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Comparative study on the prebleaching of bamboo and hardwood pulps produced in Kharnaphuli Paper Mills

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Abstract: In order to lower bleaching costs, various prebleaching methods have been investigated. In the current work 3 prebleaching methods, peroxyformic acid, oxygen, and xylanase, were investigated in bamboo and hardwood kraft pulp produced by Kharnaphuli Paper Mills. Among these 3 methods, peroxyformic acid showed the most promising results. Peroxyformic acid prebleaching reduced kappa numbers by 38% and 30% and increased brightness by 12.2% and 8.6% in hardwood and bamboo pulp, respectively. Using 30 kg ClO_2 t^{-1} of pulp, hardwood pulp attained 77.2% brightness, while peroxyformic-acid–prebleached pulp attained 86% brightness without a reduction in viscosity in $D_0E_pD_1$ bleaching sequences. To achieve 80% brightness, peroxyformic acid prebleaching saved 33% ClO_2, while oxygen prebleaching saved 17% ClO_2. Xylanase prebleaching was not an efficient method for these pulps. Bamboo pulp showed lower bleachability than hardwood pulp. The papermaking properties of the bleached pulps did not show significant variation after prebleaching, with the exception of tear index in peroxyformic-acid–prebleached pulp. When considering bleachability and papermaking properties, peroxyformic acid was the best prebleaching option for reducing ClO_2 consumption.

Key words: Mixed hardwood and bamboo pulp, prebleaching, peroxyformic acid, brightness

1. Introduction

One of the biggest enterprises in Bangladesh, Kharnaphuli Paper Mills (KPM), uses bamboo and mixed hardwood as its main raw materials, and pulping is done by kraft process. Unfortunately, the brightness of the produced pulp does not meet consumer demand. Pulping conditions can affect residual lignin nature, which may play a key role in the development of pulp brightness. The bleachability of bamboo pulp was improved when pulping was performed with a higher active alkali charge and sulfidity (Jahan et al. 2007).

The bleaching section of a pulp mill is the most critical area from an environmental point of view. Conventional bleaching practices are based on elemental chlorine-containing chemicals that generate large quantities of highly toxic, organically bound chlorine compounds, usually classified as adsorbable organic halides (AOX); however, the substitution of chlorine dioxide (ClO_2) for elemental chlorine for bleaching reduces AOX production substantially. As a result of global trends and customer demand for cleaner bleach pulp, interest in elemental chlorine-free (ECF) and total chlorine-free (TCF) bleaching is growing. Prebleaching reduces chemical consumption in subsequent bleaching stages, which reduces the total effluent load (Viikari et al. 1986, 1994; Ikeda et al. 1999a, 1999b, 1999c; Jahan et al. 2006).

Ikeda et al. (1999a, 1999b, 1999c) have extensively studied the possibility of using sulfuric acid for removing the lignin that remains with the pulp after kraft pulping. Removal of this lignin by acid treatment improved bleaching performance (Siddhartha et al. 2010).

Oxygen delignification is a modern and environmentally friendly process that is usually used before ECF and TCF bleaching sequences to continue delignification, reducing lignin in pulp by 35%–55% prior to bleaching (Samuelson 1994).

Worldwide interest in xylanase pretreatment to reduce the costs of pulp bleaching is also growing. Xylanase-aided bleaching was originally designed to reduce consumption of chlorine-based bleaching chemicals, as a response to growing environmental public concern regarding chlorinated organic compounds in bleach mill effluents (Viikari et al. 1986, 1994). When xylanase is used as a pretreatment in bleaching, it removes xylan from the surface of the fiber. Xylan in hemicelluloses is initially removed during pulping but is redeposited on the fibers

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at the end of pulping (Kantelinen 1993). Redeposited xylan consumes a significant amount of ClO_2 in the first bleaching stage. Xylan concentration on the fiber surface and in the secondary wall is dramatically reduced during the enzyme treatment and increases the permeability of the fiber surface, thereby increasing bleachability (Gliese et al. 1998).

Another promising lignin-selective reagent is peracetic acid (Sun et al. 2000). Peracetic acid converts lignin to soluble fragments by 2 different mechanisms. First, peracetic acid reduces the molecular weight of lignin polymers by cleaving β-aryl ether bonds and carbon–carbon and carbon–oxygen bonds linked to the aromatic rings (Lawrence et al. 1980). Second, peracetic acid causes other reactions that increase the water solubility of lignin: dealkylation of O-methyl groups, introduction of hydroxyl groups to aromatic rings, and cleavage of aromatic rings into muconic acids (Lawrence et al. 1980). These reactions increase the polarity of lignin and create water-soluble lignin fragments that wash away from the lignocellulosic biomass. Due to the selective delignification nature of peracid, it is also gaining popularity for the prebleaching of pulp.

