimarães et al. (2011) adopted laccase from the ascomycete *Myceliophthora thermophila* as a catalyst to oxidise the polymerization 'in situ' of catechol and catechin, and the enzyme-generated polymers were capable to over dyeing the denims. Different colours were acquired based on the phenolic used, ranging from brown to green-yellow for catechol and catechin, respectively. Such enzyme-based over dyeing processes have launched new approaches for denim over dyeing with the same level of durability as obtained with direct dyes, at the same time increasing the fabric's hydrophobicity.

Stain removal in laundry

A peroxidase-based system for the inhibition of dye transfer during washing with laundry detergents was developed by Conrad et al. (1997). The mechanism of dye-transfer inhibition by peroxidases involves oxidation and decolourisation of released dyes. To enhance the dye decolourisation ability of the enzymes, phenothiazine-10-propionic acid was used as a mediator. The peroxidases

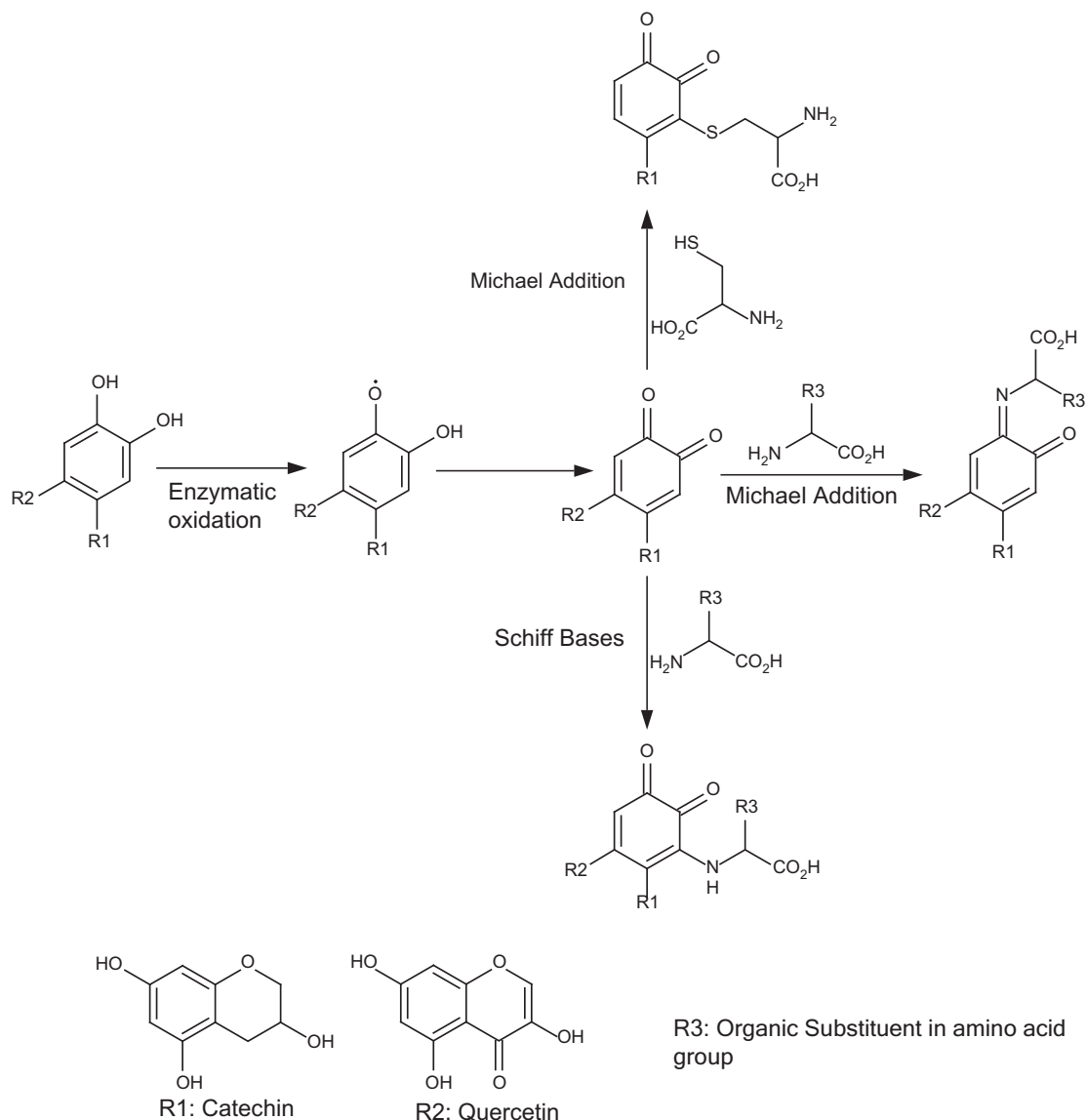


Figure 5. Schematic representation of enzymatic and non-enzymatic conjugation of flavonoids and reactive amino acids (adapted from Kim & Cavaco-Paulo 2011).

