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# Biobleaching of high quality pulps with laccase mediator system: Influence of treatment time and oxygen supply

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ABSTRACT

In this study we examined the influence of the treatment time and addition of oxygen on the efficiency of a laccase mediator system (L) applied to flax pulp at atmospheric pressure. The redox potential and the dissolved oxygen concentration during L tests are measured. After L stage, an alkaline extraction (E) is carried out. The pulp properties (kappa number, brightness and viscosity) and the effluents properties (color and COD) were measured in order to evaluate the environmental impact of this enzymatic treatment.

The biotreatment involves two distinct stages in both L and LE sequences; in the beginning the pulp exhibits a fast delignification and a slow viscosity decrease that is followed by slow delignification in the second. Pulp brightness changed differently during L stage and LE sequence. Initially brightness after the L stage decreased with respect to the initial pulp; then, it increased rapidly and eventually leveled off. After the LE sequence, brightness increased rapidly in the beginning and more gradually afterwards. The results show that supplying the medium with oxygen and increasing the oxygen concentration in it, influence the kinetics of the process.

Based on CIE L*a*b* color coordinates study, the enzyme treatment not only removes lignin, but also alters the structure of the pulp by causing the formation of chromophoric groups giving color. Such groups are removed in an E stage.



## 1. Introduction

The use of enzymes appears as a promising approach for clean bleaching process. In fact, xylanases have already demonstrated their effectiveness on the biobleaching procedures [1]. Some oxidative enzymes, such laccases, have provided an alternative to xylanases acting directly on lignin. However, this process is not fully developed due to the availability of efficient and stable in industrial conditions enzymes, the high cost and potential toxicity of the mediators and the long reaction times involved [2,3]. Moreover, oxidative enzymes have scarcely been used to bleach non-wood pulp [4–8]; also, most kinetic studies on their effects have focused on the action of laccase mediator systems (LMS) in reactions with lignin model compounds for short times [9,10]. In fact, studies on pulp delignification with LMS have largely failed to examine cellulose degradation via viscosity measurements; also, no COD or color data for the resulting effluents have seemingly been reported previously. Characterizing such effluents is important on account the ability to close circuits in TCF (totally chlorine free) sequences.

Previous studies on the influence of the treatment time with a LMS on the extent of pulp delignification on reactions with lignin model compounds or eucalyptus kraft pulp revealed that the process involves two distinct stages [10–12]. In the initial stage, the pulp is rapidly delignified to a limiting kappa number similarly as in ozone-based treatments [13,14]; in the final stage, delignification is slow but the oxygen uptake continues to be high, which suggests the presence of active chemical species in the system not reacting with residual lignin, but rather interacting with lignin fragments via side reactions [9,10].

Some authors have found raising the oxygen pressure in the reactor to result in increased delignification of the pulp [12,15,16]. Also, using a pressurized reactor was found to result in increased delignification and decreased viscosity in LP flax pulp relative to using the reactants in a flask [7,8]. However, the influence of supplying the medium with oxygen or the dissolved oxygen concentration on flax pulp delignification and optical properties, as well as effluent properties, with a LMS has never to date been studied. An atmospheric delignification system would allow the application of LMS

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system in different points of the bleaching sequence without carrying important changes in the process.

The purpose of this work was to identify and quantify the variables influencing the kinetics of the process with a view to helping optimize industrial biobleaching treatments. Specifically, the performance of a laccase mediator treatment (L) in the biobleaching of flax pulp was examined and the influence of the treatment time and of supplying the medium with oxygen on various properties of the resulting pulp (kappa number, brightness and viscosity) and effluents (color and COD) was studied. The CIE L*a*b* color coordinates were also calculated. The redox potential of the system and the dissolved oxygen concentration were measured, which required designing appropriate equipment for biobleaching at atmospheric pressure.

## 2. Experimental

### 2.1. Raw material

The unbleached flax pulp used was supplied by CELESA mill (Spain) and obtained by soda-anthraquinone (NaOH-AQ) chemical cooking. Before the bleaching study the pulp was acidified in order to remove residual liquor not eliminated by industrial washing and to bring the pulp to the pH required for the L stage. The properties of the washed pulp were 10.1 of kappa number, 35.5%ISO of brightness and 952 mL $g^{-1}$ of viscosity.

### 2.2. Laccase mediator treatment (L)

The enzyme used in this study was laccase from *Trametes villosa* available from Novozymes® (Ref. NS-51002; 0NN002; FS-002). Its initial activity was 47 U $mL^{-1}$ (one activity unit was taken to be the amount of enzyme needed to convert 1 mmol of the substrate ABTS per minute). The mediator used was 1-hydroxybenzotriazole (HBT) from Fluka (Ref. 54802, grade: purum).

