

Enzyme and Alkali-Aided ECF Bleaching of Kraft Bamboo Pulp

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Unbleached kraft bamboo pulp was pretreated by a xylanase and laccase (X/L) treatment, as well as a joint treatment of X/L and alkali, prior to element chlorine free (ECF) bleaching. In comparison with the control test, the joint treatment of X/L and alkali (X/L+0.1%) had more potential to reduce absorbable organic halide (AOX) levels (29.79%) and COD content (21.55%), in addition to improving bleached pulp properties (56.88% decrease in kappa number and 8.94 %ISO increased in brightness). Moreover, the treatment of X/L+0.1% removed more lignin and HexA than X/L treatment. The analysis of XPS indicated that the X/L treatment could noticeably remove the surface lignin of pulp, but the joint treatments of X/L and alkali could promote the production of superficial lignin. FTIR results showed that pretreatments only reduced part of the lignin and carbohydrate contents, but did not change their structures. The joint pretreatment of enzymes and diluted alkali (X/L+0.1%) had more appealing advantages to produce bleached kraft bamboo pulp.

Keywords: Xylanase; Laccase; Alkaline treatment; AOX; Surface lignin; FTIR

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INTRODUCTION

Absorbable organic halide (AOX) is seriously harmful to both the environment and human beings. It is produced when hypochlorous acid (or mixtures of hypochlorous acid and chlorine) in ECF bleaching agents reacts with residual lignin in pulp (Nie *et al.* 2014a). Furthermore, efforts to decrease residual lignin prior to bleaching have the potential to reduce the production of AOX, depending on how much of the lignin remains in the pulp. A decrease in lignin of the unbleached pulp inevitably leads to a reduction of AOX discharge in effluents. Alternatively, the elemental chlorine free (ECF) bleaching processes can avoid the formation of highly toxic AOX during bleaching. ECF sequences could control the release of toxic substances (Agnihotri *et al.* 2012; Paprakash 2012).

Biotechnology is an important tool in the pulping processes. The application of enzymes, such as xylanase and laccase in pulp bleaching, can improve the brightness of pulp, as well as decrease the kappa number and hexenuronic acids (HexA) (Valls and Roncero 2009). Xylanase is a hydrolytic enzyme. It can break down hemicellulose, help to dissolve out the residual lignin, and save about 30 to 40% of the bleaching chemicals during bleaching. Also, xylanase treatment prior to ECF bleaching could reduce the production of AOX in effluent, enhance pulp properties, and save bleaching costs (Gangwar *et al.* 2014). Therefore, xylanase pretreatment could be established as the most suitable stage to facilitate pulp ECF bleaching (Comlekcioglu *et al.* 2014).

The application of fungal laccase must be conducted in the presence of redox mediators and oxygen pressure due to its low redox potential. 1-hydroxybenzotriazole (HBT), 2,2-azino-bis(3-ethyl-benzothiazole-6-sulfonic acid, ABTS), and N-hydroxyacetanilide (NHA) have been the most common mediators for the laccase reaction (Valls *et al.* 2010a). Laccase exhibits a high selectivity to degrade lignin directly, reducing the kappa number and enhancing the brightness of kraft pulp (Dwivedi *et al.* 2010). However, laccase biobleaching of pulp is impeded, owing to its limited availability, high cost, and potential toxicity of mediators that are released into effluents (Valls and Roncero 2009). Furthermore, xylanase partly hydrolyzes hemicellulose prior to laccase treatment, granting greater permeability to the pulp, facilitating the removal of residual lignin, and leading to a large reduction of AOX in bleaching effluent (Gangwar *et al.* 2014). The joint processes of xylanase and laccase treatment allowed easy lignin removal and saved more chemical agents in the subsequent ECF bleaching.