oxidise phenothiazine-10-propionic acid to a highly reactive species responsible for oxidising and decolourising dyes in solution. A comparison of enzymatic and non-enzymatic dye-transfer inhibition systems showed that the enzymatic method is, in many cases, more effective than the non-enzymatic method (Conrad et al. 1997).

Dye synthesis through oxidative polymerization

The enzymatic polymerization phenomenon can be described as the synthesis of polymers '*in vitro*' via non-biosynthetic pathways, catalysed by enzymes (Reihmann & Ritter 2006). Since 1985, enzymatic oxidative polymerization of aromatic compounds has

been widely investigated and anticipated to be an alternative method for the production of conventional phenolic resins, which typically involves the use of toxic formaldehyde (Aktas et al. 2000). Enzyme catalysis introduces the possibility of 'Green polymer chemistry' (Kumar et al. 2005; Reihmann & Ritter 2006).

The principal mechanism of both peroxidases and laccases is one electron oxidation of phenolic compound to form phenoxy radicals using an oxidising reagent. However, the main difference between peroxidases and laccases is the type of oxidising agent, which is hydrogen peroxide and oxygen, respectively. The phenoxy radical may react with a second radical to form *o*-quinones, which are highly reactive electrophilic molecules and further spontaneously polymerize in a non-enzymatic pathway (Figure 5) (Amić et al. 2003; Uyama & Kobayashi 2002).

Phenolic polymers require specific functional properties of molecular weight, dispersity, degree of crosslinking, crystallinity, and inter- and intramolecular bonding (Aktas et al. 2000). Laccases and peroxidases are able to catalyse the transformation of phenol derivatives through an oxidative coupling reaction, resulting in the formation of less soluble and high molecular weight polymer compounds (Gianfreda et al. 2003). The polymerization of phenols catalysed by horseradish peroxidase (HRP) is fairly well understood based on published research (Adam et al. 1999; Hewson & Dunford 1976a, b; Poulos 1993; Van Deurzen et al. 1997). The oxidation of aromatic electron donors in the presence of peroxide is an important step in peroxidase catalysed synthesis (Reihmann & Ritter 2006; Tawaki et al. 2005). Peroxidases are able to yield chromogenic products and show relatively good stability characteristics (Worthington 2011).

Compared with peroxidases, the range of laccase substrates is very wide. Basically, any substrate possessing characteristics similar to *p*-diphenol will be oxidised by laccases. Moreover a few fungal laccases can oxidise monophenols such as cresol and some are able to oxidise ascorbic acid (Mayer & Staples 2002). Using oxygen as an oxidation reagent and having a wide range of substrates is a valuable feature of laccase applications.

Forte et al. (2010) and Pogni et al. (2010) applied laccase from *Cerrena unicolor* to catalyse the one step bioconversion of 3-amino-4-hydroxybenzenesulfonic acid into a water soluble phenoxazine dye having the structure of 2-amino-3-oxo-3H-phenoxazine-8-sulfonic acid. The initial mixture changed from yellow ochre to red. They claimed that the biocatalytic system offered eco-sustainable synthesis of complex polymers.

