

Biobleaching in dissolving pulp production

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SUMMARY

The biobleachability of industrial sulphite pulp from a dissolving pulp producing mill was studied using two strains of the white-rot fungus *Ceriporiopsis subvermispora* and the xylanase preparation from the yeast *Aureobasidium pullulans* Y-2311-1. It was found that the fungus can brighten the pulp very effectively, thus eliminating the need of a second chlorine dioxide stage during ECF-bleaching in sequence OD₂E₂D₂H₂; however, some cellulose degradation also occurred. On the other hand, pretreatment of pulp with xylanase and subsequent bleaching with reduced amounts of active chlorine resulted in improved pulp properties such as brightness, pentosan content and α -cellulose.

INTRODUCTION

Biobleaching of pulps is performed with either hemicellulolytic enzymes, in particular xylanases (1) or lignin-degrading fungi and their enzymes (2), while xylanases hydrolyze hemicellulose (xylan) in pulp thereby enabling the bleaching chemicals an easier access to lignin (3), white-rot fungi and their ligninolytic enzymes directly attack and depolymerize lignin in pulp (4). However, in both cases the aim is to enhance delignification and therefore facilitate the subsequent bleaching of pulp by applying reduced amounts of bleaching chemicals, especially chlorine and chlorine-containing compounds (5). Here we report on the use of the white-rot fungus *Ceriporiopsis subvermispora* and xylanases from the yeast *Aureobasidium pullulans* in biobleaching of sulphite pulps for dissolving pulp production (6).

MATERIALS AND METHODS

Unbleached sulphite pulp produced from *Eucalyptus grandis* wood was obtained from SAPPI SAICCOR (Pty.) Ltd., South Africa. The fungus *C. subvermispora* (strains L-14807 SS-3 and CZ-3) was obtained from the Forest Products Laboratory, Madison, WI, USA and maintained on PDA slants at 4°C. Plate PDA cultures were inoculated from these slants and incubated at 27°C and 65% relative humidity for 10 days (7). Fungal treatment of pulp (80% w/w moisture content) was carried out in a static-bed bioreactor with liquid inoculum preparation of *C. subvermispora* (0.1% on a dry weight basis) for 14 days at 27°C and a specific aeration rate of 0.05 L.L⁻¹ min⁻¹ (7). The maintenance of *A. pullulans* NRRL Y-2311-1, inocula preparation, enzyme production and preparation were carried out as reported before (8). One unit of xylanase activity, determined by the release of reducing sugars from oat spelts xylan (8), was defined as that amount of enzyme which catalyzes the release of 1 micromole of xylose equivalents per min. Enzyme treatment of pulp was performed with 15 IU xylanase/g dry pulp at a temperature of 55°C, pH of 4.7 (50 mM sodium acetate buffer) and a pulp consistency of 9% for 1 h. Reducing sugars of pulp filtrates were determined spectrophotometrically

according to the Somogyi-Nelson method (9,10). Chemical bleaching of pulp was accomplished in sequence OD₁E₀D₂H. The bleaching conditions are presented in Table 1. After each treatment step pulp was thoroughly washed until neutral pH of wash waters. Pulp properties were measured according to TAPPI Test Methods (pentosan content: T223 cm-84; kappa number: T236 cm-85; brightness: T452 om-87; α -cellulose: T203 om-88).

Table 1. Conditions for chemical bleaching of sulphite pulp in sequence OD₁E₀D₂H

Stage	Consistency (% w/w)	Temperature (°C)	Time (min)	pH	Charge on pulp
O	11	100	60	11	1.5% NaOH + 0.8% O ₂
D ₁	10	65	40	2.4	1.1% act.Cl or less
E ₀	11	100	140	12	4% NaOH + 0.8% O ₂
D ₂	11	65	180	4	0.6% act.Cl or less
H	12	55	120	12	0.65% act.Cl

RESULTS AND DISCUSSION

Sulphite pulp was bleached effectively with the two strains of *C. subvermispota* (Table 2). Strain SS-3 was able to remove 85% of lignin (as kappa number), whereas CZ-3 reduced lignin by 88%. In terms of pentosan removal from pulp, strain SS-3 was more successful (13%) than strain CZ-3 (5%). Brightness of fungus-treated samples increased by 42% (strain SS-3) and 47% (strain CZ-3), respectively, compared to the control samples. However, the α -cellulose content was reduced by 5 (SS-3) and 4 (CZ-3) points. When *A. pullulans* xylanase preparation was used, the pentosan content was lowered by 13% and α -cellulose enriched by 1 point, respectively, after 1 h of enzyme treatment with 15 IU xylanase/g pulp. At the same time, the impact of xylanase treatment on brightness and kappa number was insignificant (Table 2).

