Reduction In Chlorine Dioxide Consumption By Xylanase During ECF Bleaching Of Mixed Hardwood Kraft Pulp

Kumar Shiv, Kumar Satish, Sharma Chhaya, Kumar Parveen

ABSTRACT

The potential of commercial xylanase was evaluated in bleaching of mixed hardwood kraft pulp. Xylanase acts on hemicelluloses, releases chromophores and reduces sugars from the pulp. Non oxygen and oxygen delignified mixed hardwood kraft pulps, pre-treated with enzymes, gave chlorine dioxide savings of up to 10% at target brightness 85% ISO.

Key words: *Bio-bleaching, ECF bleaching, xylanase, chlorine dioxide, brightness.*

Introduction

The pulp bleaching plant, which is the most contaminating section in the paper manufacturing process, has gone through a number of changes which cause adverse impact on environment. In this, xylanase has played a crucial role in pulping and bleaching processes (Herpoel *et al.*, 2002; Roncero *et al.*, 2000, 2003) to control the production of various toxic pollutants. Xylanase pre-treatment facilitates subsequent chemical bleaching and reduces the bleach chemical demand without affecting the target brightness of the pulp was reported first time by Viikari *et al.* (1986) and this is considered to be the main benefit of this finding. One of the most successful applications has been the use of xylanase as a pre-treatment for chlorine dioxide bleaching sequences. Based on numerous laboratory experiments (Pedersen *et al.,* 1991), Skerker *et al.* (1991) and mill studies by Senior *et al.* (1992), it is now well established that pre-treatment of kraft pulps with xylanase significantly enhances the bleachability of these pulps in chlorine-based bleaching sequences such as ODED and DED. The most significant bleaching benefits found from xylanase pre-treatment include higher pulp brightness, reduction in the amount of bleaching chemicals needed to achieve target brightness, and reduced amount of organo-chlorine compounds in bleach plant effluents.

Department of Paper Technology, IIT Roorkee, Saharanpur Campus, Saharanpur - 247001, U.P., India.

Table 1: Oxygen delignification conditions.

Parameter	Oxygen stage
Oxygen pressure (kg/cm^2)	6
Temperature (^{0}C)	100
Consistency (%)	10
Retention time (min.)	75
Alkali charge (%)	1.2
Magnesium sulphate (%)	0.2
Kappa No. (Initial)	15
Kappa No. (Final)	8

Table 2: Enzyme pretreatment conditions.

Parameter	Enzyme Stage (X)
pH	6.5
Temperature (^{0}C)	50-55
Consistency (%)	10
Retention time (min.)	120
Dose (IU/g)	16
Buffer	Sodium citrate 0.5M

The pre-treatment of kraft pulps with xylanase followed by high chlorine dioxide substitution or complete replacement in the early stages of pulp bleaching provides a facile method of addressing current environmental concerns. Nonetheless, it remains uncertain if these practices will be acceptable in the future as more stringent environmental regulations are drafted. In response to these environmental concerns, a variety of non-chlorine bleaching procedures are being investigated.

Materials and methods

Pulps

Mixed hardwood kraft (Eucalyptus & Poplar) pulp was obtained from a nearby paper mill and prior to use, pulp was screened and thoroughly washed with water until a neutral pH of the wash water was attained. Washed pulp was analysed for kappa number (using the Tappi Test Methods, 1998) and the brightness of finally bleached pulps were determined with an TECHNIBRITE ERIC 950, Technibrite Corporation, USA. The washed unbleached pulp was oxygen delignified as pre-treatment conditions given in Table 1. Oxygen delignified and non oxygen pulps both were used for chlorine dioxide bleaching.

Xylanase enzyme characterisat - ion

A liquid xylanase enzyme preparation (Aquabrite, Star Enterprises, Meerut, U.P., India.) was taken. Pre-treatment optimisation for pH, temperature and stability for the xylanase were conducted as described by Singh *et al.* (2000). Xylanase activity was determined using citrate buffer (pH 6.5), at 55 ^{0}C for 2h. The activity of xylanase enzyme (466.81 IU/ml) was determined by estimating the release of reducing sugars according to Bailey *et al.* (1992), incubating the diluted

Table 3: Bleaching conditions for DED bleaching stage*

Parameters	Sequence		
	D_1*	E*	D_2*
Temperature (^{0}C)	70	70	70
Consistency (%)	10	10	10
Retention time (min.)	180	90	180
pH	3-4	11	3-4

*D_1, chlorine dioxide; E, alkali extraction; D_2, chlorine dioxide.

xylanase enzyme at pH 6.5 and at 55 ^{0}C with 1% oat spelts xylan (Sigma, Aldrich chemical corporation, Inc.). One unit of xylanase activity is defined as the amount of enzyme that catalyses the release of 1 μmol xylose equivalents per min of reaction.

