Effects of Residual Phenolic Compounds on Xylanase-assisted ClO_2 Bleaching of Hardwood Kraft Pulp

Paul Hsieh,[a] Chia-Ru Liu,[b] Chun-Han Ko,[b,*] Bing-Yuan Yang,[b] and Po-Heng Lin [c]

In both pulping and bleaching processes, lignin in the pulp fiber is degraded into smaller molecules that need to be rinsed away. However, despite the installation of automatic washing equipment, the small phenolic compounds among other lignin degradation products can hardly be completely removed from the brownstock. Among the myriad of small phenolic compounds degrading from lignin, some are water-soluble and highly reactive with bleaching reagents. To understand the impact of residual phenolic compounds from black liquor on pulp bleaching, six monomeric phenolic model compounds were tested in this study. Catechol and vanillin showed inhibitory effects on xylanase activity, while catechol, vanillin, and guaiacol interfered with the delignification reaction in the chlorine dioxide (D) and alkaline extraction (E) stages of the bleaching sequence, thereby preserving the integrity of cellulose in the pulp. Because the efficiency of xylanase and bleaching reagents is hindered by the presence of these phenolic compounds, higher operational cost and more bleaching reagents are needed, which are incompatible with modern environmental policies in the world. Nonetheless, the presence of remaining soluble phenolic compounds in the brownstock can improve the bleaching selectivity important for the production of high-quality pulp with less-degraded cellulose chains.

Keywords: Bleaching selectivity; Phenolic compounds; Catechol; Guaiacol; Vanillin; Xylanase; ClO_2; Brownstock

Contact information: a: Institute for Preservation and Conservation of Chinese Ancient Books, Fudan University, Shanghai 200433, People's Republic of China; b: Department of Forestry and Resource Conservation, National Taiwan University, Taipei 10617, Republic of China; c: Forest Utilization Division, Taiwan Forestry Research Institute, Taipei, Republic of China;
** Corresponding author: chunhank@ntu.edu.tw*

INTRODUCTION

With the increased public awareness of environmental protection, governments around the globe have reinforced strict laws against industrial pollution. Because chlorine-based bleaches produce high concentrations of toxic chloride and chlorinated organic compounds (AOX, dioxins), technologies including oxygen delignification, elemental chlorine free (ECF) bleaching using chlorine dioxide followed by alkaline extraction, lignin modified enzyme (LME)-based, and/or xylanase-assisted biobleaching have been developed and have largely replaced the highly contaminating chlorine-based bleaching (Vidal *et al*. 1997).

Xylanase is one of the major enzymes used for pulping and bleaching (Senior and Hamilton 1992; Tolan and Canovas 1992; Gangwar *et al.* 2014). It degrades xylan in the fiber pores, enhancing the permeation of bleaching reagents into the fiber. Xylanase can also cleave the lignin-carbohydrate bonds, rendering lignin fragments extractable in bleaching and washing processes. A reduced demand for bleaching chemicals, and thus

mitigation of the toxic pollutants such as absorbable organic halides (AOX) can be thus achieved (Gangwar *et al.* 2014; Sharma *et al.* 2020).

Although most modern pulp and paper mills wash the brownstock with automatic equipment, residual black liquor that contains lignin and its degradation products consisting of small aromatic compounds are difficult to remove completely (Santos and Hart 2014). The lignin degradation fragments, such as cinnamic acid, *p*-coumaric acid, caffeic acid, ferulic acid, 4-hydroxybenzoic acid, vanillin, tannic acid, syringaldehyde, gallic acid, guaiacol, acetovanillone, protocatechuic acid, and a myriad of monomeric phenolic compounds, may affect xylanase activity and xylanase-assisted bleaching (Niemelä and Alén 1992). The role of lignin fragments and small phenolic compounds relative to xylanase activity has been closely investigated in the past two decades. Soluble monomeric phenolic compounds, such as ferulic acid, prefer to bind to the thumb region of the xylanase protein, causing conformational change of the enzyme and influencing the fitting between xylanase and substrates, such as lignin-carbohydrate complexes and xylans (Boukari *et al.* 2011; Monclaro *et al.* 2019). The content of hydroxyl and methoxyl radicals in phenolic compounds also contributes to the affinity between the phenolic compounds and xylanase (Boukari *et al.* 2011). While many scientists have observed an inhibitory or deactivation effect of small phenolic compounds on xylanase activity (Buokari *et al.* 2011; Souza Moreira *et al.* 2013; Michelin *et al.* 2016; Ladeira Azar *et al.* 2018; Hamann *et al.* 2020), Kaya *et al.* (2000) earlier reported the benefits of black liquor and lignin degradation products for xylan hydrolysis by xylanase during the kraft pulping process.

This study investigated the impact of remaining monomeric phenolic compounds in brownstock on not only xylanase activity, but also pulp properties in the subsequent xylanase-assisted chlorine dioxide bleaching, attempting to elucidate the interactions between the enzyme, the inhibitor(s), and the pulp bleachability. The results might be useful for the design, control, and optimization of enzymatic treatment of lignocellulosic fibers in pulp and paper mills employing xylanase or laccase-mediator system (LMS), where the mediators are usually small phenolic compounds, such as vanillin, *p*-coumaric acid, guaiacol, syringaldehyde, acetosyringone, and trans-ferulic acid (Moldes *et al.* 2008; Fillat *et al.* 2010; Barnetto *et al.* 2012; Ladeira Azar *et al.* 2018; Singh and Arya 2019).

EXPERIMENTAL

Materials

The pulp

The pulp used in this study included unbleached and oxygen-bleached hardwood kraft pulp supplied by Chung-Hwa Pulp Corporation (Taiwan), consisting of Tasmania eucalypt (58.9%), Indonesian rhizophora (15.9%), Thai eucalypt (10.2%), Vietnamese eucalypt (9.4%), and Chinese northeast hardwoods mixture (5.6%). The pulp was thoroughly rinsed with water to remove residual chemicals before entering the bleaching sequence. The initial Kappa numbers of the unbleached and oxygen-bleached kraft pulp were 15.9 and 9.9, respectively.