Alkaline pretreatment prior to bleaching can improve the effects of the bleaching process (Chen *et al.* 2000; Solar *et al.* 2011). NaOH is one of the most commonly used alkali sources due to its low cost. NaOH pretreatment opens part of the hydrogen bonds, which are located in the cell wall of the pulp, and increases the access to the cell walls. This process could promote the penetration of chemicals during the bleaching process, as well as improve the physical strength of bleaching pulp. The combination of X/L and alkali to pre-treat kraft bamboo pulp improved the efficiency of the following ECF bleaching (Ibarra *et al.* 2010). The enzyme treatment delignified and modified the residual lignin structure, which made it easier to remove lignin in the subsequent alkaline treatment (Eugenio *et al.* 2010). On the other hand, some HexA in xylan-lignin complexes were extracted easily under alkaline conditions, and the joint treatment of X/L and alkali had more potential to release HexA, which helped to reduce the production of AOX (Costa and Colodette 2007).

As the demand for paper products rapidly grows in China, it becomes more difficult for wood raw materials to meet the production requirements. Consequently, the development and application of non-wood raw materials in papermaking is becoming urgent. Bamboo is one of the fastest growing natural resources and has great potential to be used in the pulp and paper making industry. Its fiber morphology and chemical composition shows good pulping performance. However, in contrast to other grass materials, bamboo pulp was difficult to bleach due to its higher hemicellulose, lignin, and other extractives, which consume more chemicals during bleaching. Moreover, the infrequent and small pores in bamboo pulp fiber also prevent the bleaching agents from penetrating into the inner fiber (He *et al.* 2014; Peng and She 2014). In addition, diluted alkali treatment has been found to be one of the most effective ways to extract the hemicellulose and dissolve the lignin in bamboo pulp (Peng and She 2014). Therefore, the pretreatments of kraft bamboo pulp with enzyme and/or alkali, prior to ECF bleaching, were conducted in this work.

In this work, the bio-bleaching effects of X/L treatment and a joint treatment of X/L and alkali on the formation of AOX and COD during ECF bleaching kraft bamboo pulp were considered. Also, the influence of pulp properties such as HexA content, lignin content, and kappa number on AOX formation was studied during the pretreatment process. Besides aiming to further analyze the influence of pretreatment on ECF bleaching, the lignin content on fiber surface and the structure changes of pulp were studied based on XPS and FTIR.

EXPERIMENTAL

Materials

Unbleached kraft bamboo pulp was kindly supplied by Guangxi Huajin Group Co., LTD (China). The kappa number of the unbleached pulp was 21.17, viscosity 1651.50 mg/L, brightness 23.97% ISO, and post-color number (PC number) 1.10.

In this study, xylanase and laccase had activities of 500 U/mL and 3510 U/mL, respectively. Both of the enzymes were supplied by the College of Biological Science of Guangxi University. Laccase was produced from an isolated white rot fungus. The mediator of laccase reaction was 1-hydroxybenzotriazole (HBT), and Tween® 80 (polyoxyethylene (20) sorbitan monooleate) was used as a surfactant. All other chemicals were purchased from the Aladdin company (Shanghai, China).

Methods

Enzymatic treatment

Kraft bamboo pulp was subjected to a joint xylanase/laccase (X/L) treatment, in which the pulp was first treated with xylanase, then with laccase. The X treatment was performed using 30 g of oven dry pulp (odp), which was treated in a polythene bag under the following conditions: 10% pulp consistency, 65 °C, 10U/g xylanase (on dried pulp), pH 9.0 (adjusted with acid anhydride), 90 min. The pulp was filtered and washed thoroughly with distilled water after X treatment. The Laccase (L) treatment was conducted in the high pressure reactor under the following conditions: 20 U/g laccase (on dried pulp), 1.5% odp HBT, 0.05% Tween® 80, 10% pulp consistency, 0.6 MPa oxygen pressure, 50 °C, pH 4.5 (adjusted with sodium acetate), stirring 60 rpm, 120 min. The pulp was also filtered and washed thoroughly with distilled water after L treatment.

Alkaline treatment

After the X/L treatment, the pulp was treated with different dosages of NaOH solution, the treatment conditions were as follows: 70 °C, 90 min, with varied dosages of NaOH solution (0.1%, 0.3%, and 1% on dried pulp). Additionally, the joint treatment of X/L+0% was not conducted because the pH of the pulp would be acidic during hot water (0% alkali treatment) (Sun *et al.* 2003). Then, the pulp was filtered and thoroughly washed with distilled water after each NaOH solution treatment. Some pulp was used to conduct the analysis, other pulp was used for ECF bleaching.

