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Ultrasonic pilot-scale reactor for enzymatic bleaching of cotton fabrics

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ABSTRACT

The potential of ultrasound-assisted technology has been demonstrated by several laboratory scale studies. However, their successful industrial scaling-up is still a challenge due to the limited pilot and commercial sonochemical reactors. In this work, a pilot reactor for laccase-hydrogen peroxide cotton bleaching assisted by ultrasound was scaled-up. For this purpose, an existing dyeing machine was transformed and adapted by including piezoelectric ultrasonic devices. Laboratory experiments demonstrated that both low frequency, high power (22 kHz, 2100 W) and high frequency, low power ultrasounds (850 kHz, 400 W) were required to achieve satisfactory results. Standard half (4 g/L H_2O_2 at 90 °C for 60 min) and optical (8 g/L H_2O_2 at 103 °C for 40 min) cotton bleaching processes were used as references. Two sequential stages were established for cotton bleaching: (1) laccase pretreatment assisted by high frequency ultrasound (850 kHz, 400 W) and (2) bleaching using high power ultrasound (22 kHz, 2100 W). When compared with conventional methods, combined laccase-hydrogen peroxide cotton bleaching with ultrasound energy improved the whitening effectiveness. Subsequently, less energy (temperature) and chemicals (hydrogen peroxide) were needed for cotton bleaching thus resulting in costs reduction. This technology allowed the combination of enzyme and hydrogen peroxide treatment in a continuous process. The developed pilot-scale reactor offers an enhancement of the cotton bleaching process with lower environmental impact as well as a better performance of further finishing operations.

1. Introduction

The purpose of cotton bleaching is to decolorize natural pigments, mainly flavonoids conferring a pure white appearance to the fibres [1,2]. This process is directly related to the success of the subsequent wet processing operations such as dyeing, printing and finishing [3]. Nowadays hydrogen peroxide, due to its biodegradability, almost entirely replaced the conventional chlorine oxidizing chemicals [1]. It is applied at alkaline pH and temperatures closed to boiling, requiring therefore high energy consumption. Radical reactions of bleaching agents with the fibres can lead to a decrease in the polymerization degree and to fiber damage. Moreover, huge amounts of water are needed to remove hydrogen peroxide from fabrics which would cause dyeing difficulties [4]. Thus, more specific processes targeting only colored substances would be advantageous. Enzyme-based systems integrating bleaching of cotton have been developed in order to overcome these concerns and reduce processing costs. Based on the assumption that fungal laccases can oxidize phenolic moieties of lignin in pulp, it has been assumed that these enzymes could also decolorize or eliminate colored flavonoids of cotton attacking phenolic hydroxyl groups. Laccases (EC 1.10.3.2) are multi-copper-containing enzymes capable of oxidizing phenols and aromatic amines, reducing molecular oxygen to water. The reaction involves three types of copper centers with different functions: type 1 (blue copper) catalyzes the electron transfer from the substrate while type 2 and type 3 form a three-member cluster that collectively activate molecular oxygen [5].

Several authors have successfully described the use of laccases on cotton bleaching as a new environmentally friendly technology at laboratory scale [2,3,6–9]. Tzanov et al. reported for the first time the enhancement of the bleaching effect achieved on cotton using laccase. This enzyme applied in short-time batch wise or pad-dry processes prior to conventional bleaching, improved the

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end fabric whiteness. They postulate that the enzyme transforms the cellulose coloring matter in another colored compounds which are more easily susceptible to oxidation with peroxide and thus more easily degraded [9]. The advantages of this system rely on the hydrogen peroxide dosage reduction as well as on the reduced bleaching temperature and time [8].

Considering that enzymatic processes of cotton textiles require transfer of mass from the bulk solution to the fabrics surface, diffusion rates can be improved by mechanical agitation. Since this type of agitation is not very efficient, ultrasounds have been undertaken for the enhancement of mass transfer and speed-up of bleaching reactions [3,6,10–14]. Indeed, the use of ultrasound promotes an improvement on chemical reactivity (higher reaction speed and output, more efficient energy usage, performance improvement of phase transfer and increase in the reactivity of reagents or catalysts) mainly caused by cavitation. This is an acoustic phenomenon which lies in the formation, growth and implosive collapse of bubbles in a liquid. Once formed, small gas bubbles irradiated with ultrasound in a bulk of liquid are grown until it can no longer absorb energy efficiently and cannot sustain itself. When the cavity implodes, an increase of the local temperature and pressure of the surrounding liquid is created. Thus, the cohesion and adhesion forces within the liquid can be overcome. Some studies have identified the formation of high-energy intermediates during this process in aqueous solutions, including $HO_2^{\cdot}$ (superoxide), $H^{\cdot}$ (atomic hydrogen), $OH^{\cdot}$ (hydroxyl), and e- (aq.) (solvated electrons). Therefore, the sonolysis of water produces strong oxidants, such as hydroxyl radicals, capable of causing secondary oxidation reactions [12].