The enzyme, reagents, and phenolic model compounds

The xylanase sample used was Pulpzyme HC$^{\bigcirc;R}$ supplied by Novozymes Company (Bagsværd, Denmark). It was produced from a genetically modified *Bacillus* bacterium *via*

submerged fermentation. Pulpzyme HC has endo-1,4-β-D-xylanase activity (E.C. 3.2.1.8) and is capable of catalyzing the hydrolysis of deacetylated xylan substrates. To measure xylanase activity, dinitrosalicyclic acid (DNS) reagent and buffers of analytical grade were used (Miller 1959). All reagents including dinitrosalicylic acid, potassium sodium tartrate tetrahydrate, xylose, xylan (Sigma Chemical Co., St. Louis, MO, USA), Tris buffer, $CaCl_2$, Tween 20, NaOH, and KOH were used as received. Six phenolic model compounds: catechol, *p*-coumaric acid, eugenol, guaiacol, syringic acid, and vanillin were acquired from Sigma Chemical (St. Louis, MO, USA) (Fig. 1).

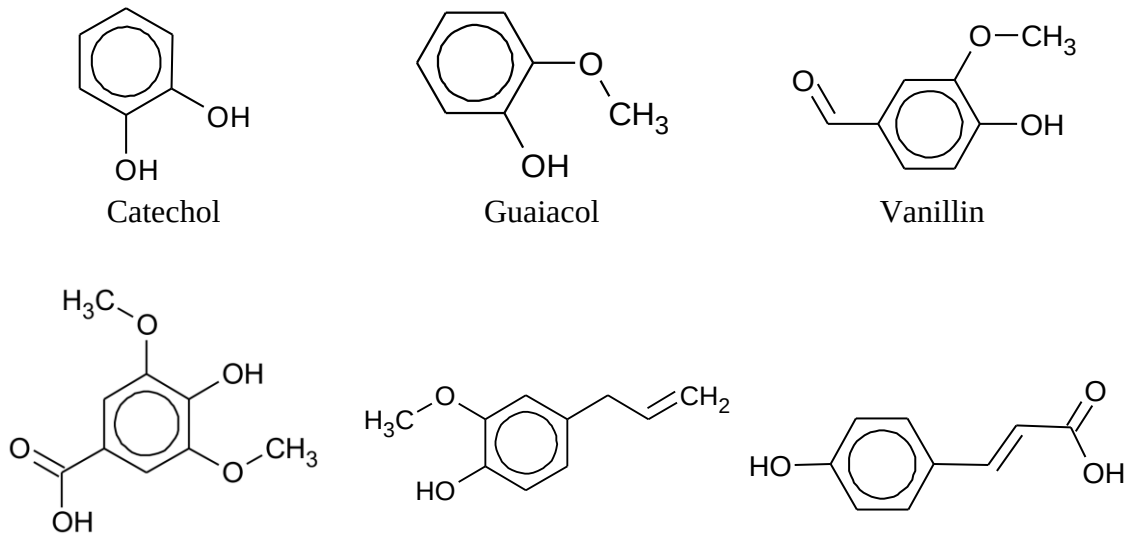

Fig. 1. Structures of the phenolic model compounds used in this study

Methods

Determination of xylanase activity affected by the phenolic compounds

The xylanase activity was determined by measuring the contents of reducing sugars released from birchwood xylan (1% w/v) by DNS method (Miller 1959). One unit of xylanase (IU) was defined as the quantity of enzyme required to release 1.0 μmol of xylose from birchwood xylan in one minute under the standard assay conditions (50 °C at pH 8).

The optimal pH and temperature for Pulpzyme HC were tested in Tris-HCl buffer. The enzyme solution with added phenolic model compounds of catechol, guaiacol, vanillin, syringic acid, eugenol, or *p*-coumaric acid (Fig. 1) was incubated at 50 and 60 °C for 30, 60, 120, and 180 min at pH 7 and pH 9. The residual activities of Pulpzyme HC were also measured by DNS method. Three independent measurements were performed to obtain a mean value.

The bleaching sequence with xylanase pretreatment stage in the presence of the phenolic model compounds

At the pretreatment stage, xylanase dosages of 6, 12, and 18 U/g ODP (oven-dried pulp) were added into 10% consistency of the kraft pulp. The reaction was continued at pH 8 and 50 °C for 3 h with 0, 5, 10, or 20 mM solutions of the phenolic model compounds in

the pulp. An aqueous solution of ClO_2 with 0.05, 0.15, 0.225, and 0.3 A.C.M. (active chlorine multiple) was then added into 8% consistency of the pulp and allowed to react at 70 °C for 1 h (D stage). Also known as Kappa factor, active chlorine multiple (A.C.M.) is defined as the ratio of the amount of (equivalent) chlorine applied in the initial chlorination stage to the amount of lignin in the pulp entering the initial chlorination stage:

$$\text{A.C.M.} = \text{Charge of } ClO_2 \text{ (wt\%)} \times 2.63 / \text{Kappa number of the pulp} \quad (1)$$

After rinsing with distilled water to remove residual reagents, the pulp was subjected to alkaline extraction with 1.5% NaOH at 65 °C for 1.5 h with 10% pulp consistency (E stage). The entire bleaching sequence and treatment procedures were repeated three times. The mean values of the three replicas were employed for pulp analysis.

Pulp analysis

The pulp's Kappa number, viscosity, and the ratio of change in Kappa number to the change in viscosity characterize the quality of pulp. Kappa number is defined as the number of volume (mL) of 0.1 N potassium permanganate solution consumed by 1 g of oven-dried pulp under the conditions specified in TAPPI T236 om-13 (2013). It can be referred to as an indication of the degree of delignification of the pulp and was used in this study to evaluate the effectiveness of bleaching operations of the kraft pulp.