Properties analysis of pulp after different treatments

The pulp samples, including those without treatment, X/L treatment, and the joint treatment of X/L and alkali, were analyzed for kappa number (TAPPI T236 om-99, 2004), viscosity (TAPPI T230 om-04, 2004), and brightness (TAPPI T217 wd-77, 2004). The chemical ingredients of pulp samples such as cellulose (T201 wd-76, 2004), poly-pentose (T223 cm-01, 2004), Klason lignin (T222 om-02, 2004), and acid-soluble lignin (T222 om-02, 2004) were determined. The content of hexenuronic acid (HexA) was estimated following the method of UV spectrophotometry (Chai *et al.* 2001).

Properties of pulp and effluent after bleaching

The pulp samples were bleached, both before and after treatments, with an ECF bleaching sequence of D0(EP)D1, where D0 denoted the first bleaching stage of chlorine dioxide, EP denoted alkaline extraction with hydrogen peroxide bleaching, and D1

denoted the second bleaching stage of chlorine dioxide. The conditions during the D0 stage were: 10% pulp consistency, 65 °C, pH 2.5-3.0, 90 min, and 3.5% ClO₂ (on dried pulp). During the EP stage, the pulp first was operated by a chelating treatment, with ethylene diamine tetraacetic acid (EDTA) and MgSO₄. Then, the pulp was bleached with NaOH and hydrogen peroxide, and the bleaching time was 60 min and 100 min, respectively. The conditions during the EP stage were: 0.3% EDTA, 0.5% MgSO₄, 2.0% NaOH, and 1.0% H₂O₂ (on dried pulp), 10% pulp consistency, 70 °C, and pH 10.5 to 11.5. The D1 stage was performed with 10% pulp consistency, 85 °C, pH 3.5 to 4.0, 120 min, and 1.5% ClO₂ (on dried pulp). The pulp was filtered and thoroughly washed with distilled water after each treatment. The properties of the bleached pulp were analyzed to determine the kappa number, viscosity, brightness, and post-color (PC) number. The PC number was detected using the standard method of TAPPI (T260 wd-98, 2004). AOX content of the bleaching effluent was determined as in previous work by the authors (Nie *et al.* 2013, 2014a,b).

XPS analysis of fiber surface

The pulp samples were prepared in sheets (diameter: 20 mm, basis weight: 80 g/m²) made using a Buchner funnel. Then the sheets were air-dried, extracted with acetone at 80 °C for 6 h, and subsequently placed on clean glass slides to air dry for 24 h, to allow for acetone evaporation. Finally, the samples were oven dried at 60 °C until their weights were constant.

The smooth sides of samples (adhered to the glass surface) were used to provide a good surface for XPS measurement. The type of XPS instrument was K-Alpha (Thermo Fisher Britain). The instrument was equipped with in a monochromatic Al K α X-ray source and operated at 15KV under a vacuum about 2 \times 10⁻⁹ mbar. The scan area was 400 μ m \times 400 μ m. The O/C ratio was determined using the low-resolution mode, with pass energy 100 eV. The quantification of different bound carbons was ascertained from high-resolution mode, with pass energy 20 eV.

FTIR analysis of fiber

The pulp samples were ground into powder. Then, the powder samples were embedded into KBr disk and subjected to Fourier-transform infrared spectra (FTIR) with a NEXUS47-ESP series (NEXUS47 FTIR ESP, Thermo Nicolet) spectrometer at room temperature.

RESULTS AND DISCUSSION

Effect of Different Treatments on AOX and COD Formation

Most of the AOX and COD constituents present in ECF bleaching effluents would seriously damage the environment. This work aimed to assess the potentiality of different treatments for lowering environmental impact, and the pulp samples included those without treatment, those subjects to X/L treatment, and those which utilize a joint treatment of X/L and alkali (X/L+0.1%, X/L+0.3% and X/L+1.0%), which were bleached with the sequences of D0(EP)D1. The contents of AOX and COD in the bleaching effluents were measured. The results are shown in Table 1.

