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Combined ultrasound-laccase assisted bleaching of cotton

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Abstract

This study evaluates the potential of using ultrasound to enhance the bleaching efficiency of laccase enzyme on cotton fabrics. Ultrasound of low intensity (7 W) and relatively short reaction time (30 min) seems to act in a synergistic way with the enzyme in the oxidation/removal of the natural colouring matter of cotton. The increased bleaching effect could be attributed to improved diffusion of the enzyme from the liquid phase to the fibres surface and throughout the textile structure. On the other hand inactivation of the laccase occurred increasing the intensity of the ultrasound. However, at the ultrasound power applied in the bleaching experiments the loss of enzyme activity was not significant enough to justify the use stabilizer such as polyvinyl alcohol. Furthermore, the polyvinyl alcohol appears to be a substrate for the laccase.

Keywords: Laccase; Ultrasound; Cotton; Bleaching

1. Introduction

Laccase (EC 1.10.3.2) is a multi-copper oxidase using a broad range of aromatic compounds as substrates and oxygen as a terminal electron acceptor [1]. Laccases have found various biotechnical and environmental applications, among which colour removal from both liquors and materials (bleaching) is of particular interest [2]. In the preparation technology of cellulose textile fibres, the bleaching process is not only concerned with brightening of the fibres, removing the natural colouring matter, e.g. fats, waxes, pectines, proteins and pigments, but it is directly related to the success of subsequent wet processing operations such as dyeing, printing and finishing. The whitening of the textiles is achieved traditionally at acidic to alkaline conditions, and in a wide temperature range, with different oxidizing agents. The whiteness level aimed in bleaching depends on the end use of the fabrics. When higher whiteness is needed it is necessary to perform a repeated oxidizing treatment. The bleaching chemicals normally are dosed in excess to the fibres, which necessitates repeated washing to remove the residual, harmful to the next processing operations, oxidants. This renders the bleaching process high chemicals, water, energy, and time consuming, discharging environmentally hazardous waste liquors. In a previous work we demonstrated that a short-time laccase pre-treatment enhanced the whiteness of cotton fabrics and reduced significantly the hydrogen peroxide dosage in subsequent chemical bleaching [2]. Enzymatic treatment of textiles involves mass transfer from the enzyme solution across the interior of the textile substrate, but in general, has low diffusion rates and the effect is concentrated on the outer fibres in the yarns [3]. Ultrasound could be a way to improve the diffusion of the enzyme to the interior of the yarns. Ultrasonic energy has been used successfully in conventional processes of desizing, scoring, bleaching, mercerization and dyeing of cotton [3,4]. Combined ultrasound/hydrolytic enzymes (e.g. cellulases, pectinases, amylases) applications provided reduction in the consumption of enzymes, shorter process time, less fibre damage and greater uniformity of the treatment [3,4]. However, data about the effect of ultrasound on the

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stability of oxidative enzymes such as laccases and their bleaching capacity have not been reported so far. The objective of the present research was to study the effect of the ultrasound on the bleaching ability of laccase as an alternative to the conventional chemical bleaching process of cotton.

2. Materials and methods

2.1. Enzyme and enzyme activity

Laccase (EC 1.10.3.2) from *Trametes villosa* (5.3 mg protein/mL) was provided by Novozymes (Bagsvaerd, Denmark). Laccase activity was assayed spectrophotometrically (Helyos γ, Unicam) by measuring the increase of absorbance at 420 nm ($\varepsilon_{420} = 3.6 \times 10^4\ M^{-1}\ cm^{-1}$) due to the oxidation of 0.5×10^{-3} M 2.2′-azinobis(3-ethylbenzthiazoline-6-sulfonate) (ABTS) (from Sigma) by a suitable amount of enzyme in 0.1 M sodium acetate buffer pH 5, at 50 °C. Enzyme activity (U) was defined as μmol of substrate oxidized per min. Lacccase activity at bleaching applications was followed by measuring the oxygen consumption (data acquired every 30 s) as a direct function of the oxidation of the colouring matter in cotton by means of CellOx 325 oxygen sensor, (from WTW GMH & Co. KG) in a thermostated, hermetically sealed vessel.