Bleaching of fungus- and xylanase-treated pulp was carried out in sequence OD₁E₀D₂H with reduced (at D₁ and D₂ stages) amounts (0-63%) of active chlorine (Table 3). Results indicated that brightness of dissolving pulp pretreated with *C. subvermispota* strains was superior to the brightness of the xylanase-pretreated dissolving pulp and the reference of dissolving pulp, obtained without biotreatments. Even the elimination of the second chlorine dioxide stage (63% reduction of total active chlorine) did not reduce the brightness values, thus indicating that the charge reduction of total active chlorine within a certain range does not exert a direct influence on the final brightness of the fungus-pretreated dissolving pulp. Also, no correlation could be observed between the reduction of active chlorine on one hand, and α -cellulose or pentosan content, on the other. Apparently, more lignin has been solubilized and removed during bleaching of pulp, pretreated with strain SS-3 than CZ-3. Although strain CZ-3 bleached sulphite pulp to a greater extent than SS-3 strain (Table 2), chemical bleaching of these samples produced just the opposite effect: brightness of SS-3-pretreated dissolving pulp was higher than that of CZ-3-pretreated dissolving pulp (Table 3). This might reflect the differences in the penetration and oxidation capabilities of the lignin-degrading enzymes (or their low molecular weight active compounds which may be responsible for lignin oxidation), secreted by both strains: ligninases of SS-3 strain may be more capable of attacking and depolymerizing lignin localized in the secondary cell wall of pulp fibres than CZ-3-secreted enzymes. Thus, the accessibility of lignin from the inner parts of the cell wall to the bleaching chemicals and lignin diffusability out of the fibres would be greater when sulphite pulp is pretreated with the SS-3 strain of *C. subvermispota*. Strain CZ-3 proved to be more selective in lignin removal than strain SS-3 (Tables 2,3). More appreciable carbohydrate (cellulose and hemicellulose) degradation of pulp was observed with strain SS-3 than CZ-3 before (Table 2) as well as after chemical bleaching (Table 3). This suggests that cellulases and hemicellulases

Table 2. Treatment of sulphite pulp with *C. subvermispota* (strains SS-3 and CZ-3) and *A. pullulans* xylanases

Pulp treatment	Kappa number	α -Cellulose (%) (w/w)	Pentosan content (%) (w/w)	Brightness (% ISO)
Sulphite pulp (control)	6.7	89.9		56.0
SS-3-treated	1.0	84.9	3.4	79.4
CZ-3-treated	0.8	86.0	3.7	82.2
Xylanase-treated	6.5	90.7	3.4	56.5

of strain SS-3 were more active on sulphite pulp than those of CZ-3. Hence, the α -cellulose and pentosan content of SS-3-treated and bleached pulp were lower by up to 3 points and 19%, respectively, than that of CZ-3-pretreated dissolving pulp.

Table 3. Biobleaching of sulphite pulp with *C. subvermispota* (strains SS-3 and CZ-3) or *A. pullulans* xylanases and reduced amounts of active chlorine in sequence OD₂E₀D₂H

Pulp treatment	% Total act.Cl reduction	α -Cellulose (%) (w/w)	Pentosan content (%) (w/w)	Brightness (% ISO)
SS-3-treated	0	85.9	1.8	94.0
	13	86.1	1.7	93.1
	23	85.5	1.8	93.7
	37	85.9	1.7	93.9
	63	87.1	1.8	93.3
CZ-3-treated	0	88.3	2.1	92.5
	13	88.3	2.1	92.3
	23	88.5	2.0	92.1
	37	88.8	1.9	92.2
	63	88.5	2.0	93.3
Xylanase-treated	0	92.4	1.9	88.5
	13	92.2	1.7	88.4
	23	92.2	1.8	89.6
	37	92.1	1.8	88.3
Control	0	91.6	2.4	87.5

Biobleaching of sulphite pulp with *A. pullulans* xylanases and chemicals in sequence OD₂E₀D₂H resulted in production of a dissolving pulp having the highest α -cellulose content (92.1-92.4%) as related to the control (91.6%) and the fungus-pretreated dissolving pulp (85.9-88.8%, Table 3). This is indicative for the high selectivity of xylanolytic enzymes of *A. pullulans* in hydrolyzing only the hemicelluloses (mostly xylan) in pulp (8) as well as for the lack of cellulase activities in the crude enzyme preparation (11). The enzyme pretreatment

of pulp contributed about 72% to the total release of reducing sugars during bleaching, with the latter being approximately 4 times greater than that released from the untreated control (Table 4). Pentosans of xylanase pretreated dissolving pulp were reduced by 25-29% when pulp was bleached with 13-37% less active chlorine than the control of enzymatically untreated dissolving pulp (Table 3). Therefore, the amount of pentosans removed from unbleached pulp by the xylanase treatment (13%, Table 2) was doubled after bleaching (Table 3). Brightness was also improved over the control by 1-2 points, in accordance with previously reported results (12).

Table 4. Reducing sugars released from xylanase (X) treated sulphite pulp during biobleaching in sequence XOD₁E₀D₂H

Pulp treatment	Reducing sugars (mg/100 g pulp)						Total
	X	O	D ₁	E ₀	D ₂	H	
Xylanase-treated	276	24	34	33	11	4	382
Control	0	23	31	29	10	3	96

Thus, pretreatment of sulphite pulp with the white-rot fungus *C. subvermispora* followed by ODE₀D₂H-sequenced ECF-bleaching (with up to 63% reduction of total act.Cl) could produce dissolving pulp with superior brightness. However, cellulose degradation also occurred, causing a decrease in the α -cellulose characteristics under the required level for dissolving pulp production. This detrimental effect can be minimized by optimizing fungal pretreatments in the near future. On the other hand, dissolving pulp, pretreated with *A. pullulans* xylanases and bleached with up to 37% less active chlorine, had improved properties such as brightness, pentosan and α -cellulose content, compared with the control. Biobleaching of sulphite pulps thus looks promising for the manufacture of dissolving pulp with an improved quality and this process may also reduce the toxicity of the bleach plant effluents.

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