Table 1. Effluent Properties after ECF Bleaching

	AOX, Kg/t				COD, Kg/t			
	D ₀	EP	D ₁	Total AOX	D ₀	EP	D ₁	Total COD
Control	0.32	0.06	0.09	0.47	1.85	3.40	0.55	5.80
X/L	0.31	0.05	0.03	0.39	1.62	3.02	0.55	5.19
X/L+0.1%	0.22	0.06	0.05	0.33	1.47	2.54	0.54	4.55
X/L+0.3%	0.23	0.06	0.05	0.34	1.54	2.54	0.53	4.61
X/L+1.0%	0.23	0.05	0.05	0.33	1.27	1.99	0.57	3.83

The results in Table 1 showed that the total contents of AOX and COD were decreased after different treatments under the same bleaching conditions, especially for the joint treatment of X/L+0.1%. Compared with the control test, the total contents of AOX and COD were reduced by 17.02% and 10.52% for X/L treatment, and 29.79% and 21.55% for X/L+0.1% treatment. The results indicated that X/L+0.1% treatment was more effective in decreasing AOX and COD than X/L treatment, which is similar to the findings of Singh and Dutt (2014). One of the most significant effects of the treatment was the delignification of the residual lignin, which enhanced the access of chemicals into the fibers and improved the removal of lignin in the subsequent alkaline treatment. Moreover, the content of lignin had a close relationship with the formation of AOX, and decreased lignin would lead to lower production of AOX (Nie *et al.* 2014a). The decreased lignin content and kappa number in Table 2 after treatments also verified the results.

On the other hand, the COD is an index of organic matter content in bleaching effluent. Most organic matter in the pulp was dissolved into the filtrates during both enzyme and alkali pretreatments, which led to a decreasing COD during the ECF bleaching (Gangwar *et al.* 2014). Therefore, the contents of AOX and COD were reduced more in the joint treatment of X/L+0.1% than in the X/L treatment, since the lignin was deeply degraded in advance.

Most of the AOX and COD were produced during the D₀ and EP stages, respectively. The reason for the AOX production was that most residual lignin still was present in the unbleached pulp prior to bleaching, although it underwent different pretreatments. Moreover, AOX was produced when the hypochlorous acid (or the mixtures of hypochlorous acid and chlorine in ECF bleaching agents) reacted with residual lignin (Nie *et al.* 2014a).

Therefore, high amounts of lignin present in the pulp would lead to equally high amounts of AOX produced in the bleaching effluents. Additionally, the amount of AOX was also relative to the kappa number of unbleached pulp and the dosage of chlorine dioxide (Nie *et al.* 2014b). Most of the COD produced in the EP stage was involved with the application of EDTA as a chelating agent (an organic compound) and gave a large amount of COD (Valls *et al.* 2010b).

Effect of Different Treatments on Pulp Properties

The chemical characteristics of pulps were analyzed after different treatments. The results are shown in Table 2.

Table 2. Chemical Characteristic of Pulps after Different Treatments

Samples	Kappa number	Cellulose (%)	Poly-pentose (%)	HexA (molx 10 ⁻⁶ /g)	Klason Lignin (%)	Acid-soluble lignin (%)
Control	21.17	83.34	20.27	23.44	3.24 ± 0.04	0.45
X/L	20.66	79.68	18.60	22.38	2.11 ± 0.03	0.39
X/L+0.1%	18.79	79.29	18.53	17.09	1.99 ± 0.03	0.39
X/L+0.3%	18.82	79.69	18.59	18.34	1.67 ± 0.02	0.40
X/L+1.0%	18.66	79.54	18.70	18.74	1.64 ± 0.02	0.40

The results in Table 2 show that the content of HexA was reduced by 4.52% and 27.09% after X/L treatment and a joint treatment of X/L+0.1%, respectively. Moreover, the content of AOX correspondingly decreased by 17.02% and 29.79% according to Table 1. Therefore, the formation of AOX had a close relationship with HexA for kraft bamboo pulp, and the decrease of HexA prior to bleaching would be very beneficial for reducing the production of AOX. The reduction of HexA was due to the xylanase treatment, which reduced part of the hemicelluloses in pulp and led to an increase in the removal rate of HexA in X/L treatment. Furthermore, HexA that was bound to xylan-lignin complexes were easily extracted under alkaline conditions (Eugenio *et al.* 2010). On the other hand, part of the HexA structures were oxidized into chlorinated organics by chlorine dioxide, which was the main contribution in the AOX formation (Costa and Colodette 2007). Consequently, the biggest reduction of HexA and AOX took place after the joint treatment of X/L and alkali, especially for dilute alkali. In addition, the pH value of pulp was nearly 7 after the treatment of X/L+0.1%, which meant that the pulp did not need to be washed further. Considering the results of Table 1 and Table 2, the treatment of X/L+0.1% had more potential to be incorporated into industrial production because of its lower cost.