Treatments with the laccase mediator system were performed with 10 g of pulp at 1.5%odp consistency in 50 mM sodium tartrate buffer (tartaric acid form Merck, Ref. 818531, for synthesis) at pH 4 containing the surfactant Tween 80 from Sigma (Ref. P1754) at atmospheric pressure. Tests were conducted in tall 1 L beakers at 30 °C and open at the top (i.e. at atmospheric pressure). Fiber suspensions were used to measure redox potentials and dissolved oxygen concentrations. The L stage was applied in three different ways, namely: in the absence of gas (Ls), by bubbling air (Lair) and by bubbling oxygen (Lo) through the medium. The laccase dose was 25 U $g^{-1}$ and the HBT dose 2.6%odp. The treatment time ranged from 0.5 to 30 h. Once treated, the pulp was filtered and residual liquor collected for subsequent analysis.

### 2.3. Alkaline extraction stage (E)

The L samples were subjected to an alkaline extraction stage in an Easydye AHIBA oscillating individual reactor from Datacolor. Treatments were done on 5 g of pulp at 5%odp consistency. The operating conditions were: 1.5%odp NaOH from Panreac (Ref. 211687, QP), 90 °C and 120 min.

### 2.4. Pulp and effluent properties

The pulp samples from L and LE sequences were characterized for brightness, kappa number and viscosity according to the applicable ISO standards, ISO 2470, ISO 302 and ISO 5351-1, respectively. Determinations also included CIE L*a*b* color coordinates. The effluents from the L stage were characterized for color and COD in accordance with ASTM D1252-00 and ASTM D1209-00, respectively. All chemicals reagents were of analytical grade from Panreac and Merck.

## 3. Results and discussion

### 3.1. Dissolved oxygen concentration

The variation of the dissolved oxygen concentration during the tests involving the addition of air (Lair) and no gas (Ls) was measured (data not shown). The oxygen concentration in the Lo test exceeded 20 ppm, which was beyond the measuring range of our oxygen meter. The oxygen concentration in Ls was 7 ppm prior to addition of the reagents, but immediately started to fall and reached 4 ppm after 40 min of treatment; beyond that point, the oxygen concentration rose to 5.5 ppm at 5 h and 6.7 ppm at 24 h. The initial oxygen concentration in Lair was 7.5 ppm; after the reagents were added, it decreased to 7 ppm, where it leveled off. Then, it rose to 8.5 ppm at 4 h and leveled off until the end of the test (9 h). The more oxygen is supplied to a medium, the higher is the dissolved oxygen concentration to be expected. The oxygen concentration measured during the treatments was found to depend on the way the gas was supplied and changed with time. Thus, in Ls and Lair, the oxygen concentration decreased from its initial value over the first few minutes of reaction and then increased to a constant level that was reached after 4 h of treatment.

### 3.2. Variation of the kappa number

No significant differences between treatments were observed during the first 3 h in kappa number after L stage (Fig. 1). At longer times, however, delignification was higher by 3–11% with Lair than with no gas (Ls). The differences between Lair and Lo were less substantial and in favour of the latter. The smallest kappa number obtained with L stage was 6.0, which corresponded to 41% delignification and was provided by Lo at the longest treatment time studied (30 h).

In LE sequence, the kappa number decreased with respect to the initial pulp from the beginning. The effect was similar to that of the L stage alone: rapid delignification during the first 5 h of treatment, by up to 40% within the first 30 min (Fig. 1), and then slower delignification to a limiting kappa number. The smallest kappa number obtained with LE sequence was 3.1, which corresponded to 70% delignification and was provided by Lo at 30 h (the longest treat-

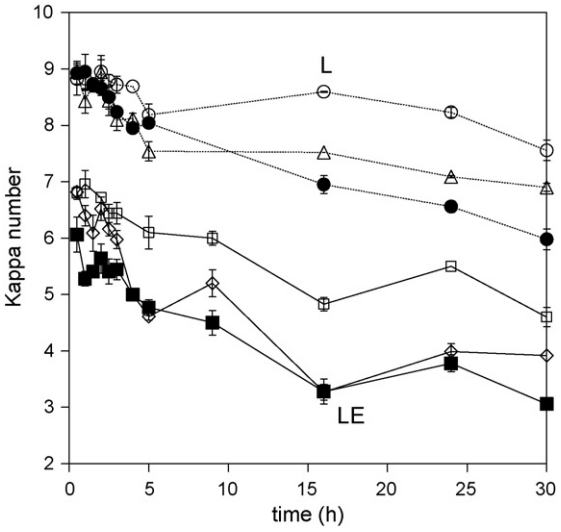


**Fig. 1.** Kappa number in the LsE, LairE and LoE treatments. In the figure, Ls (○), Lair (△), Lo (●), LsE (□), LairE (◊) and LoE (■).