Xylanase treatment of pulp

Pulp sample (70 g dry weight) was treated with enzyme (16 IU/g) as per treatment conditions given in Table 2. After completion of reaction, the pulp was filtered and filtrate was analysed for the release of chromophoric material spectrophotometrically at 465 nm in terms of reducing sugars by dinitroslicylic acid method (Miller *et al.*, 1959).

Bleaching chemicals preparation
Materials

Chlorine dioxide was produced *in situ* from sodium chlorite ($NaClO_2$). NaOH solution was used for alkaline extraction of pulp.

Analytical methods

The analysis of bleach liquor and residuals were carried out according to standard procedure. The following standard analytical procedures were used: kappa number of pulp - Tappi T 236, disintegration of chemical pulps for testing SCAN C 18 : 65, forming hand sheets for physical testing of pulp SCAN C 26 : 76, brightness of pulp ISO Standard 2469, preparation of indicators and standard solutions T 610 om-87.

Chemical bleaching of pulp

The four pulp samples viz. untreated, enzyme pre-treated, oxygen delignified and oxygen delignified enzyme pre-treated pulps were further bleached in a multistage elemental chlorine-free (ECF) bleaching process using a chlorine dioxide (D), alkali extraction (E), chlorine dioxide (D) treatment sequence under the treatment conditions summarised in (Table 3) .

Table 4: Brightness of xylanase pre-treated and untreated oxygen delignified and non oxygen bleached pulp.

S. No.	Parameter	Bleaching Sequences			
		DED	XDED	ODED	OXDED
1.	Brightness (% ISO)	84.9	85.2	85.2	85.1
2.	Enzyme dose (IU/g)	-	16	-	12
3.	Chlorine dioxide (ClO_2) charge (kg/t)	45	40.5	23.2	21.6

Results
Enzyme characteristics

The crude xylanase retained 100% activity i.e. 466.81 IU/ml, after incubation at 55 ^{0}C for 2 h. The optimum temperature and pH of the enzyme was 55 ^{0}C and 6.5, respectively (Table 6).

Brightness boost

The xylanase enzyme was efficient in improving the final pulp brightness of mixed hard wood kraft pulp by 2-3 points at an enzyme dose of 16 IU/g (Table 4).

Reduction in chlorine dioxide consumption

The xylanase was effective on both the pulps oxygen and non oxygen mixed hardwood kraft pulp (Table 5). Xylanase reduced the chlorine dioxide consumption on non oxygen mixed hardwood kraft pulp by 4.5 kg/t pulp at brightness of 85% ISO. Similarly, xylanase decreased the chlorine dioxide dose on oxygen delignified pulp by 1.6 kg/t at the same pulp brightness.

Table 5: Chlorine dioxide charge of enzyme pre-treated and control bleaching sequences

S. No.	Bleaching Sequence	Chlorine dioxides (kg/t)	AOX (kg/t)
1.	DED	45	0.94
2.	XDED	40.5	0.69
3.	ODED	23.2	0.40
4.	OXDED	21.6	0.30

Table 6: Optimization of pH for xylanase enzyme (16 IU/g)s

S. No.	pH	Reducing sugars (mg/g)
1.	4.5	13.41
2.	5.5	14.75
3.	6.5	19.0
4.	7.5	17.33
5.	8.5	12.58
6.	9.5	6.31

Discussion

The use of xylanases constitute a very important technological improvement and enhances the bleaching effect of chemical reagents, thereby affording substantial savings and, more important it reduces the production of pollutants during bleaching process (Amin, 2006; Roncero *et al.*, 2005) by decreasing the bleach chemical consumption. In the present enzyme pre-bleaching study which is performed on non oxygen and oxygen delignified mixed hardwood kraft pulps; it has been observed that after enzyme pre-bleaching, chlorine dioxide consumption decreased in bleaching sequences. This suggests that the decrease of the chlorine dioxide consumption during bio-bleaching with xylanase is dependent on the particular pulp type used. Various researches on xylanases and their use in pulp bleaching support the feasibility of their industrial application (Bajpai, 2004; Popovici *et al.*, 2004). Pretreatment of kraft pulp with xylanase enzyme prior to bleaching produced savings of chlorine dioxide of 4.5kg/t and 1.6kg/t of pulp in DED and ODED respectively.