Viscosity of pulp gives an estimate of the average degree of polymerization of cellulose in the pulp. It indicates cellulose integrity and the relative molecular weight during pulping/bleaching process. The cellulose in the pulp was dissolved in cupriethylenediamine (CED) solution according to the protocol given in "viscosity of pulp (capillary viscometer method)" (TAPPI T230 om-19 2019), measured by using Cannon-Fenske capillary viscometer (Model AK46460-200, Kimble$^{\bigcirc;R}$, DWK Life Sciences Inc., Rochester, NY, USA).

Bleaching selectivity is defined as the ratio of the reduction of the Kappa number to the loss of viscosity of the pulp during the pulping/bleaching process. Because the lignin content and the integrity of cellulose would both reduce during bleaching, the value of bleaching selectivity reveals the bleachability of the pulp.

Statistics

The means and standard deviations of each three-replica of independent measurements were obtained by MS Excel software. The means from a single plot were compared with each other by one-way ANOVA and post-hoc Scheffé test using OriginLab software to determine if the means are significantly different from each other at 5% significance level. Means that do not share a letter are significantly different from one another.

RESULTS AND DISCUSSION

Influence of the Phenolic Model Compounds on Xylanase Activity

Figure 2 illustrates the effect of catechol and vanillin on the relative activity of Pulpzyme HC. While guaiacol, syringic acid, eugenol, and *p*-coumaric acid did not noticeably affect Pulpzyme HC activity (figure not shown), the enzyme was deactivated by catechol and vanillin (Fig. 2). Pulpzyme HC was more susceptible to catechol in alkaline

condition than in neutral condition (Fig. 2a), whereas vanillin deactivated Pulpzyme HC to a similar extent in both neutral and alkaline conditions (Fig. 2b). Statistical analysis showed that xylanase activity was more susceptible to catechol than to vanillin. Generally, vanillin with concentration lower than 2.5 mM had no clear influence on xylanase activity; for instance, 2.5 mM vanillin in the first and the third diagrams (Fig. 2b) all shared the same letter a, while catechol with concentration as low as 0.5 mM could significantly reduce xylanase activity as illustrated by the different letters (Fig. 2a).

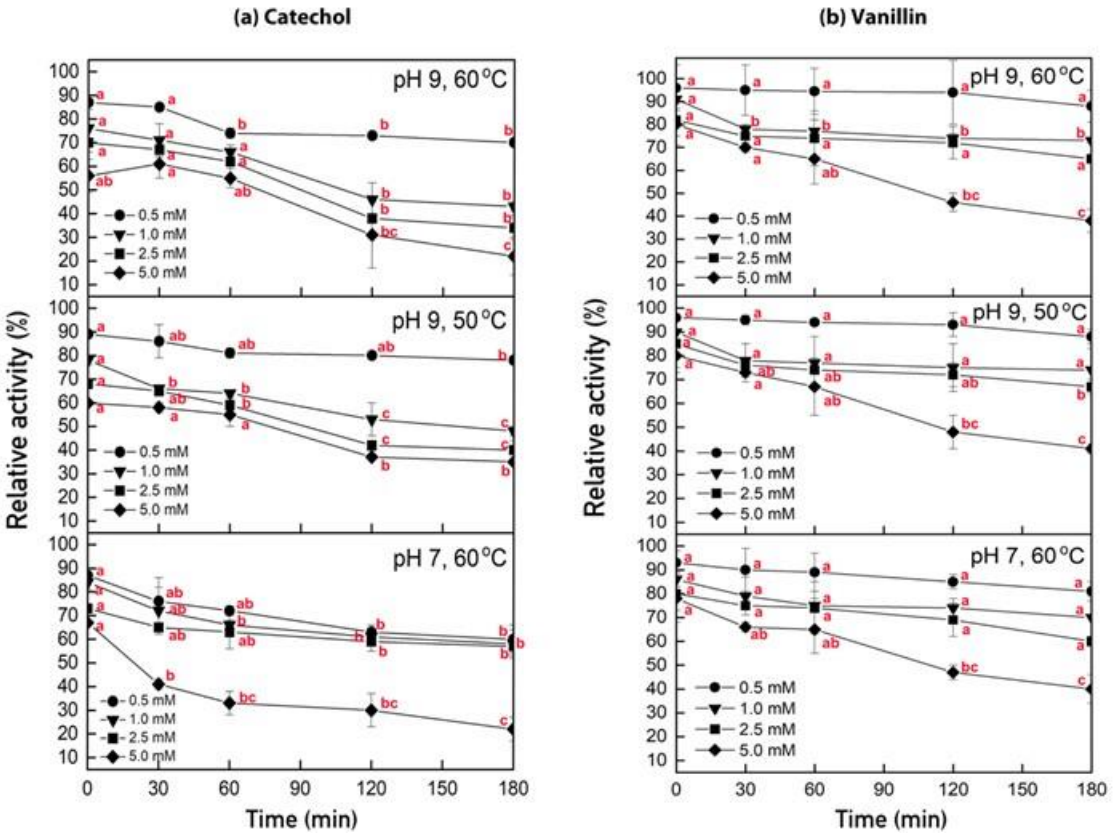

Fig. 2. Effect of (a) catechol and (b) vanillin concentrations on xylanase activity in neutral and alkaline warm conditions. Each dot represents the mean of three independent measurements and was compared within the same line at 5% significance level.

There are several factors contributing to xylanase activity, such as pH, temperature, pulp consistency, intensity of agitation, and lignin degradation products in pulp. Kaya *et al.* (2000) found that the addition of lignin degradation products, including vanillin and guaiacol, at concentrations ranging from 0.005% to 0.2% (equals to 0.33 to 13.2 mM for vanillin) increased the rate of xylan hydrolysis. Through using circular dichroism spectroscopy, they found that xylanase had interacted with black liquor, changing the molecular structure of the protein.

