Improvements in ECF bleaching: Use of activated oxygen species and xylanase

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ABSTRACT

Softwood and hardwood kraft pulps were pretreated with xylanase followed by treatment with hydrogen peroxide, dimethyidioxirane (DMD), or hydrogen peroxide reinforced with nitrilamine (Pnt). The resulting pulps were then further bleached with a DEDED sequence. Bleaching studies demonstrated that activated peroxide in the form of DMD or Pnt was an effective method of reducing the total applied charge of chlorine dioxide while still achieving 90+ ISO brightness values.

Application:

This paper gives preliminary results on studies of enzymes and peroxide agents as alternative ECF bleaching protocols to further reduce AOX.

CHANGES IN PUBLIC POLICY *(1)* and new market demands *(2, 3)* have increased the interest in developing low-effluent adsorbable organic halide (AOX) bleaching technologies for kraft pulps. In response to these demands, a variety of new pulping and bleaching technologies are being studied *(4–13)*. Despite these advances, there remains a need to develop alternative bleaching protocols that could further reduce the levels of AOX generated from modern chlorine dioxide–based bleaching sequences. We recently reported that xylanase pretreatments were an effective method of improving the bleaching properties of several nonchlorine-based bleaching agents, including dimethyidioxirane *(14)* and ozone *(15)*. In this report, we have examined the bleaching interactions between xylanase, peroxide-based bleaching agents, and chlorine dioxide for softwood and hardwood kraft pulps.

EXPERIMENTAL

Materials

Oxone™ ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), 30% hydrogen peroxide, nitrilamine, acetone, aqueous H_2SO_4, NaOH, and $NaHCO_3$ were purchased from Aldrich and used as received. Conventional kraft pulps were prepared in the laboratory from an Eastern Canadian wood source (hardwood kraft pulp: kappa no. 18.0 and viscosity 49.5 cp; softwood kraft pulp: kappa no. 27.4 and viscosity 37.0 cp).

Cellulase-free xylanases, prepared by Primalco Biotech Ltd. and ICI Canada Inc., were used for all enzymatic treatments. The microbial source for the enzyme was *Streptomyces lividans* [plAF 20] for the DMD studies and Ecopulp® X-200 for the nitrilamine and hydrogen peroxide studies.

Xylanase and control treatments

Xylanase treatments (X-stage) and control treatments (W-stage) were performed following literature procedures *(14, 15)*.

DMD pretreatment (I-stage)

Pulp was bleached with a 0.7% charge of DMD (0.10 N DMD acetone solution) following literature procedures *(16–18)*. [Note: All studies were performed following standard laboratory practices for handling peroxides *(19)*.]

Nitrilamine-activated peroxide treatment (Pnt-stage)

Pulp samples were bleached with a 0.9% charge of NaOH, 0.7% charge hydrogen peroxide, and 0.2% nitrilamine following Sturm's procedure.

Hydrogen peroxide treatment

The P-stage was executed in the same manner as the Pnt-stage except that the nitrilamine was omitted.

Chlorine dioxide and caustic extraction stages

Standard literature procedures *(8)* were used for all D- and E-stage bleaching treatments. The kappa factors are listed in Table I *(20)*. All brightness values, kappa numbers, and viscosity measurements of the pulp were determined using standard TAPPI and CPPA methods.

RESULTS AND DISCUSSION

Xylanase/activated peroxide bleaching

Although the benefits of xylanase pretreatment for chlorine dioxide bleaching of kraft pulps are now well established, their application for oxygen-based bleaching protocols is still undergoing active investigation. Studies by Eriksson *(21)*, Joyce *(22)*, and others *(23)* have clearly highlighted the potential benefits of xylanase pretreatments for ozone and hydrogen peroxide–based bleaching sequences. This report summarizes our preliminary studies directed at evaluating the interactions between xylanase and two novel peroxide agents, dimethyidioxirane (DMD) and isoureaperoxide. The chemical pathways by which these reagents are generated are summarized below. The DMD generation mechanism is as follows *(24)*:

[SEE PAGE 234 FOR EQUATION 1]

The proposed iso-ureaperoxide generation mechanism is as follows *(25)*:

[SEE PAGE 234 FOR EQUATION 2]

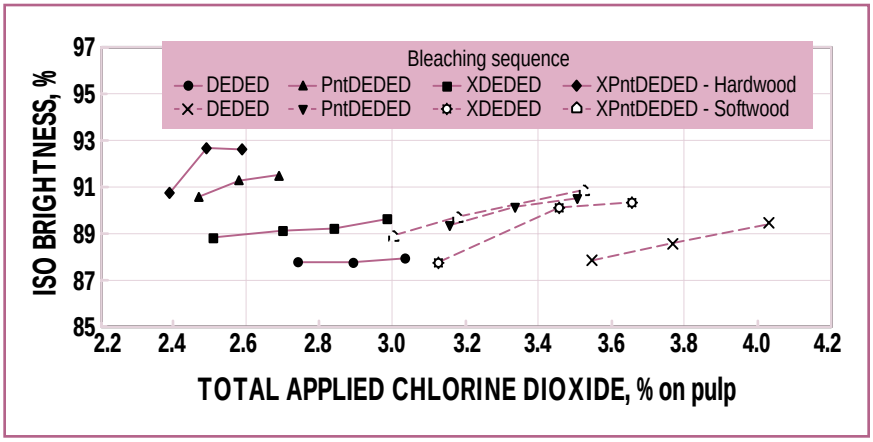
Both of these oxidative bleaching agents have been shown to exhibit improved bleaching properties over hydrogen peroxide *(24, 26–30)*.