Conclusions

Xylanase preparations used in this study have shown potential in bleach boosting and reducing the consumption of chlorine dioxide in ECF bleaching sequence. It has been demonstrated that the use of enzymes for pulp bleaching could enhance pulp brightness or alternatively decrease the amounts of bleaching chemicals consumed during the bleaching sequence. This has also reduced the amount of adsorbable organic halogens (AOX) and in chloro-organic compounds of the bleach waste-waters to alleviate the environmental impact of the industry.

References

1. Amin H.M., "Extended usage of xylanase enzyme to enhance the bleaching of softwood kraft pulp", Tappi Journal, Vol. 5 (1); (2326p), 2006.
2. Bailey M.J., Biely P. and Poutanen K., "Interlaboratory testing of methods for assay of xylanase activity", Journal of Biotechnology, Vol. 23; (257 270p), 1992.
3. Bajpai P., "Biological bleaching of chemical pulps", Critical Reviews in Biotechnology, Vol. 24: (158p), 2004.
4. Bajpai P., Bhardwaj N.K. and Bajpai P.K., "The impact of xylanases on bleaching of eucalyptus Kraft pulp", Journal of Biotechnology, Vol. 38; (16p), 1994.
5. Christov L.P. and Prior B.A., "Research in biotechnology for the pulp and paper industry in South Africa", South African Journal of Science, Vol. 94; (195200p), 1998.
6. Herpoel I., Jeller H., Fang G., Petit-Conil M., Bourbonnais R., Robert J.L., Asther M. and Sigoillot J.C., "Efficient enzymatic delignification of wheat straw pulp by a sequential xylanase-laccase mediator treatment", Journal of

Pulp and Paper Science, Vol. 28; (6771p), 2002.
7. Miller G.L., "Use of dinitrosalicylic acid reagent for determination of reducing sugar", Analytical Chemistry, Vol. 31; (426428), 1959.
8. Pedersen L.S., Elm D.D., Nissen A.M. and Chorea P.P., "Bleach boosting of kraft pulp using alkaline hemicellulases", Proceedings of the International Pulp and Bleaching Conference, Stockholm, Sweden, Vol. 2; (107-121p), 1991.
9. Roncero M.B., Torres A.L., Colom J.F. and Vidal T., "Effects of a xylanase treatment on fibre morphology in totally chlorine-free bleaching (TCF) of Eucalyptus pulp", Process Biochemistry, Vol. 36; (4550p), 2000.
10. Roncero M.B., Torres A.L., Colom J.F. and Vidal T., "Effect of xylanase on ozone bleaching kinetics and properties of eucalyptus kraft pulp", Journal of Chemical Technology and Biotechnology, Vol. 78; (10231031p), 2003.
11. Roncero M.B., Torres A.L., Colom J.F. and Vidal T., "The effect of xylanase on lignocellulosic components during the bleaching of wood pulps", Bioresources Technology, Vol. 96; (2130p), 2005.
12. Skerker P.S., Farrell R.L. and Chang H.M., "Chlorine-free bleaching with Catazyme TM HS treatment", Proceedings of the International Pulp and Bleaching Conference, Stockholm, Sweden, Vol. 2; (93-105p), 1991.
13. Senior D.J. and Hamilton J., "Biobleaching with xylanases brings biotechnology to reality", Pulp Paper, September; (111-114p), 1992.
14. Singh S., Pillay B. and Prior B.A., "Thermal stability of β-xylanases produced by different *Thermomyces lanuginosus* strains", Enzyme Microbiology and Technology, Vol. 26; (502508p), 2000.
15. Viikari L., Ranua M., Kantelinen A., Linko M. and Sundquist J., Proceedings 3rd International Conference of Biotechnology in the Pulp and Paper Industry, Stockolm, (6769p), 1986.
16. Popovici C., Messier M., Thibault L. and Charron D., "Multiples avantages du xylanase dans une usine nexfor papiers fraser de pâte kraft de feuillus", Pulp and Paper Canada, Vol. 105; (78281p), 2004.