However, the current study demonstrated the opposite effects of phenolic compounds on xylanase activity. Further, after Kaya's report in 2000, quite a few studies have also shown the deactivation of xylanase by various phenolic compounds. Boukari *et al.* (2011) tested the effects of cinnamic acid, *p*-coumaric acid, caffeic acid, ferulic acid, and 3,4,5-trimethoxy-cinnamic acid on endo-β-1,4-xylanase, and observed strong negative impacts of all the five phenolic compounds on xylanase activity. Kinetic analysis revealed

a non-competitive multi-site inhibition mechanism, resulting in conformational alterations of the enzyme protein, thus inducing steric inactivation. Hamann *et al.* (2020) demonstrated that the thermal stability of endo-β-1,4-xylanase from *Clostridium thermocellum* was reduced by ferulic acid, syringaldehyde, cinnamic acid, 4-hydroxybenzoic acid, and *p*-coumaric acid. Tannic acid presented the strongest deactivation effect on the xylanase by reducing 80% of activity. Ladeira Azar *et al.* (2018) tested the tolerance of the 1:1 ratio enzyme mixture from *Chrysoporthe cubensis* and *Penicillium pinophilum* against five individual phenolic compounds of vanillin, *p*-coumaric acid, ferulic acid, tannic acid, and gallic acid. After incubation for 24 h, the enzyme mixture lost 60% to 65% of xylanase activity when 25 mM phenolic compound was present, and it lost approximately 80% activity with 75 mM phenolic compound in the system. The phenolic solution from alkali-treated sugarcane bagasse had even stronger inhibitory effect on xylanase. Michelin *et al.* (2016) showed that hemicellulases, including endoxylanase, were inhibited and deactivated by water-soluble and acetone-extracted phenolics from sugarcane bagasse. Moreover, Souza Moreira *et al.* (2013) compared the resistance of two β-xylanases from *Aspergillus terreus*. All six phenolic compounds, ferulic acid, *p*-coumaric acid, vanillin, cinnamic acid, tannic acid, and 4-hydroxylbenzoic acid, negatively inhibited one xylanase whereas the other xylanase was resistant.

The inconsistent effects of phenolic compounds on xylanase activity observed by various researchers may be attributed to the type of xylanase enzymes and the type of xylan used as the substrate. Monclaro *et al.* (2019) demonstrated that the opposing effects of phenolic compounds on xylanase activity could be explained by different types of xylan substrate. In the presence of phenolic compounds, the xylanase from *Aspergillus tamarii* was deactivated when oat spelt xylan was used as the substrate and activated when birchwood xylan or beech xylan was used.

The work of Monclaro *et al.* (2019) is important for this study. Because birchwood xylan is employed to determine xylanase activity in this study (Miller 1959), it only shows the hydrolysis of birchwood xylan but it cannot reflect the actual impact of phenolic compounds on xylanase hydrolysis of the hardwood xylans from *Eucalyptus* and *Rhizophora* spp. Therefore, more parameters rather than just xylanase activity have been examined in this study to obtain a thorough understanding of the influence of monomeric phenolic compounds on pulp quality and bleaching efficiency in the DE bleaching process.

Effect of the Phenolic Compounds on DE Bleaching Sequence with Xylanase Pretreatment

Among the six phenolic compounds tested, eugenol, *p*-coumaric acid, and syringic acid had no clear influence on DE bleaching sequence (data not shown), while catechol, guaiacol, and vanillin decreased the efficiency of the bleaching reagents. The effectiveness of DE bleaching sequence was adversely affected by the dissociation of the phenolic compounds in the system. At ambient temperature, for instance, the solubility in water for catechol, guaiacol, and vanillin that could decrease bleaching efficiency are 450 g/L, 15 g/L, and 10 g/L, respectively, whereas eugenol is insoluble and *p*-coumaric acid has weak solubility of 1.0 g/L. Although syringic acid has mild solubility of 5.8 g/L, like *p*-coumaric acid, they are both carboxylic acids, which are generally inactive with ClO_2 (Gan *et al.* 2020). The value of the slope of Kappa number over A.C.M. of ClO_2 decreased when catechol, guaiacol, or vanillin was added; higher concentration of ClO_2 was needed to oxidize a certain amount of lignin in the presence of the small phenolic compounds (Fig. 3). For instance, 0.3 A.C.M. ClO_2 lowered the Kappa number of the unprebleached pulp

from 16 to 5.2 when no monomeric phenolic compounds were added in the system. With the addition of 20 mM vanillin, in contrast, the Kappa number could only be reduced to 10.8 by 0.3 A.C.M (Fig. 3a). The influence of the small phenolic compounds on lignin removal in the oxygen pre-bleached pulp was still negative even though the slope was not as steep as that of the unprebleached pulp (Fig. 3b). The statistical analysis revealed that unprebleached pulp was more susceptible to ClO_2 bleaching than was oxygen prebleached pulp, as the letters assigned to the unprebleached pulp were much more diverse compared to the oxygen prebleached pulp (Fig. 3). Higher concentrations of monomeric phenolic compounds tended to reduce the efficacy of ClO_2. For instance, in the presence of 20 mM either catechol, guaiacol, or vanillin, different concentrations of ClO_2 had no significant effect on lignin removal, as illustrated by the shared letter a; without the presence of the monomeric phenolic compounds, in contrast, the effect of ClO_2 became significant as illustrated by the diverse letters (Fig. 3b). The monomeric phenolic compounds affected lignin removal from unprebleached pulp by ClO_2 also in the same trend (Fig. 3a).