In this study, bamboo and mixed hardwood pulps produced by KPM were prebleached by oxygen, peroxyacid, and xylanase, and then prebleached pulp properties were evaluated. The effect of different prebleaching methods on $D_0E_pD_1$ bleaching was also studied.

2. Materials and methods

2.1. Raw materials

Bamboo and mixed hardwood pulps were collected from KPM and stored in a refrigerator until use. Kappa number, viscosity, and TAPPI brightness of unbleached pulps were determined according to TAPPI test methods. All chemicals used in this study were purchased from E-Merck, India. The purity of the hydrogen peroxide, hydrochloric acid, sulfuric acid, sodium chlorite, and sodium hydroxide was as follows: 30%, 37%, 98%, 78%, and 98%, respectively. The chlorine dioxide was prepared in the laboratory by reacting sodium chlorite with hydrochloric acid. The concentration of the chlorine dioxide was 15 g L^{-1} as ClO_2.

2.2. Oxygen prebleaching

Oxygen delignification (OD) was carried out in a thermostatically controlled digester, rotating at 1 rpm. OD conditions were 110 °C, retention time 60 min, pulp consistency 10%, NaOH 2%, $MgSO_4$ 0.3%, and O_2 pressure 3.5 kg cm^{-2}. The kappa number and viscosity of the resulting pulp was determined in accordance with TAPPI test methods T 236 om-99 and T 230 om-99, respectively.

2.3. Peroxyformic acid prebleaching

Bamboo and mixed hardwood pulps were further delignified with peroxyformic acid (PFA) at 80 °C for 120 min and maintained at 10% pulp consistency. The reaction was carried out in a thermostatic water bath. The peroxyformic acid was prepared by adding 90% formic acid with 4% H_2O_2. After pulping was completed the pulp was filtered off and washed with 80% fresh formic acid and then water. The kappa number and viscosity of the resulting pulp was determined in accordance with TAPPI test methods T 236 om-99 and T 230 om-99, respectively.

2.4. Xylanase prebleaching

The xylanase pretreatment was carried out at a pulp consistency of 10% with a xylanase charge 2 IU g^{-1} of OD pulp (pH 5) at 50 °C for 1 h. The kappa number and viscosity of the resulting pulp was determined in accordance with TAPPI test methods T 236 om-99 and T 230 om-99, respectively.

2.5. Bleaching

Oxygen, PFA, and xylanase prebleached pulps were bleached by $D_0E_pD_1$ bleaching sequence. The ClO_2 charge varied from 1% to 2%, and temperature was 70 °C for 60 min in the D_0 stage. The pH was adjusted to 2.5 by adding dilute H_2SO_4. In the alkaline extraction stage the temperature was 70 °C for 60 min, and NaOH and H_2O_2 charges were 2% and 0.5%, respectively. In the final D_1 stage, the ClO_2 charge varied from 0.5% to 1%, and pH was adjusted to 4.5 by adding diluted H_2SO_4.

2.6. Strength properties

The bleached pulps were beaten in a PFI mill to about 40° SR, and handsheets were made for determining tear index (T414 om-98), tensile index (T404 cm-92), and burst index (T403 om-97). All properties were determined according to the TAPPI standard methods given in parenthesis.

3. Results

In order to reduce bleaching costs, hardwood and bamboo pulps obtained from KPM were prebleached with peroxyformic acid, oxygen, and xylanase. Results are shown in Table 1.

3.1. Peroxyformic acid prebleaching

The peroxyformic acid treatment reduced the kappa number by 30% in hardwood pulp and 37% in bamboo pulp, while brightness increased by 12.2% and 8.6%, respectively (Table 1). Another study of organic solvent-based delignification showed that peroxyacetic acid is a good delignifier as well as a good brightening agent (Mire et al. 2005).

3.2. Oxygen prebleaching

The oxygen delignification prior to bleaching reduced the kappa number by 30% in hardwood pulp and 38% in bamboo pulp. The viscosity of oxygen-delignified pulp was slightly better than that of peroxyformic-acid–delignified pulp (Table 1). Oxygen delignification significantly increased pulp brightness, and the brightness increased

Table 1. Effect of different prebleaching methods of hardwood and bamboo pulps.