Mustafa et al. (2005) used the laccase oxidation of ferulic acid in a biphasic hydro-organic medium containing well-mixed ethyl acetate and sodium phosphate buffer and obtained intermediate stable yellow coloured products from the organic phase, with the ability to bind to macromolecules like pectin, hemicellulose etc (Craven et al. 1981; Taylor & Clydesdale 1987a, b). Normally, when the laccase oxidation of phenolic and polyphenolic compounds (ferulic acid, gallic acid, caffeic acid and catechin) takes place in aqueous medium, the colour of the oxidation products goes from an intermediate yellow, green or orange to a final brown hue. However, the presence of an organic solvent in the reaction medium decreased both the laccase activity and non-enzymatic reaction rates, resulting in a major improvement in stability of the intermediate products. Therefore, the laccase-based synthesis of colorants may be expanded to other phenolic and polyphenolic compounds with this medium. In addition, a biphasic hydro-organic medium helped the preven-

tion of browning and increased product solubility. The authors claimed an improved control of polymer synthesis. Recently, Polak and Jarosz-Wilkolazka (2010) tried to apply immobilized white rot fungal strains as cheaper industrial-grade biocatalysts for dye synthesis. Such biomass was able to catalyse the transformation of benzene and naphthalene derivatives and generate stable and non-toxic polymers with good dyeing properties, highlighting the possibility to replace isolated enzymes by fungal biomass to transform precursors into dyes in a more efficient and simple way (Polak & Jarosz-Wilkolazka 2010). Enaud et al. (2010) synthesized a sulfonic azoanthraquinone through the coupling of aromatic amine monomers in the presence of the *Perenniporia ochroleuca* MUCL 41114 laccase, Laccase Acid Red 1 (LAR1). Such enzymatically created dyes were not mutagenic and showed lower toxicity than other commercial red dyes. A crude preparation of this new acid eco-colourant could be used directly and demonstrated good dyeing properties on polyamide. This work opens the way to safe and environmentally friendly routes to azo dye biosynthesis. Horseradish peroxidase (HRP) and soybean peroxidase (SBP) can also produce polymers from the flavonoids quercetin, rutin and catechin in the presence of H₂O₂ (Lorenzo et al. 2002).

Laccase and peroxidase based colouration

The first notable activity of heme peroxidases that led to their discovery was the observation by Planche in 1810 of their ability to catalyse the formation of a beautiful blue colour when a tincture of gaiac resin came into contact with fresh horseradish root, long before the enzyme was known (Nyanhongo et al. 2010). Similarly with respect to laccases, Chinese lacquer artwork from more than 6000 years ago reveals the use of laccase (Hüttermann et al. 2001). Recently, there has been growing interest in using these oxidative enzymes to improve the aesthetic look of fabrics. Dyes are colorants applied to textile substrates in a molecularly dispersed form (AATCC 1997, 375). Colour is derived from the conjugated double bonds in the molecular structure of the dyes (Clifford 1986; Bille & Phyllis 1997). The dyes which are mainly used are classified as azoic dyes (naphthol dyes), direct dyes, vat dyes, sulphur dyes and reactive dyes (Bille & Phyllis 1997). Different dyes are appropriate for the requirements for dyeing various substrates. The enzymatically polymerized phenolic compounds with high molecular weight are less soluble (Gianfreda et al. 2003) and tend to have a characteristic colour attributed to the formation of a large conjugated structure along the main chain (Shin

et al. 2001), which offers great potential for application in colouration. The enzymatically produced polyphenols generally possess mixed structures with phenylene and oxyphenylene units resulting from the C–C and C–O coupling of phenols, respectively (Mita et al. 2003). Such enzyme-catalysed polymerization for polymer production is regarded as an ‘environmentally friendly’ synthetic process (Kobayashi et al. 2001) for colorant production.

Colouration of cellulosic fibres (cotton and flax)

In situ direct colouration on cellulosic materials. Fixation of dye molecules ‘*in situ*’ generated on the fibre surface can take place when a decrease in solubility their release during wet processing (Hadzhiyska et al. 2006). The key to achieving higher dye fixation on cellulosic materials depends on suitable molecular reactions of dye precursors for enzymatic coupling (Hadzhiyska et al. 2006). Generally, enzymatic oxidation of dye intermediates dominantly leads to homo-molecular reactions at equimolar ratios of precursors. However, the higher the concentration of compounds that can transform into less soluble products upon laccase oxidation, the higher the fixation that may be achieved (Hadzhiyska et al. 2006). It is reported that increasing the concentration of phenol component benefits oxidative self-polymerization into less soluble products (Aktas & Tanyolac 2003; David et al. 1996; Dubey et al. 1998). Tzanov and coworkers have undertaken a series of studies on laccase-assisted dyeing of cotton since 2006, and demonstrated for the first time a permanent colouration of cotton fabrics with polymeric dyes generated *in situ* by oxidative coupling of 1-hydroxyphenol (catechol) and colourless 2,5-diaminobenzenesulfonic acid (2,5-DABSA) in the presence of laccase (Calafell et al. 2007; Hadzhiyska et al. 2006). With an excess of catechol, the cross-coupling occurs in higher yield (Calafell et al. 2007). They suggested that at least four-fold excess of catechol was required for satisfactory dye fixation on cotton and proposed the reaction pathway for the laccase-catalysed oxidative coupling of the reagents shown in Figure 6. Laccase catalysed the conversion of catechol to highly reactive quinone species which undergo homo-molecular C–O–C coupling, and then non-enzymatic C–N coupling with 2,5-DABSA took place through 1,4 nucleophilic addition of the latter to the quinoid rings (Calafell et al. 2007).