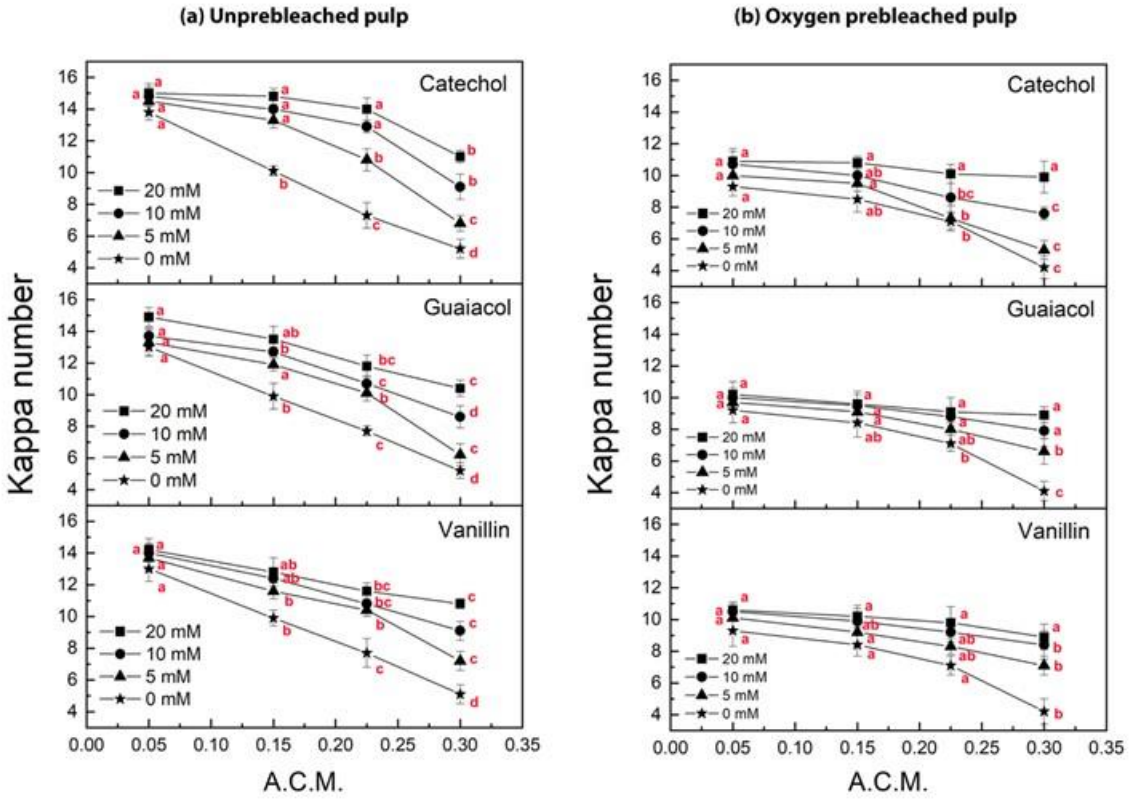

Fig. 3. Effect of the concentrations of phenolic compounds on Kappa number of (a) unprebleached pulp and (b) oxygen prebleached pulp with DE bleaching sequence. Each dot represents the mean of three independent measurements and was compared within the same line at the 5% significance level.

The negative impact of the residual phenolic compounds from the black liquor on the reduction of Kappa number during DE bleaching sequence could be attributed to the high reactivity of the dissolvable phenolics. Phenols react rapidly with ClO_2 at rates of 10^3 to 10^8 M^{-1} S^{-1} at neutral pH. The reaction rate constants of dissociated phenols with ClO_2 are generally around 6 orders of magnitude higher than those of undissolved phenols (Yu *et al.* 2015; Gan *et al.* 2020). Chlorine dioxide may react with the colorless residual

phenolic compounds and diffuse into the air in the form of $HOCl_{(g)}$, which may contribute to up to 50% of the total ClO_2 consumption (Rougé *et al.* 2018), thus decreasing the bleaching efficiency of the reagents for the chromophoric lignin.

Although the formation of organic halides (AOX) in ClO_2 bleaching process is as low as 15% to 25% of the conventional chlorine bleach (Zhang *et al.* 2019), it is reported that AOX in ClO_2 bleaching are mainly generated from chlorination of HOCl, lignin fragments (phenolic compounds), and hexenuronic acid (Rada *et al.* 2006). The presence of small phenolic compounds in DE bleaching sequence may contribute to AOX formation. However, it has been demonstrated that AOX formation in ClO_2 bleaching process can be reduced by 22% by the addition of ammonium thiosulfate, which consumes the excess ClO_2 in the system (Li *et al.* 2020). Because monomeric phenolic compounds also consume excess ClO_2, they might help reduce the formation of AOX. The actual role that phenolic compounds play on AOX formation/reduction deserves further investigation.

Because ClO_2 is consumed by catechol, guaiacol, and vanillin prior to reaching the pulp fiber, the components of the fiber become less accessible to the bleaching reagents. This leads to an ineffective removal of lignin from the fiber and results in higher Kappa number (Fig. 3). However, the bleaching reagents degrade the cellulose to a lesser extent. The presence of catechol, guaiacol, and vanillin in the pulp reduce the decline of pulp viscosity, which is in turn related to the molecular weight and average degree of polymerization of cellulose (TAPPI T230 om-19, 2019) (Fig. 4).