Although the reported effectiveness of the combined laccase-hydrogen peroxide/ultrasounds system on cotton bleaching, the scale-up of this process has not been successfully achieved. The existing conventional designs still do not give substantial efficiency at larger operation scales [15,16], since an intense cavitational activity is obtained very close to the transducers. Moreover, a lack of expertise is required in diverse fields, namely material science, acoustics and chemical engineering for scaling-up successful reactor design and scale-up strategies.

The main proposal of this work was to join the knowledge of experts in several areas, namely ultrasound field, enzymology and industrial engineering to scale-up a laccase-hydrogen peroxide system assisted by ultrasound for cotton bleaching. Standard operational conditions were optimized, namely temperature, processing time and hydrogen peroxide amount. All the process was studied at laboratory scale and further transferred to a pilot sonochemical reactor by adjusting existing dyeing machinery. Ultrasonic devices with different geometry and operational mode of action were tested. The final reactor was designed considering the optimal conditions attained at laboratory scale.

2. Materials, equipment and methods

2.1. Materials

100% of desized woven cotton fabrics and auxiliary products used on cotton bleaching experiments were supported by an industrial company, Acatel (Portugal). Laccase (EC 1.10.3.2) from ascomycete *Myceliophthora thermophila*, Novozym® 51003 (17 g protein/L, 4500 U/mL, at 50 °C), was obtained from Novozymes (Denmark). All the others chemical products were purchased from Sigma Aldrich and Panreac without further purification.

2.2. Equipment

The high frequency experiments were carried out using an ultrasonic power generator type K8 (850 kHz, 120 W) coupled with an ultrasonic high-power bath Type 5/1575 equipped with high-performed ultrasound plan-transmitter, double glass cylinder cooling system, ceramic, stainless construction and Titan-membrane (Fig. 1A). The maximum temperature reached by this equipment is 60 °C. Both equipments were purchased from Meinhardt Ultraschalltechnik (Germany). Low frequency assays were performed using piezoelectric transducers of mono-frequency (22 and 38 kHz) and multi-frequency (40–90 kHz), both with 400 W (Fig. 1B). Also magnetostrictive transducers of 40 kHz and 1400 W were used (Fig. 1C). All the equipment were made with stainless steel and equipped with temperature controlled vessels. One robotic arm was introduced on the ultrasonic systems to promote the agitation of bath solutions.

A prototype jet dyeing machine was adapted for the pilot scale experiments at Centre de Recerca i Innovació de Catalunya, SA – CRIC, Spain. Ultrasounds interact at two different levels, with concurrent effects. During pretreatment, ultrasounds are supposed to

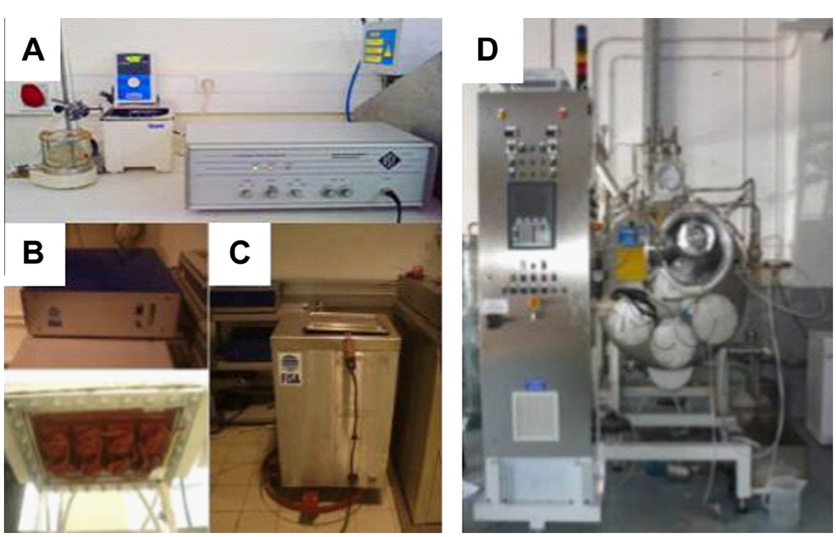

Fig. 1. (A) High frequency ultrasonic device (850 kHz, 120 W); (B) low frequency/high power ultrasonic devices: piezoelectric transducers with ultrasounds power supply (mono-frequency 22 kHz and 38 kHz, multi-frequency 40–90 kHz, 400 W); (C) vessel equipped with magnetostrictive transducers (40 kHz, 1400 W); (D) cotton bleach prototype containing low frequency/high power intensity (22 kHz, 140–2100 W) and high frequency (850 kHz, 400 W) devices.