The bioboosting interactions between xylanase and DMD-activated peroxide reagents were examined using softwood and hardwood kraft pulps. Pulp samples were pretreated with xylanase following well-established literature procedures *(8–10)*. As a control, a second series of pulps were treated in an analogous manner, except that the enzyme was omitted. The resulting pulps were then bleached with a 0.7% charge of dimethyidioxirane or its molecular equivalent of hydrogen peroxide or hydrogen peroxide/nitrilamine. The results of these bleaching studies are summarized in Table II.

KAPPA FACTOR

Pretreatment	Softwood	Hardwood
Control	0.18, 0.20, 0.23	0.16, 0.18, 0.20
Pnt, I, P	0.18, 0.20, 0.22	0.16, 0.18, 0.20
X	0.15, 0.18, 0.20	0.13, 0.16, 0.18, 0.20
XI, X(Pnt), XP	0.16, 0.18, 0.20	0.16, 0.18, 0.20

I. Kappa factor (20) used for bleaching softwood and hardwood kraft pulps



1. Effects of xylanase and nitrilamine-reinforced hydrogen peroxide treatments on DEDED bleaching properties for hardwood and softwood kraft pulps

The bleaching results for DMD were reported after an alkaline extraction stage since the I-stage is performed at neutral pH, whereas the P- and Pnt-stages are performed under alkaline conditions. Analysis of the bleaching data from various xylanase/peroxide treatments indicates that the enzyme-treated hardwood pulps responded more favorably to either the I- or Pnt-stages than the softwood pulps. Interestingly, the xylanase pretreatment prior to peroxide bleaching was beneficial to both the hardwood and softwood kraft pulps. A comparison of the bleaching results for WIE vs. W(Pnt) for the softwood and hardwood kraft pulps suggests that the bleaching efficiency of these two agents at low charges is comparable. Indeed, in the case of the softwood kraft pulp, it appears that the nitrilamine/peroxide treatment was slightly more effective at delignifying the kraft pulp at these relatively low peroxide charges.

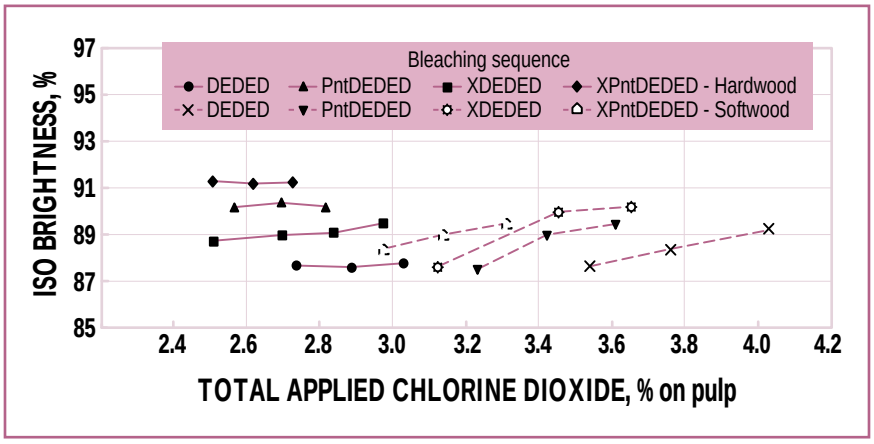
To explore the bleachability of these pulps, each sample was subsequently treated with a DEDED bleach sequence. The kappa factor for the D_{100} stage ranged from 0.13 to 0.23, depending on the pulp; these values are summarized in Table I. The D_1 stage featured a 1.2% charge of chlorine-free chlorine dioxide while the final D_2 stage had a 0.2% charge of chlorine dioxide for the softwood pulps and 0.4% for the hardwood pulps. The brightness results for the xylanase/nitrilamine-reinforced peroxide studies are summarized in Fig. 1.

An examination of these results indicates that the enzymatic pretreatment, combined with the Pnt-stage, significantly raises the brightness ceiling of the pulps. For target brightness values of 89% ISO, the use of XI reduces the totally applied chlorine dioxide (TAC) stage by approximately 15–23%, and even greater reductions were observed at 90% ISO brightness values. A comparison of the nitrilamine-reinforced bleaching studies with the hydrogen peroxide bleaching experiments, summarized in Fig. 2, further illustrates the benefits of activating hydrogen peroxide with nitrilamine. For both the hardwood and softwood kraft pulps, the X(Pnt) DEDED bleaching sequence yielded higher brightness pulps while reducing the TAC used.