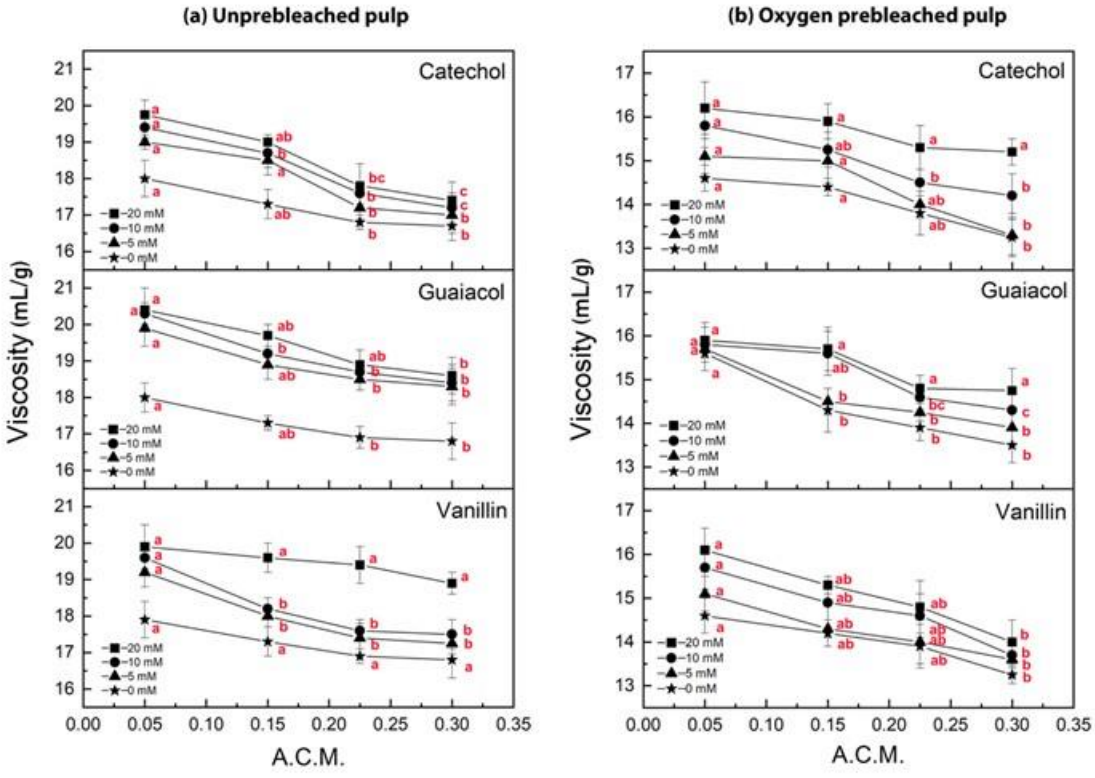

Fig. 4. Effect of the concentrations of phenolic compounds on the viscosity of (a) unprebleached pulp and (b) oxygen prebleached pulp with DE bleaching sequence. Each dot represents the mean of three independent measurements and was compared within the same line at 5% significance level.

The unprebleached kraft pulp had a viscosity of 18 after bleached by 0.05 A.C.M. in DE bleaching sequence without the additional monomeric phenolic compounds; however, when 20 mM vanillin was present, for instance, the pulp could preserve its viscosity at 20 (Fig. 4a). Catechol and guaiacol shared the similar trend with vanillin in reducing the loss of pulp viscosity in both the unprebleached and oxygen-prebleached kraft pulp, which is confirmed by the statistical analysis when most of the measurements shared the letters a, ab, or b, no matter the different kinds of phenolic compounds influencing either unprebleached pulp or oxygen prebleached pulp (Fig. 4).

Despite the fact that the phenolic compounds can decrease the degradation of cellulose in DE bleaching sequence, they also reduce the delignification efficiency of ClO_2. Hence, to evaluate the pros and cons of residual small phenolic compounds on pulp quality during bleaching, the ratio of the reduction of Kappa number to the reduction of pulp viscosity, known as bleaching selectivity, is calculated and discussed in the next session.

Xylanase has been applied to the removal of the lignin-carbohydrate complex (LCC) generated in the kraft process that acts as a physical barrier to the entry of bleaching chemicals (Yamasaki *et al*. 1981; Paice *et al*. 1992). In a pulp and paper mill, xylanase is usually added after the oxygen prebleaching stage to improve the bleaching efficiency of the reagents. As shown in Fig. 5, the addition of xylanase in DE bleaching sequence reduced Kappa number in both the unprebleached and oxygen prebleached pulps. Noticeably, without the addition of ClO_2 (*i.e.*, A.C.M. = 0), xylanase alone was able to decrease the Kappa number. Even though xylanase cannot degrade lignin directly, it attacks the LCC structure and renders lignin fragments in LCC easier to rinse away in the subsequent washing and bleaching processes, thereby reducing the demand for bleaching charge. It can be observed from the statistical analysis that without the addition of xylanase, ClO_2 removed lignin from the pulp more effectively, as illustrated by the high diversity of letters (Fig. 5a, the uppermost line). When 18 IU/mL xylanase was applied, ClO_2 became less effective in lignin removal, as illustrated by the assignment of only 2 letters (Fig. 5b, the bottom line).