The cellulose and poly-pentose contents were reduced by 4.39% and 8.24% after the X/L treatment, respectively. Also, the cellulose and poly-pentose were not further degraded with the application of alkali treatment, compared with the X/L treatment. Because lignin was coexistent with cellulose and poly-pentose, xylanase could help to dissolve the residual lignin when it broke down part of the hemicellulose. The laccase could directly oxidize the lignin, so Klason lignin was reduced after X/L treatment, which also resulted in decreases in the kappa number. Additionally, HexA was formed from 4-O-methylglucuronoxylan during cooking, which interfered with the determination of the kappa number of the pulp (Li *et al.* 2002).

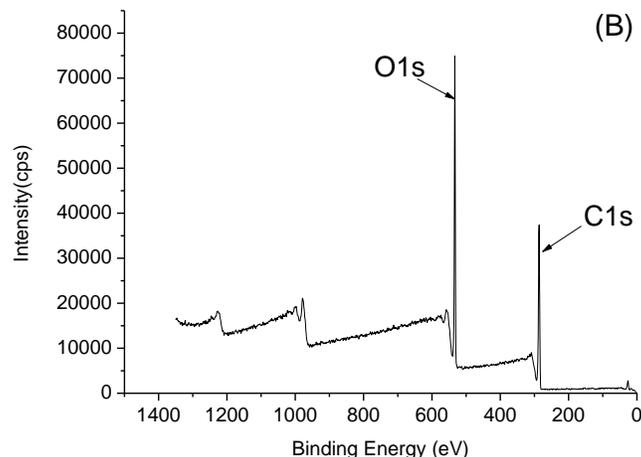
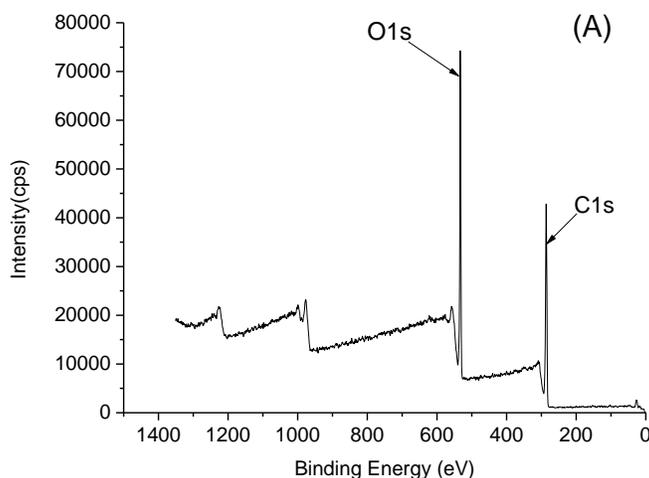
Another important observation to be extrapolated from Table 2 was that the joint treatment of X/L and alkali was more beneficial for decreasing the lignin content and kappa number. The reasoning behind the results was similar to the studies of Eugenio *et al.* (2010).

XPS Analysis of Pulp Surface

X-ray photoelectron spectroscopy (XPS) had been applied to quantify the surface compositions of the lignocellulosic materials (Ji and Lee 2013). The known theoretical O/C ratios were found to be 0.83 for pure cellulose, hemicellulose, and pectin, and 0.35 for pure lignin (Peng *et al.* 2010; Mou *et al.* 2014). In this study, the pulp samples (including those without treatment, X/L, X/L+0.1%, X/L+0.3%, and X/L+1.0% treatments) were detected by XPS.

As can be seen in Fig. 1, there were characteristic peaks for C atoms and O atoms, detected by XPS in those samples. Element C had four combination modes in the fibers (C1, C2, C3, and C4), which had different binding between each element C (Gruian *et al.* 2012; Babu *et al.* 2014; George *et al.* 2014; Wu *et al.* 2014).