Non-toxic and non-harmful phenolic substrates such as flavonoids (rutin, morin and quercetin) have been used to coat and colourise cotton and flax fabrics. The laccase-oxidised flavonoids can graft onto the surface of the cotton and provide a yellow to brown colour of different colour strength, depending on the

type of external flavonoids used and the reaction conditions (Kim et al. 2007a). Rutin flavonoids gave poor colour appearance on the surface of cotton fabric in the presence of laccase compared with morin and quercetin (Kim 2009) since the oxidation rate of rutin is lower than the other flavonoids (Friedman 1996) and the aqueous solubility of the enzyme-catalysed poly(rutin) reduced the chance for coupling to the cellulosic fibre surface (Kim 2009). Rinsing and washing conditions also influenced the colour visual inspection, and a remarkable colour vanish was detected in a high temperature process (Kim 2009). The washing and friction fastness test of flavonoid colourised cotton showed satisfactory results confirming the feasibility of this new and promising colouration technique (Kim 2009). Moreover, their application on the surface of fabrics introduces new functions on the fabrics such as antioxidant and antimicrobial properties, and therefore, increasing their potential.

Significantly, for all flavonoids tested, a higher increase in colour appearance and superior colour fastness was obtained when laccase treatment was carried out in the presence of scoured cotton fibres, rather than the scoured/bleached fibres (Kim et al. 2007a). Similar results were obtained in the colouration of flax fabrics with polymerized flavonoids. The scoured flax fabrics gave better colour strength and colour fixation in comparison with scoured and bleached fabrics (Kim 2009). Natural flavonoids present in cotton and flax may serve as grafting points or anchors to attach the intermediates (quinones) formed during oxidation by laccase (Friedman 1996; Makris & Rossiter 2002), promoting colouration. However, the traditional bleaching pretreatment of cotton removes these natural flavonoids from cotton and flax. Elimination of the bleaching treatment results in savings of chemicals, water, energy, giving an environmentally friendly textile process (Kim et al. 2007a). Flax is thought to have a better affinity for oxidised flavonoids due to the higher quantity of lignin compounds on its surface compared with cotton (Kim 2009). A high temperature and the presence of salt improved polymer absorption onto the flax fabrics. Compared to morin, the quercetin flavonoid is more effective for colouration of flax fabrics. However, considerable colour vanished during the washing processes since the newly incorporated polymers had not deeply penetrated through the fibre structure and no strong covalent bonds were formed between the fibre and oxidised compounds, leading to a poor affinity (Kim 2009; Kim et al. 2009). In addition, polymers from laccase-catalysed polymerization of lignosulfonates were applied on the lignin-containing surface of flax fibre. However, the affinity of the resulting polymers towards the fibres was low since their high molecular weight