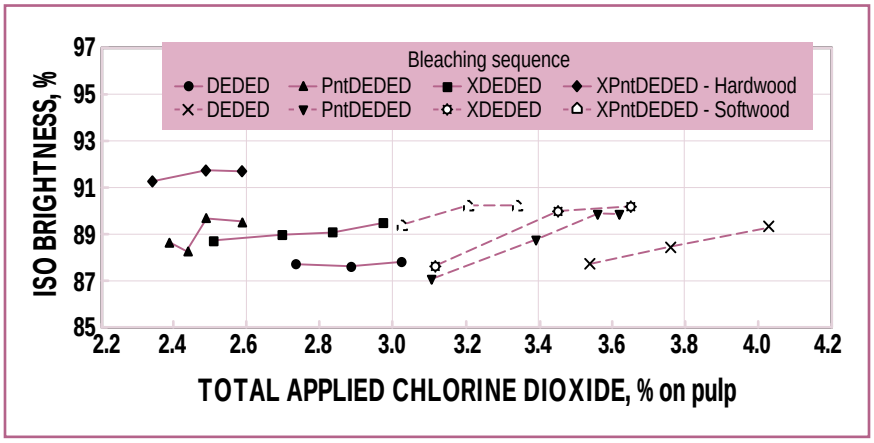
The DMD-treated pulps also afforded higher brightness values at reduced TAC than comparable peroxide-bleached pulps, as shown in

Treatment	HARDWOOD Brightness, % ISO	HARDWOOD Kappa no.	HARDWOOD Viscosity, cp	SOFTWOOD Brightness, % ISO	SOFTWOOD Kappa no.	SOFTWOOD Viscosity, cp
W	34.7	18.0	49.5	29.7	27.4	37.0
X	35.1	17.3	51.0	30.6	26.7	38.5
WIE	46.4	14.1	40.7	32.3	24.9	35.0
XIE	48.6	13.0	51.0	32.3	24.6	36.6
W(Pnt)	46.1	14.3	38.8	32.6	22.7	25.4
X(Pnt)	46.0	13.0	41.4	32.4	23.0	30.0
WP	41.6	16.0	-	32.9	24.1	-
XP	42.2	14.9	-	32.2	22.7	-

II. Characteristics of pulp samples bleached with DMD, hydrogen peroxide, or nitrilamine/hydrogen peroxide



2. Effects of xylanase and hydrogen peroxide treatments on DEDED bleaching properties for hardwood and softwood kraft pulp



3. Effects of xylanase and DMD treatments on DEDED bleaching properties for hardwood and softwood kraft pulp

Fig. 3. Interestingly, a comparison of the Pnt- and DMD-treated pulps suggests that the nitrilamine/peroxide-treated pulps respond slightly more favorably to the DEDED bleached sequence than the DMD-treated pulps.

CONCLUSIONS

The use of activated peroxide species, such as DMD or nitrilamine-reinforced peroxide followed by DEDED, allowed 2–5% ISO brightness gains in hardwoods and 2–3% ISO brightness gains for softwood kraft pulps. The use of xylanase pretreatments also improved the delignification properties for all forms of peroxide studied. In light of the relative ease of incorporating nitrilamine-reinforced peroxide stages in modern bleaching operations, we plan to continue exploring the application of X(Pnt) stages as pretreatments for low-AOX chlorine dioxide bleaching technologies. TJ

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KEYWORDS
Alkaline pulps, bleaching, chemical pulps, chemical treatment, chlorine dioxide, chlorine free bleaching, enzymes, hardwood pulps, hydrogen peroxide, kraft pulps, multistage process, oxides, peroxides, pretreatment, processes, proteins, pulps, softwood pulps, xylanase.

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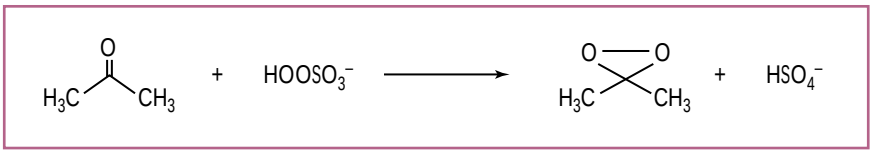
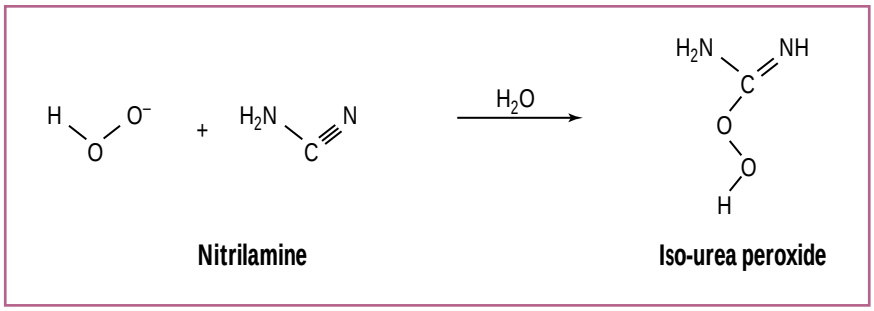
EQUATION 1



EQUATION 2



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