The amount of C1 (C-C, C-H, C=C) represented the lignin content on the fiber surface, and existed only in lignin after extractives were completely removed by acetone in advance. The results in Table 3 showed that the amount of C1 was noticeably decreased by 30.34% after X/L treatment. Hence, the X/L treatment had a significant effect on removing surface lignin in pulp, due to the biobleaching effects of xylanase and laccase. However, changes in the decrease in the lignin content were not significant after different joint treatments of X/L and alkali.



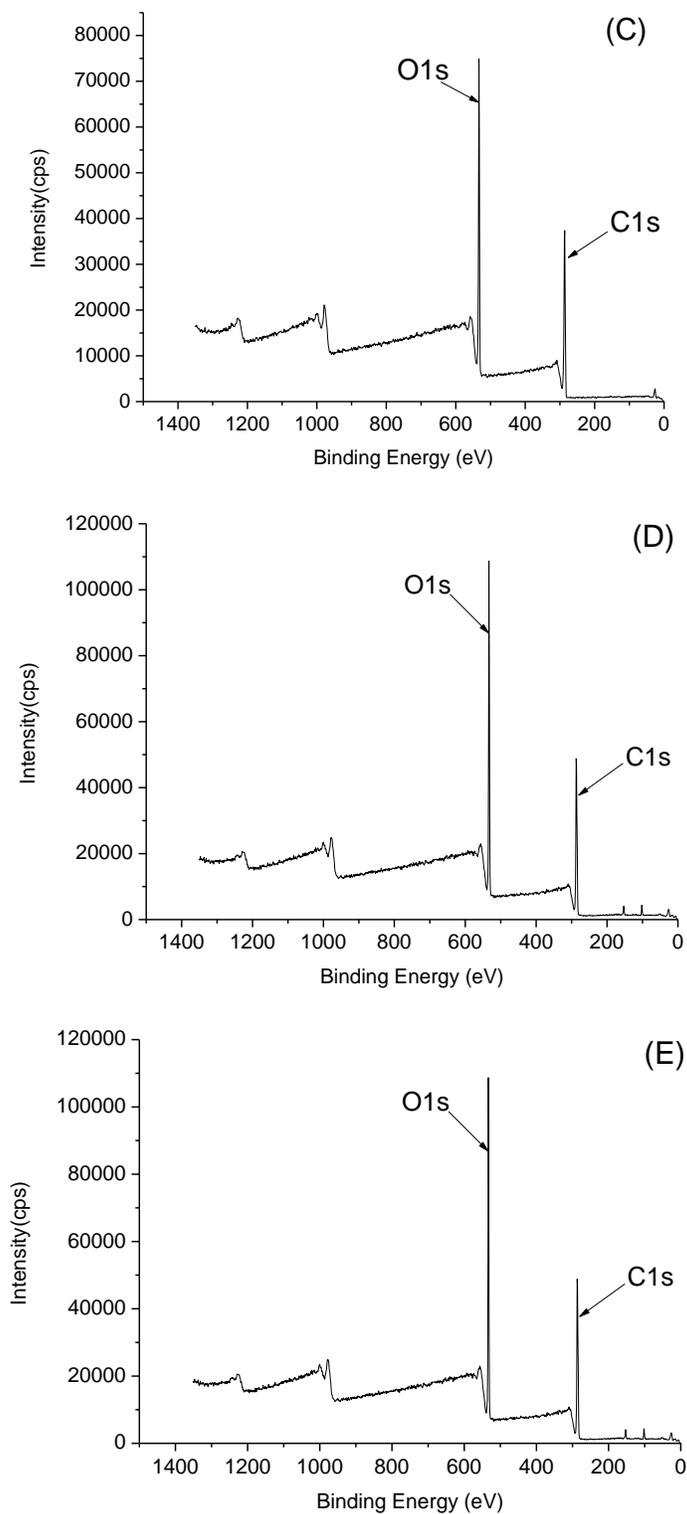


Fig. 1. XPS spectra of samples: low resolution survey scans of C1s and O1s, (A) without treatment, (B) X/L treatment, (C) X/L+0.1% treatment, (D) X/L+0.3% treatment, and (E) X/L+1.0% treatment