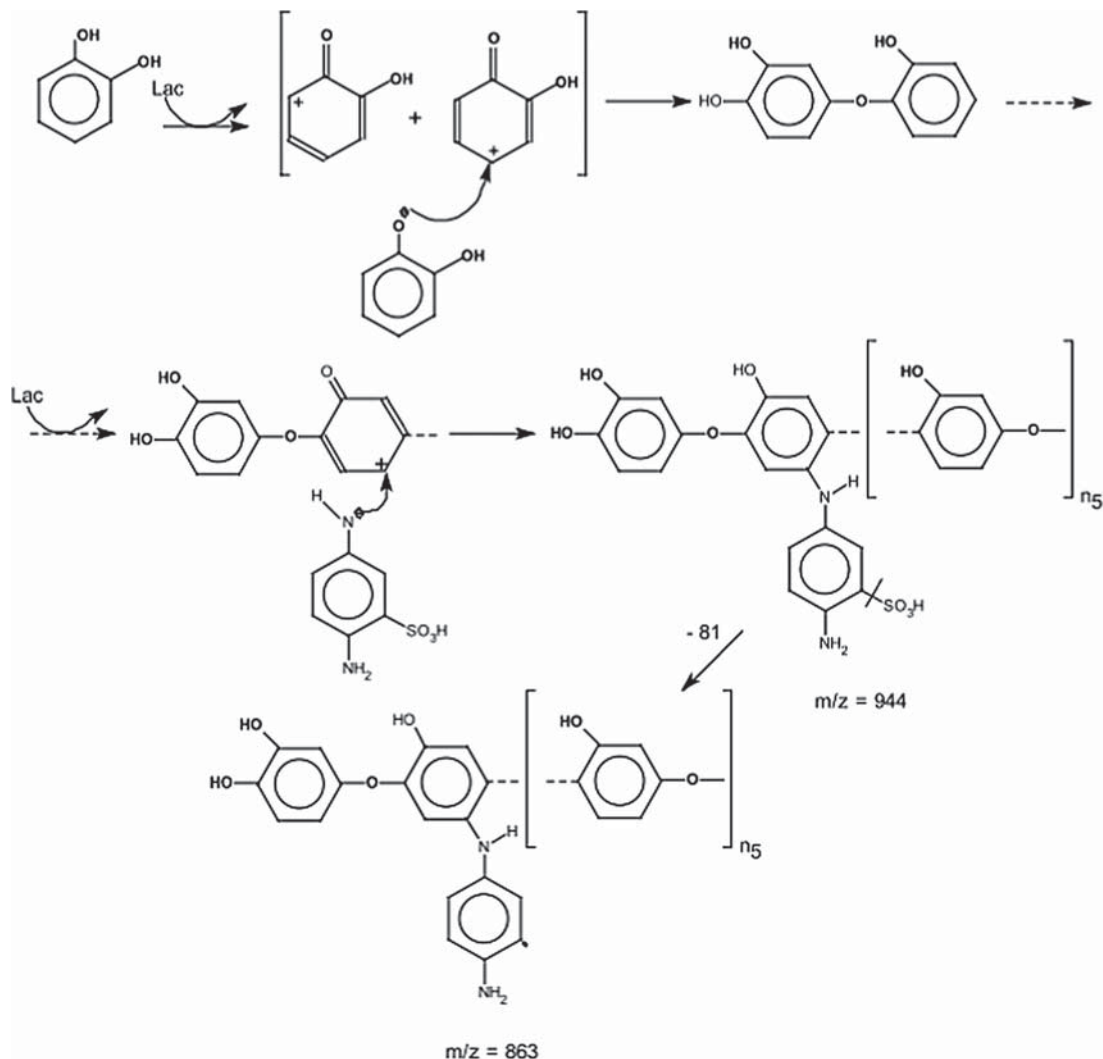


Figure 6. Proposed reaction pathway for laccase-catalyzed oxidative cross-coupling of 2,5-DABSA and catechol, and splitting pattern of the resulting product identified by MALDI-TOF MS (Adapted from Calafell et al. 2007).

affected interaction with the fibre structures. Therefore, the colour strength level was not so satisfactory (Kim 2009). In very recent work, polyoxometalates (POMs), namely $K_5[SiW_{11}VVO_{40}] \cdot 11H_2O$ and $H_5[PMo_{10}V_2O_{40}] \cdot 13H_2O$, were employed as inorganic mediators in the laccase-oxidative polymerization reaction to form a relatively high molecular weight polycatechol. The polymers synthesized by the laccase-mediator system allowed better colour fixation and colour resistance for flax compared to that obtained by conventional synthesis with laccase solely or with addition of an organic mediator (1-hydroxybenzotriazole) (Kim et al. 2011).

Preparations of cellulosic fabrics for improving polymer affinity

A major constraint for enzymatic colouration of cellulosic materials is the lack of affinity between the

laccase-generated dyes and cellulosic materials, since no chemical bonding occurs. Various surface modification techniques like amination, pre-oxidation, cationisation, etc. have been employed to improve cellulose fibre-matrix adhesion (Tsubokawa et al. 2000; Zhou et al. 2005). These functional groups have chemical affinity to enzymatically produced polymers thus enhancing 'dyeability' (Chhagani et al. 2000; Mohorcic et al. 2004).