Pulp type	Parameter	Unbleached pulp	Prebleaching		
			Peroxyformic acid	Oxygen	Xylanase
Hardwood pulp	Kappa number	21.9	15.3	17.2	19.1
	Brightness (TAPPI %)	23.2	35.4	35.7	25.5
	Viscosity (mPa s)	15.4	12.4	12.9	14.2
Bamboo pulp	Kappa number	30.0	18.7	15.7	20.8
	Brightness (TAPPI %)	20.5	29.1	35.0	23.5
	Viscosity (mPa s)	17.3	14.5	16.1	16.4

by 12.5% and 14.5% for hardwood and bamboo pulps, respectively.

3.3. Xylanase prebleaching

It is remarkable that the bleaching action (i.e. direct brightening and delignification) was already observed immediately after the enzymatic stage, pointing to the beneficial effects of xylanase treatment of bamboo and hardwood pulp. It is necessary to note that there were some change in bamboo pulp properties, reductions in kappa number of up to 13%, and increases in pulp brightness by about 2.3%. The most striking result was observed for hardwood pulp, in which the kappa number was reduced by 30%. The exclusive effect of xylanase action was therefore assessed through comparison with control samples.

3.4. $D_0E_pD_1$ bleaching

The unbleached and prebleached pulps from hardwood and bamboo were subsequently bleached by $D_0E_pD_1$ bleaching sequences. The total ClO_2 charge was 3 kg t^{-1} of pulp. The investigation began with the first ClO_2 bleaching stage. The initial challenge was to determine the intensity required in the D_0 stage. Prebleaching resulted in a lower kappa number and should allow for an easier final pulp bleaching. All prebleached pulp showed better final brightness than the control of unbleached pulp (Table 2). In both pulps, peroxyformic acid treatment showed the best bleachability among the 3 prebleaching processes, as shown in Table 2. Hardwood pulp after peroxyformic acid treatment showed 82% brightness using only 20 kg ClO_2 t^{-1} of pulp, while unbleached pulp had a final brightness of 77% using 30 kg ClO_2 t^{-1} of pulp (Figure 1). At 30 kg ClO_2 charge t^{-1} bamboo pulp had an increase in final brightness from 70% to 85% with peroxyformic acid prebleaching. Peroxyacid treatment increases the phenolic hydroxyl group of pulp, which subsequently accelerates bleachability of the pulp (Jahan et al. 2007). Similarly, oxygen prebleaching also showed promising results in both hardwood and bamboo pulps (Figure 2).

Xylanase prebleaching did not create much improvement in final brightness in this study. The performance of xylanase depends substantially on the wood and pulping method used (Suurnakki et al. 1994).

3.5. Papermaking properties

The papermaking properties of bleached hardwood and bamboo pulps were determined after beating in a PFI mill for 1500 revolutions (Table 3). Only 1500 PFI revolutions increased the °SR value above 40. Organic acid pulp becomes brittle, which increases easy beatability (Jahan et al. 2005). In both species, PFA-prebleached pulp had a better tensile index than pulps prebleached with oxygen and xylanase. However, the tear index of PFA-treated pulp was lower than in the other prebleached pulps.

Table 2. Effect of prebleaching on the final brightness of $D_0E_pD_1$ bleached pulp from hardwood and bamboo (total ClO_2 charge was 3%).

Pulp type	Prebleaching	Final brightness (TAPPI %)	Final viscosity (mPa s)
Hardwood pulp	Control	77.2	10.3
	Peroxyformic acid	86.0	10.8
	Oxygen	83.2	11.1
	Xylanase	79.1	11.5
Bamboo pulp	Control	68.8	11.3
	Peroxyformic acid	84.4	11.6
	Oxygen	82.2	11.4
	Xylanase	69.2	12.9

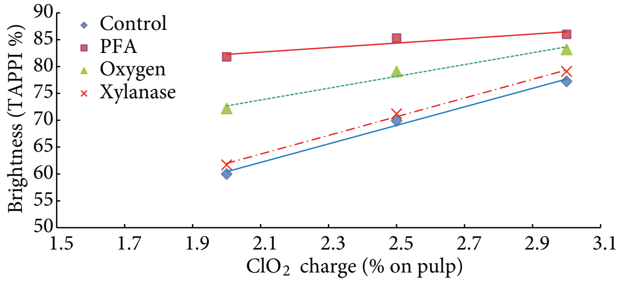

Figure 1. Effect of ClO_2 charge on the final brightness of hardwood pulp.