Table 3. XPS Data Following Different Treatments of Pulps

Samples	Atomic ratio (O/C)	C1s total=100%			
		C1(%)	C2(%)	C3(%)	C4(%)
Control	0.522	17.96	31.91	12.42	2.43
X/L	0.594	12.51	33.22	13.47	2.96
X/L+0.1%	0.558	17.87	34.28	9.99	1.83
X/L+0.3%	0.527	17.47	33.91	11.74	1.29
X/L+1.0%	0.599	15.55	36.79	9.64	---

Combined with the results of Table 2, due to the obvious decrease of kappa number and klason lignin in pulp, the limited decrease of C1 can be attributed to the lignin dissolved from cell wall matrix becoming partly redeposited again on fiber surfaces during the alkaline pretreatment and washing process. The results were similar to some previous studies (Ji and Lee 2013; Mou *et al.* 2013).

C2 (C-O or C-O-C) and C3 (C=O or O-C-O) mainly are deemed to represent cellulose and hemicellulose. Compared to the control test, the increase of C2 and C3 after X/L treatment showed that more cellulose, hemicellulose, and hydrophilic groups were exposed. However, the joint treatment of X/L and alkali only had a slight effect on increasing the carbohydrates on the fiber surface, according to the amount of C2 and C3, which corresponded to the results for lignin redeposition. C4 mainly consists of carboxylic acid. In contrast to the control test, the increased amount of C4 after X/L treatment showed that much carboxylic acid was exposed on the fiber surface. According to the increase of C2 and C3, the exposed carboxylic acid should be bound on the cellulose and hemicellulose. However, the C4 was decreased after the joint treatment. It was for this reason that the carboxylic acid was neutralized by the added alkali. Therefore, with the increasing alkali dosage, carboxylic acid on the fiber surface was reacted thoroughly by the alkali and the C4 was not detected after X/L+1.0% treatment.

Moreover, the lignin concentration on the fiber surface can be obtained from the O/C ratios in XPS. A higher O/C ratio generally indicated lower lignin concentration (Peng *et al.* 2010). The results in Table 3 showed that in contrast to the control test, the O/C ratios were increased after treatments, indicating that surface lignins were decreased after treatments. Additionally, in comparison with the X/L treatment, the surface lignin contents were increased after the joint treatment of X/L and alkali. The results were coincident to the decrease of C1.

FTIR Analysis of Pulp Chemical Structures

To further investigate the improvement of different treatments on ECF bleaching, the chemical structures of pulp, both before and after treatment, were analyzed with FTIR. The results are shown in Fig. 2.

The FTIR spectra of lignocellulosic materials were influenced by three main polymers, including lignin, cellulose, and hemicellulose (Sindhu *et al.* 2014). Compared to the control test, an appreciable reduction of intensities at all peaks after treatments was observed in Fig. 2, especially after the joint treatment of X/L and alkali. Also, the peaks were only shifted minutely. The results indicated that the pretreatments prior to bleaching only reduced the part contents of chemical constituents, but did not change their structures.

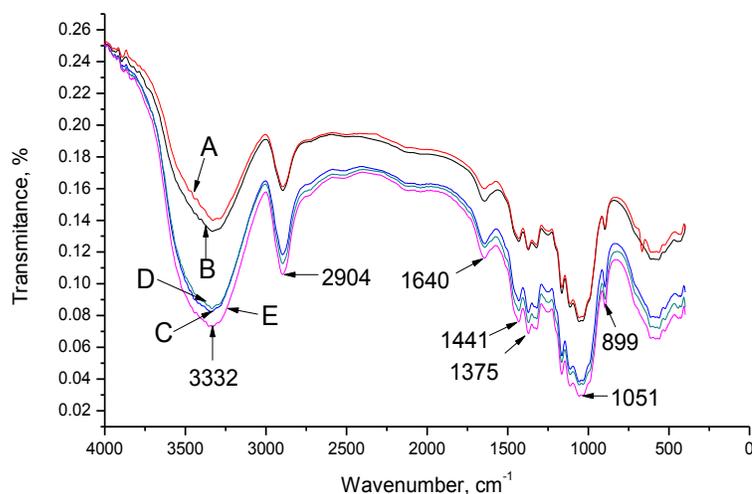


Fig. 2. FTIR spectra of pulps: (A) without treatment, (B) X/L treatment, (C) X/L+0.1% treatment, (D) X/L+0.3% treatment, and (E) X/L+1.0% treatment