Based on its relatively low cost and wide utilization as a dye in the textile industry, Reactive Black 5 dye (RB5), a di-azo vinyl sulphonc dye, is normally adopted for amination (Mohorcic et al. 2004). Initially, RB 5 is covalently attached onto the cellulose fabric via a nucleophilic addition reaction (Chhagani et al. 2000) and then covalently attached RB5 molecules are chemically reduced to form aminic functional groups on the fabric surface (Chhagani et al. 2000; Kim et al. 2007b) as shown in Figure 7.

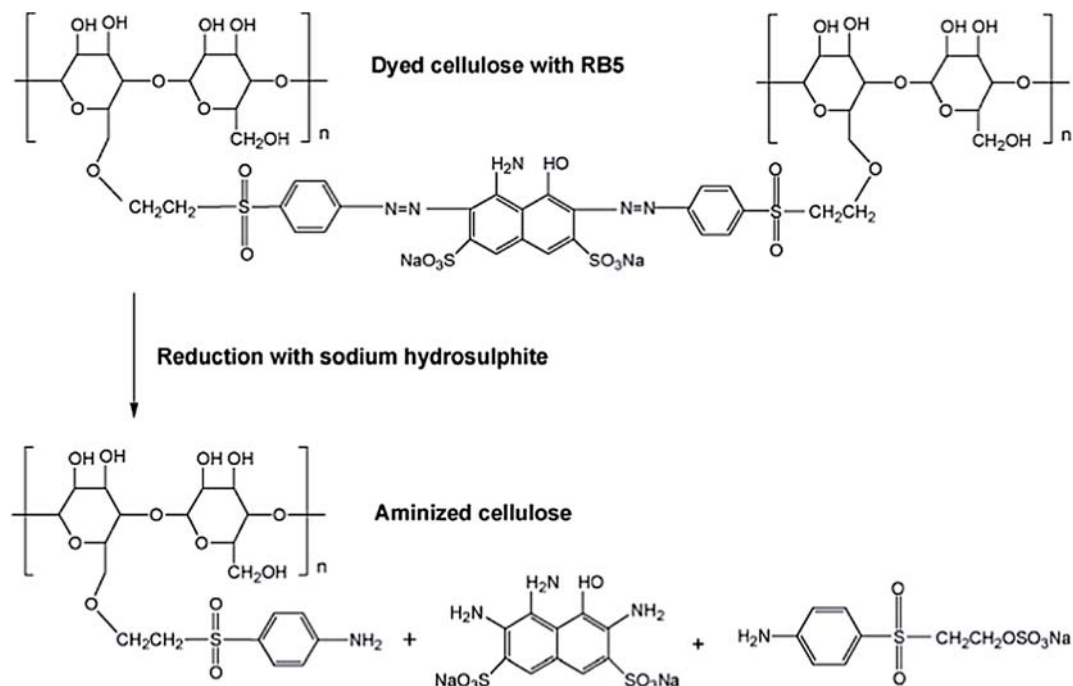


Figure 7. Mechanisms of chemical-reductive cellulose functionalization (adapted from Kim et al., 2007b).

Reduction of the two azo groups of RB5 produces three compounds containing amino groups: one compound covalently linked to cellulose and the other two dissolving in water. Decolorisation of the fabric can be observed during the reduction process, since the reduction of azo bonds resulted the formation of non-colourful amine groups. The amino groups on the cellulose can be exploited for coupling polyphenols obtained through enzymatic oxidation (Kim et al. 2007b). Compared with unfunctionalised cotton fibres, the aminised cotton fibres develop a much darker-brown colour after coating 'in situ' with laccase-synthesised polycatechol, which reflects the high level of coupling sites on the functionalized surface (Kim 2009). Meanwhile, coated functionalized-cellulose showed greater resistance to cellulase hydrolysis since the polymeric network on the fibre surface can sterically block the binding activity of cellulase (Kim 2009; Kim et al. 2007b).

Blanco et al. (2009) examined tosylation of the surface of cotton fabrics with subsequent amino group introduction with 2,5-DABSA through nucleophilic displacement of the tosyl groups in a quantitatively controlled way. The aminised cotton showed about 20% enhancement in dyeability compared to the unmodified fabric and allowed up to 95% pigment fixation on the fabric in the laccase catalysed process for fibres colouration.