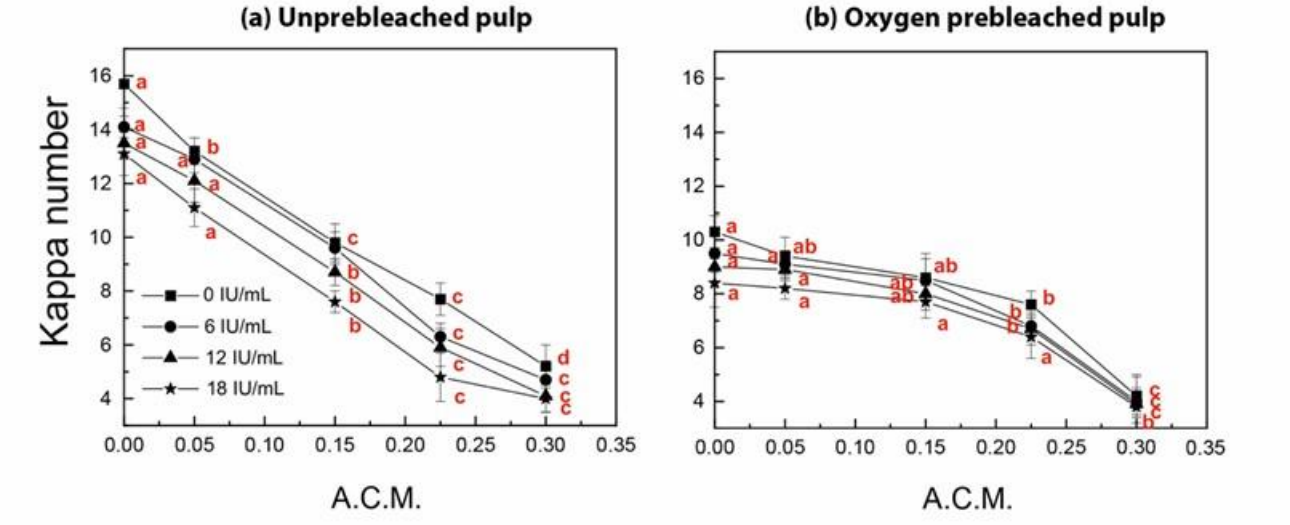

Fig. 5. Effect of xylanase concentration on Kappa number of (a) unprebleached pulp and (b) oxygen prebleached pulp with DE bleaching sequence. Each dot represents the mean of three independent measurements and was compared within the same line at 5% significance level.

Impact of the Phenolic Compounds on Bleaching Selectivity in DE Bleaching Sequence Pretreated with Xylanase

Bleaching selectivity represents the degree to which the bleaching agent can remove lignin without dissolving or removing the cellulose and hemicellulose in the fiber. It can be determined as the ratio of the reduction of Kappa number to the reduction of pulp viscosity during bleaching (Tavast *et al.* 2011).

Figure 6 illustrates that the DE bleaching sequence has a negative impact on the selectivity of the hardwood kraft pulp pretreated with xylanase (Pulpzyme HC); a higher A.C.M. of ClO_2 resulted in a lower achieved value of the bleaching selectivity. In comparison with the unprebleached pulp (Fig. 6a), oxygen prebleaching further reduced the selectivity in DE bleaching sequence (Fig. 6b). Moreover, xylanase pretreatment also negatively affected the bleaching selectivity of DE bleaching sequence for the kraft pulp as demonstrated in Fig. 7. The pulp pretreated with 18 IU/mL xylanase generally had lower bleaching selectivity in DE bleaching sequence than the pulp pretreated with 6 IU/mL xylanase. For instance, DE bleaching sequence with 0.15 A.C.M. of ClO_2 had bleaching selectivity of 1.6 for the pulp pretreated with 18 IU/mL xylanase in the presence of 20 mM catechol whereas the bleaching selectivity rose to 1.9 when xylanase dosage was reduced to 6 IU/mL.

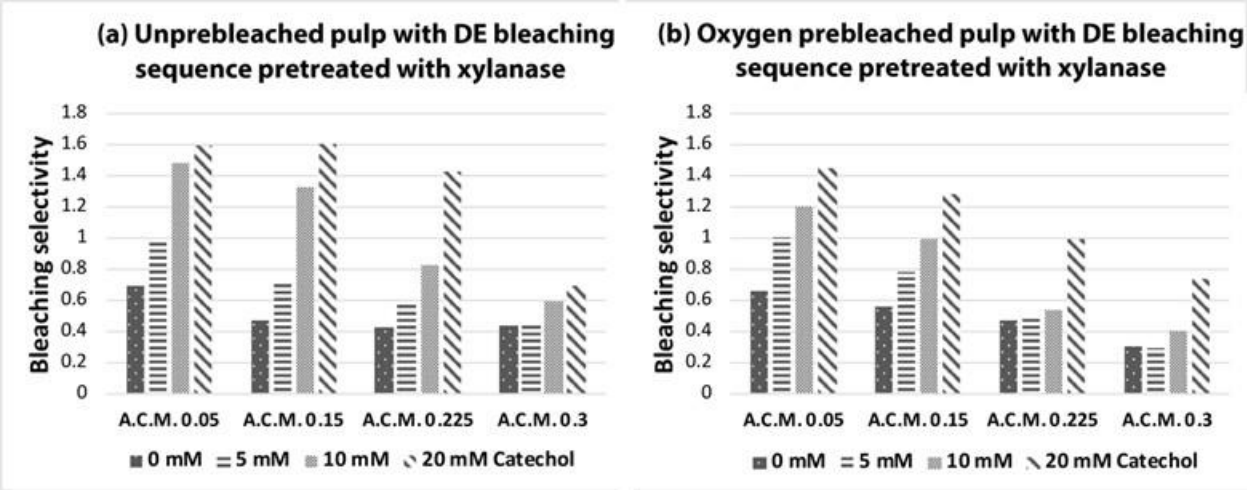

Fig. 6. Effect of catechol concentration on bleaching selectivity of DE bleaching sequence pretreated with 18 IU/mL xylanase for (a) unprebleached pulp and (b) oxygen prebleached pulp

Nevertheless, it is noteworthy that the presence of catechol in the pulp promoted the selectivity of DE bleaching sequence for both the oxygen prebleached (Fig. 6b) and the unprebleached pulps (Figs. 6a, 7); a higher concentration of catechol resulted in greater selectivity obtained in the DE bleaching sequence. As shown in Figs. 6a and 7, for instance, the presence of 20 mM catechol in the pulp pretreated with 18 IU/mL xylanase promoted the selectivity of 0.15 A.C.M. of ClO_2 from the original 0.47 without catechol to 1.6 in DE bleaching sequence. It has been observed that both guaiacol and vanillin promoted the bleaching selectivity of D.E. bleaching sequence with 18 IU/mL xylanase pretreatment in a trend the same as catechol (figure not shown). Syringic acid, eugenol, and *p*-coumaric acid did not demonstrate clear influence on the bleaching selectivity of D.E. bleaching sequence because acids generally do not react with ClO_2, and eugenol is insoluble in the system (Gan *et al.* 2020).