2.2. Ultrasound equipment

The equipment (Fig. 1) is composed of an electrical generator (Sonics & Materials, USA) with fixed frequency of 20 kHz and power intensity ranging from 7 to 100 W supplied by a piezoelectric transducer with probe diameter 13 mm. The diameter of the thermostated (50 ± 2 °C) glass cell, where all experiments were conducted, was 60 mm and the height was 200 mm. The ultrasound intensity used in this study and the distance between the transducer and the sample were selected according to preliminary experiments (ultrasound with intensity of 7, 30, and 50 W was applied to aluminium foil samples fixed perpendicularly at 0–2 cm from the transducer in acetate buffer pH 5.0 for 30 min) and the data for laccase stability in presence of ultrasound. The optimal distance between the transducer and material surface, providing maximum affected area (about 35%) was 0.5 cm for the intensity power of 7 W. The perpendicular positioning of the sample to the probe was chosen due to the specific application – to improve the diffusion of the biocatalysts towards and throughout the pores of the textile material, while a parallel positioning of the fabric would promote the removal of impurities from the surface [5] and not the biocatalyst/fibre contact.

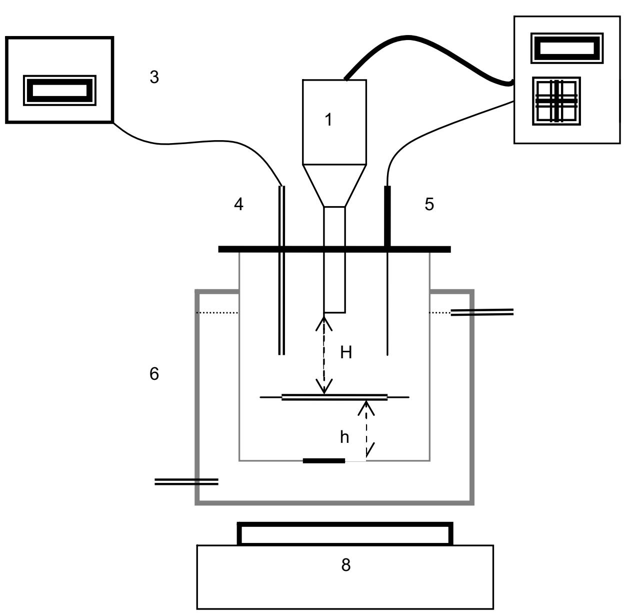

Fig. 1. Experimental set-up: (1) ultrasound probe, (2) ultrasonic generator, (3) oxygen measuring apparatus, (4) oxygen sensor, (5) temperature sensor, (6) thermostated and hermetically sealed vessel, (7) sample, (8) stirring equipment, (H) distance between the sample and the probe and (h) distance from the sample to the bottom of the reaction vessel.

2.3. Stability of laccase in the presence of ultrasound

Laccase solutions (125 mg prot./L) prepared in 0.1 M acetate buffer pH 5 were subjected for up to 40 min to ultrasound with intensity of 7, 30 and 50 W at 20 kHz, and 50 °C. Then the activity of the enzyme was measured against ABTS as described above. The enzyme was further stabilized using 1%, 5% and 10% w/v of high-hydrolyzed grade polyvinyl alcohol (DP. 682–1591 from Sigma).

2.4. Combined laccase/ultrasound assisted bleaching of cotton

The textile substrate used in the experiments was alkali scoured, twill weave, 120 g/cm^2, 100% cotton fabric. Samples of 1 g (60 mm × 60 mm) were fixed perpendicularly to the ultrasound transducer at a distance of 0.5 cm and treated simultaneously with 125 mg prot./L laccase and 7 W, 20 kHz ultrasound in 0.1 M acetate buffer pH 5, at 50 °C for 30 min. The oxygen consumption during the reaction was followed continuously.

The fabrics were bleached chemically afterwards following the recipe: 1.75 g/L Na-silicate, 0.5 g/L Na_2CO_3, 1 g/L NaOH, and 2 g/L 35% H_2O_2 (all reagents are from analytical grade). The bleaching was carried out at 90 °C for 1 h, in Ahiba Spectradye-Datacolor dyeing apparatus at liquor to fabric ratio 20:1. The whiteness index Berger (W*) of the fabrics was determined using a reflectance measuring Datacolor apparatus at standard illuminant D_{65} (LAV/Spec. Excl., d/8, D_{65}/10°).

3. Results and discussion

Most of the physical and chemical effects of ultrasound are due to the cavitation phenomenon, e.g. collapsing of