Recently, Silva et al. (2011) described the application of natural compounds for aminization, using chitosan. In the presence of laccase, the amino

functional groups of chitosan can covalently link with unbleached flax fabrics previously oxidised with laccase. The pre-oxidation of flax fabrics using laccase might develop grafting points for chitosan attachment by oxidation of natural phenolic compounds in flax to introduce reactive sites. The previously laccase-oxidised flax fabric had enhanced washing durability and higher grafting levels on the surface and, thus had a higher concentration of catechin polymers grafted onto the surface giving higher colour strength (Silva et al. 2011). In the study of Kim and Cavaco-Paulo (2011), the cationisation of flax fabrics using a polyanion was introduced for modification of flax fabrics by anchoring of protein-flavonoid conjugates produced by laccase catalysis. The cationised fabrics reacted with protein-flavonoid conjugates through strong ionic interactions. In the reaction medium, the proteins are negatively charged at pH 7.4 with high affinity for the cationised surface of fabrics. The conjugates onto fibres had acceptable durability in terms of washing resistance and the surface became hydrophilic when α -casein-catechin was applied (lower contact angle 48°). The final products with new colour generation and antioxidant activity (> 93%) were obtained by anchoring the protein-flavonoid conjugates onto flax fibres.

In addition to chemical pre-modification, mechanical agitation can also greatly influence the affinity of coloured polymers. Strong vertical agitation promotes the breakage of filaments on fibre

surfaces increasing the accessible surface area for attachment of polymerized flavonoids (Kim 2009).

Dyeing of keratinous fibres (wool and hair)

Wool and hair are the most common keratinous fibres in textile and cosmetic applications, respectively. Enzymes like laccase or horseradish peroxidase can be applied for their colouration. The enzymatic dyeing process, when carried out at a mild pH and low temperature does not damage keratinous fabric, is an economically and environmentally attractive alternative to the conventional process (Tzanov et al. 2003b; Zille 2005).

Wool dyeing. Characteristic colours are determined by the use of different phenolic compounds for the enzymatic dyeing, such as hydroquinone (brown-blacks), catechol (greys), dopamine (greys), guaiacol (colourless) and ferulic acid (yellows) after treatment with HRP (Shin et al. 2001). Shin et al. (2001) found that wool fabric previously treated with hydroquinone and ferulic acid can be coloured by laccase (or HRP), in which the hydroquinone on the fabric was enzymatically oxidised, forming dimers, oligomers and polymers. The colour depth of enzymatically dyed wool fabrics could be adjusted by the amount of hydroquinone previously added to the wool fabric. Mordant processing with chromium compounds and boiling under acidic conditions assisted the strong fixation of the coloured hydroquinone and ferulic acid derivatives to the wool fabrics.

Later, Tzanov et al. (2003b) and Zille (2005) optimized a novel laccase-assisted wool dyeing process performed in a dye bath using a dye precursor (2,5-diaminobenzenesulfonic acid) and dye modifiers (catechol and resorcinol) and laccase, without any dyeing auxiliaries. Varying the concentration of the modifiers and the time of laccase treatment generated different hues and depths of shades on the wool fabric. The wool fabrics dyed with catechol (modifier) showed redder and bluer colours, while the fabric dyed with resorcinol gave yellower and greener colours. The highest colouration value for catechol was achieved at the highest concentration of modifier, laccase amount and dyeing time, while the highest colouration value for resorcinol was attained at the highest concentration of laccase and dyeing time but lowest concentration of modifier. It was pointed out that the duration of the enzymatic reaction appeared to be the most important factor in the dyeing process. Darker colouration of the wool fabric could be achieved by increasing the reaction time and minimizing the enzyme and modifier loading.

Such laccase-catalysed colorant can penetrate into the mass of wool fibres.

More recently, Munteanu et al. (2007) found that the cyclic voltammetry had a synergetic effect on wool staining using 2,2'-Azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) enzymatic oxidation when coupled with ultrasound and resulted in higher colour depth (K/S value). The K/S value of staining wool in the system with the combination of cyclic voltammetry and ultrasonic irradiation was the sum of the values obtained in the presence of cyclic voltammetry and ultrasonic irradiation alone. However, the cumulative value was exceeded when wool colouration was carried out under continuous stirring and cyclic voltammetry, since mass transport of the active species to/from the working electrode was improved in the presence of ultrasound and formed a higher amount of $ABTS^{2+}$ which was easily transported to the wool surface resulting in wool colouration.