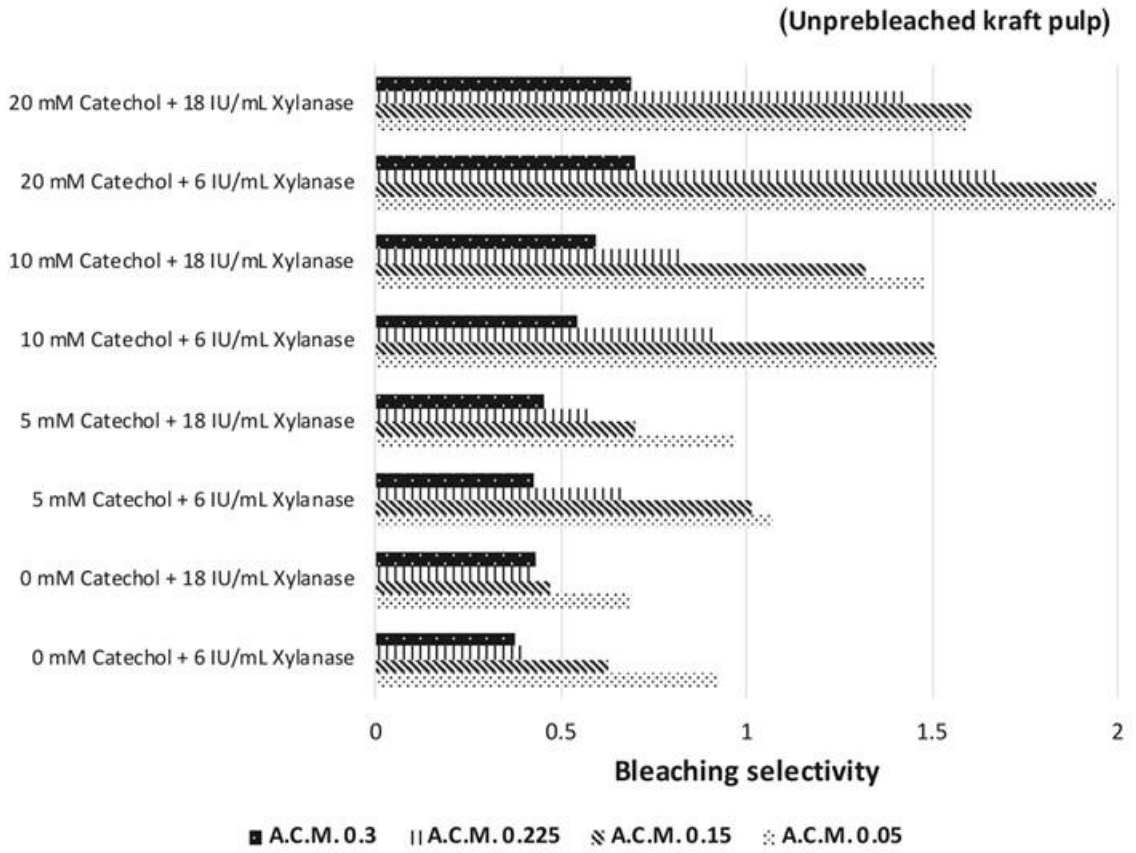

Fig. 7. Effect of various catechol and xylanase dosages on bleaching selectivity of DE bleaching sequence for the unprebleached kraft pulp

Although phenolic compounds do not directly react with the lignin and cellulose in the fiber, they inhibited the xylanase activity and thereby interacted rapidly with ClO_2, as discussed in the previous sessions. Because ClO_2 and xylanase both have negative consequences on bleaching selectivity, the presence of phenolic compounds in the pulp may serve as a buffer that decreases the activity and efficiency of the enzyme and bleaching chemicals detrimental to bleaching selectivity. In terms of pulp quality, the presence of residual monomeric phenolic compounds from black liquor may benefit the preservation of cellulose integrity by interacting with both xylanase and ClO_2 in the xylanase-assisted DE bleaching sequence.

CONCLUSIONS

1. Monomeric phenolic compounds are small lignin fragments commonly found in the brownstock. They are highly reactive with the bleaching chemicals such as ClO_2 that are consumed by these phenolic compounds before the chemicals can reach the pulp fiber.
2. Soluble phenolic compounds, such as vanillin and catechol, inhibit xylanase (Pulpzyme HC) activity, while guaiacol, syringic acid, eugenol, and *p*-coumaric acid show no obvious effect on the xylanase. The consumption and inactivation of ClO_2 and xylanase

by small phenolic compounds would inevitably increase the need for a higher amount of bleaching reagent and enzyme charge in xylanase-assisted DE bleaching sequence, thus raising the operation cost and the emission of toxic chemicals, like $HOCl_{(g)}$, that are against environmental policies in most countries.

3. The rare contribution of the residual small phenolic compounds from black liquor to pulping and papermaking seems to be the improvement of pulp properties. The small phenolic compounds "buffered" the bleaching system and make it less aggressive to cellulose by quickly reacting with ClO_2 and inhibiting the xylanase activity.
4. With the presence of the monomeric phenolic compounds, such as catechol, guaiacol and vanillin, the viscosity of the pulp can be preserved and the bleaching selectivity is enhanced. Although the other monomeric phenolic compounds tested did not demonstrate clear trends on bleaching selectivity, their presence did not reduce bleaching selectivity either. Nonetheless, due to the negative impacts of the phenolic compounds on xylanase activity, chemical efficiency, and the environment, it is not advisable to ignore a thorough washing of the brownstock or to use additional monomeric phenolic compounds to improve pulp quality. Environmental-friendly reagents should instead be tested to protect the cellulose integrity during xylanase-assisted DE bleaching.

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