The absorption bands at 3332 cm^{-1} and 2904 cm^{-1} were mainly assigned to the O-H and C-H stretching vibration of lignin and hemicellulose, respectively (Wu *et al.* 2012; Mou *et al.* 2013). The band at 1640 cm^{-1} was ascribed to the stretching of guaiacyl ring (C=C) and carbonyl groups (C=O) in aromatic rings of lignin. The significant decrease of the aforementioned peaks' intensities indicated that the lignin was reduced after treatments, especially after the joint treatment of X/L and alkali. The results were coincident with the decreased results of lignin and kappa number in Table 2. Some peaks of carbohydrates (such as those at 1441 cm^{-1} , 1375 cm^{-1} , 1051 cm^{-1} , and 899 cm^{-1}) were decreased after different treatments, indicating that these treatments partly degraded the carbohydrate of pulp. Some similar results were also obtained by Mou *et al.* (2013).

Effects of Different Treatments on Pulp Properties

The effect of different treatments on the properties of ECF bleaching pulp was analyzed. The results are shown in Table 4.

Table 4. Effects of Different Treatments on Pulp Properties

	Kappa number	Viscosity, ml/g	Brightness, %ISO	PC number
Control	2.69 ± 0.05	1272.5	71.02	1.10 ± 0.06
X/L	1.31 ± 0.03	1260.5	78.36	1.10 ± 0.05
X/L+0.1%	1.16 ± 0.02	1253.0	79.96	0.96 ± 0.04
X/L+0.3%	1.16 ± 0.03	1239.5	80.36	0.81 ± 0.04
X/L+1.0%	1.13 ± 0.02	1220.5	83.34	0.78 ± 0.05

In contrast to the control test, the results in Table 4 showed that these pretreatments had noticeable effects on enhancing the brightness of kraft bamboo pulp and reduced the kappa number during the $D_0\text{EPD}_1$ bleaching, especially for the joint treatments of X/L and alkali. One of the main reasons was that the process of enzyme treatment enhanced the access to the inner fiber and facilitated the bleaching agents to react with the inner lignin. Moreover, alkali pretreatment could extract parts of the lignin,

and the lignin would easily precipitate again on the fiber surface, which promoted the production of superficial lignin and resulted in easy removal by the bleaching agents (Angayarkanni *et al.* 2006). Additionally, alkali treatment had the potential to extract the colored materials in pulp and led to a reduction in the PC number after ECF bleaching. These pretreatments had a slight effect on decreasing the viscosity, regardless of the enzyme and alkali treatments.

A slight increase in viscosity was observed after xylanase treatment, but there was a slight decrease after laccase treatment, so no variation on pulp viscosity has been found after X/L treatment of bleached pulp (Valls *et al.* 2011). On the other hand, the hydroxyl radicals, which were produced in laccase treatment stage caused the formation of carbonyl groups after the X/L treatment, and the carbonyl groups could break the cellulose chain and lead to a decrease of viscosity in the subsequent alkaline treatment stage (Valls *et al.* 2010c).

CONCLUSIONS

1. Unbleached kraft bamboo pulp was pretreated with a xylanase and laccase (X/L), coupled with a joint treatment of X/L and alkali, prior to element chlorine free (ECF) bleaching. In contrast to the control test, the joint treatment of X/L and alkali (X/L+0.1%) had greater potential to reduce AOX and COD, and improve the properties of bleached pulp as well. Additionally, the treatment of X/L+0.1% was more adept at removing lignin and HexA than the X/L treatment.
2. XPS analysis indicated that the joint treatments of X/L and alkali could promote the production of superficial lignin due to the dissolved lignin redepositing on the fiber surface during the alkaline treatment and washing process. FTIR results showed that pretreatments only partly reduced the contents of some chemical constituents, such as lignin and carbohydrate, but did not change their structures.
3. The joint pretreatment of enzymes and very dilute alkali (X/L+0.1%) exhibited appealing advantages to produce bleached kraft bamboo pulp.

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