When laccase (Denilite II S) was applied to modify the physical properties of wool fabric, Majid Montazer et al. (2009) found that the wool fabric changed colour, showing a redder and yellower colour with increasing laccase, due to the progressively higher oxidation of wool. Additionally, they found that the dyeing of laccase pre-treated wool fabric with madder gave a lower lightness since the laccase pretreated wool fabric was more hydrophilic and could adsorb higher amounts of water soluble dye in the dye bath. This suggested that the laccase-based pre-treatment was effective for fabric colouring when dyed with madder.

Hair dyeing. Hair is mostly proteinaceous in nature mainly consisting of fibrous α -keratin proteins (Araújo et al. 2011). Hydrogen peroxide (H_2O_2) and phenylenediamines are the most widely used oxidising agent and dye precursor for hair dyeing (Wall 1972), respectively. However, it has been recognized that the strong oxidation power of H_2O_2 under high alkalinity conditions causes severe hair damage (Araújo et al. 2011; Takada et al. 2003) and phenylenediamines are allergenic and carcinogenic (Chen et al. 2006; Marcoux et al. 2002; Huang et al. 2007). Therefore, it is high desirable to develop new approaches for hair dyeing to overcome these problems.

Various patents have claimed the oxidation dyeing of keratinous fibres and, in particular, human keratinous fibres (such as hair) in the presence of enzymes (Lang & Cotteret 2007; Onuki et al. 2004). Oxidases such as peroxidase and laccase can be used to generate useful hair dyes. Laccase-based hair dyes are less irritant and easier to handle than current hair dyes (Aaslyng et al. 1997; Koike 2002; Lang & Plos

2002; Lang & Cotteret 1999, 2004; Onuki et al. 2000; Pereira & Burgaud 2005; Plos 2001, 2004a, b; Pruche et al. 2000; Shichiri et al. 2003; Riva 2006; Roure et al. 1992; Sorensen 2001; Tsuji et al. 2002; Xu 1999). However, phenylenediamines or other synthetic dye precursors which may be toxic to humans are still in use (Lang & Cotteret 2007; Onuki et al. 2004).

Recently, Jeon et al. (2010) studied laccase-catalysed polymerization of natural phenols to form products for hair dyeing, overcoming the current problem with H_2O_2 - and phenylenediamine-based dyeing systems. They found that the novel combinations of natural phenols derived from edible plant fibres for polymeric dye synthesis can result in useful and diverse colours in hair dyeing. The colour of compounds obtained from two-monomer polymerizations was more diverse than that from single-monomer polymerizations due to the formation of heteropolymer or homopolymer mixtures. Three kinds of two-monomer combinations, namely gallic acid/syringic acid, catechin/catechol and ferulic acid/syringic acid, generated brown, black and red colourations, respectively, showing commercial value for grey hair dyeing. The catechin/catechol mixture could be particularly useful as an alternative to *p*-phenylenediamine for hair blackening, as both materials are natural polyphenols. The authors indicated that the laccase-catalysed polymerization of natural phenols to produce polymeric hair dyes would be a promising and applicable 'green' technology in the cosmetic industry.

Conclusion and future outlook

The potential of enzyme-based dyeing processes has been demonstrated in this review. Laccase and peroxidase, in particular, are able to catalyse the oxidative transformation or polymerization of various amine or phenolic compounds to generate coloured polymers '*in situ*' to dye fabrics like cotton, flax, wool and hair. The enzymatic colouration takes place at low temperature, neutral pH and without pressure, addition of acid or alkaline products and toxic reagents. Moreover, biological colouration of lignocellulosic fibres allows elimination of the conventional bleaching process that uses alkaline conditions and other chemicals. Consequently, substitution of chemical processes with enzymes holds the promise of simpler, more economic and more environmentally friendly colouration processes. Additional functions, such as antioxidant antimicrobial activity, obtained through the attachment of polymers produced by enzymatic catalysis, can also add value to these products.

The discovery of novel laccases/peroxidases with different substrates specificities to extend the range of accessible colored compounds and discovery of more suitable, less polluting redox mediators remain as future challenges.

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