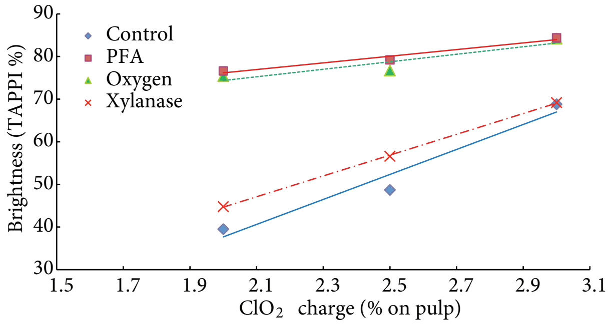

Figure 2. Effect of ClO_2 charge on the final brightness of bamboo pulp.

Table 3. Effect of prebleaching on the final bleached pulp properties obtained from hardwood and bamboo.

Pulp type	Pretreatment	°SR	Tensile index (N m g^{-1})	Tear index (mN m^2 g^{-1})	Burst index (kPa m^2 g^{-1})
Hardwood pulp	Control	43	39.3	12.2	3.8
	PFA	49	39.4	10.0	3.5
	Oxygen	40	38.4	15.0	3.9
	Xylanase	41	35.3	13.7	3.8
Bamboo pulp	Control	40	34.6	19.3	3.3
	PFA	51	38.9	15.4	4.4
	Oxygen	41	38.5	21.8	4.7
	Xylanase	42	37.6	20.8	4.2

4. Discussion

4.1. Prebleaching

Delignification of lignocelluloses has also been reported to produce pulps with excellent peroxide bleachability (Perez et al. 1998). During peroxyformic acid treatment, electrophilic HO^+ ions are formed ($HCOOOH + H^+ = HCOOH + HO^+$). According to model compound studies the main reactions for the HO^+ ions with lignin are expected to be ring hydroxylation, oxidative ring opening, substitution of side chains, cleavage of β-aryl ether bonds, and epoxidation (Gierer et al. 1982; Hortling et al. 1991; Strumila and Rapson 1975; Yuan et al. 1998b).

In oxygen delignification, the first stage of lignin degradation by oxygen and alkali is believed to be the formation of phenoxy radicals from phenolate anions present in the lignin under alkaline conditions (Gierer and Imsgard 1977; McDonough 1996). Thus, it would be easy to assume that the bleachability of pulp by oxygen would be dependent on free phenolic group content in the residual lignin from pulp. Oxygen delignification of soda–AQ bagasse pulp reduced the kappa number by almost 50% with only marginal yield loss (Mohta et al. 1998). The effectiveness of an oxygen delignification stage is limited to 50% delignification. Beyond this level, severe cellulose degradation takes place, resulting in the deterioration of pulp viscosity and strength characteristics (Masura 1993; McDonough 1996).

The key function of xylanase pretreatment (X-stage) is to enhance the bleaching effect of other chemicals (so-called bleach boosting) in subsequent bleaching stages. The mechanism of xylanase-aided bleaching is not yet fully understood. One hypothesis is that xylanases degrade the redeposited xylan on the surface of the fibers, thereby opening up the pulp structure to access by bleaching chemicals (Kantalinen 1991).

4.2. $D_0E_pD_1$ bleaching

To achieve 80% brightness, peroxyformic acid prebleaching saved 33% ClO_2, while oxygen prebleaching saved 17% ClO_2. This would certainly reduce the bleached effluent load. Gustavsson et al. (1999) concluded that a high content of beta-*O*-4 structures in unbleached residual lignin contributed to better pulp bleachability in ECF and TCF bleaching. Chlorine dioxide is able to depolymerize both phenolic and nonphenolic lignin structures (Lindgren 1971; Brage et al. 1991). Oxygen and PFA prebleaching produced more phenolic hydroxyl units and beta-*O*-4 structures, which improved bleachability in subsequent ClO_2 bleaching.

4.3. Papermaking properties

The tear index of bamboo pulp was superior to that of hardwood pulp due to longer fiber length. However, PFA-prebleached pulp showed a lower tear index than pulps prebleached with oxygen and xylanase, which can be attributed to degradation and changes in cellulose structure (Fernandez 1996; Young 1996). Our results for tear index after PFA prebleaching also conform to the results of Sahin and Young (2008). The authors concluded that acidic pulping was harmful to the strength properties of jute fiber pulp. This may be due to damage to fibers during acidic pulping. A similar result was found in the acetic acid pulping of wheat straw (Pan and Sano 2005). Acetic acid is a very good solvent. It is assumed to promote the solvation of lignin fragments; however, it also reduces swelling of the predominantly carbohydrate fibers (Young 1986), which may also be the cause of poorer strength properties.

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