Fiber Surface Chemistry in Relation to the Efficiency of Chlorine Dioxide Bleaching

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Relationships between fiber surface chemical components and the efficiency of chlorine dioxide bleaching were studied using chemical analysis in combination with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The amount of surface lignin decreased quickly at the beginning of the bleaching, and the brightness increased during the bleaching. Surface oxidation took place immediately, and the amount of lignin on the fiber surface decreased during the bleaching, especially in the first 5 min. The ratio of aromatic carbons to aliphatic carbons also decreased, which indicated that the lignin was degraded and new aliphatic carbons formed that might noticeably deposit on the surface of the fiber. The aliphatic carbons reacted with the in-situ formed hypochlorous acids, and thus affected the bleaching efficiency. Further bleaching led to the deposition of more acidic functional groups on the fiber surface with increased acidity-basicity ratios, which also affected the whole efficiency of bleaching.

Keywords: Bagasse pulp; Fiber surface chemistry; Chlorine dioxide bleaching; ATR-FTIR; XPS

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INTRODUCTION

Knowledge of the distribution of chemical components in pulps is important to improve existing bleaching processes. The unbleached pulp mainly consists of cellulose, hemicellulose, and a small number of residual lignin and extractives (Casey 1980). It has been shown that the residual lignin of chemical pulp is difficult to remove by bleaching (Matuana et al. 2001). Most of the residual lignin and extractives are enriched on the surface of the unbleached pulp fibers (Orblin and Fardim 2010). These lignin and extractives will reduce the reactivity of bleaching chemicals to pulp fibers. In fact, lignin and extractives are not evenly distributed in the fibers of unbleached pulp; it is an inherent property of wood as a consequence of its cellular structure (Sjöström 1981). Chlorine dioxide is currently used as the principal bleaching agent in the element chlorine free (ECF) bleaching process (Nie et al. 2014a,b; Yao et al. 2017). The surface chemistry of pulps plays an important role in chlorine dioxide bleaching. Surface reactions, rather than the liquid phase reactions, at fiber walls are a key step in removing the chromophore (Song et al. 2016; Nie et al. 2017). The surface charge of pulps increases during chlorine dioxide bleaching because of lignin oxidation and new carboxylic groups forming (Sundberg et al. 2000).

For the past few years, many approaches have been employed to determine the surface properties of pulps. Spectroscopic methods, such as X-ray photoelectron
spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and Fourier transform infrared (FTIR) spectroscopy (Matuana et al. 2001; Dchesne et al. 2003; Nakamata et al. 2010; Orblin and Fardim 2010; Yao et al. 2015), have been employed to characterize the surface chemistry of pulps. A combination of different spectroscopic methods could provide better insight into the complex fiber surface and more chemical information. X-ray photoelectron and FTIR spectroscopy are best suited for studying the surface of lignocellulosic fibers (Matuana et al. 2001). For wood fibers, only oxygen and carbon can be analyzed by XPS, and the results are usually reported as differences in the ratios of oxygen to carbon (O/C), allowing discrimination between carbohydrates, lignin, and extractives (Dchesne et al. 2003).

The chemical properties of chlorine dioxide bleached bagasse pulp and their correlation to surface properties have not been reported. The goal of this work is to study the changes taking place in the surface chemistry of bagasse pulps during chlorine dioxide bleaching. The attenuated total reflectance- Fourier transform infrared spectrum (ATR-FTIR) spectroscopy and XPS were employed to monitor changes in the surface chemistry of the pulp. The ratio of aromatic carbons to aliphatic carbons and ratio of acidity to basicity were investigated, and important information was provided on how pulp surface chemistry changes during chlorine dioxide bleaching.

EXPERIMENTAL

Materials

Unbleached pulp was obtained from a bagasse pulp mill of Nanning, China and air-dried in the laboratory. The bagasse pulp had an initial brightness of 43.2% ISO and a Kappa number of 9.89. The assay reagents were obtained from Sigma (San Francisco, CA, USA). All the other chemicals used in this work were purchased from Chong Qing Kawahigashi Chemical Co., Ltd. (Chongqing, China). All of the chemicals were of analytical grade.

Bleaching operation

The chlorine dioxide bleaching was conducted at 10% consistency and performed in plastic bags. The initial pH was 3.5, and the temperature was maintained at 60 °C during the bleaching. The bag was then placed in a water bath (60 °C) and kneaded at 10 min intervals. The bleaching liquor and pulp were sampled when reacting for 0 min, 5 min, 15 min, and 30 min. After bleaching, the bag was cooled to room temperature and opened. The pulps were extracted by acetone and kept dry for ATR-FTIR and XPS analysis.

Methods

ATR-FTIR spectra analysis

The ATR-FTIR spectra of untreated and chlorine dioxide-treated pulps were obtained on a NEXUS 470 FTIR spectrometer (Nicolet, Madison, WI, USA) and ZnSe crystal ATR (Nicolet, Madison, WI, USA). The spectra were obtained with 4 cm\(^{-1}\) resolution and 256 scans were carried out for the sample spectra. All infrared spectra were recorded in the 4000 cm\(^{-1}\) to 450 cm\(^{-1}\) range (Nie et al. 2015).
XPS analysis
The XPS analysis was performed according to the authors’ previous studies. It was performed on a Leybold Max200 XPS system (Leybold, Cologne, Germany). The samples were flattened and dried after being fully washed. After drying, samples were put into the Soxhlet device and extracted for 4 to 6 hours with acetone and distilled water. The samples were then placed on clean smooth metal slides, pressed lightly, and dried at room temperature.

The smooth sides were used for XPS measurement. The X-radiation source was obtained by electron bombardment of Al under 12 or 15 kV and at 15 to 25 mA. The XPS spectra were obtained with a vacuum of $1138 \times 10^{-7}$ Pa, and a photoelectron take-off angle of 90°. The oxygen and carbon atoms ratio (O/C) was calculated by a low-resolution X-ray photoelectron spectroscopy, where the pass energy was 192 eV. The sensitivity factor of carbon was 0.32 and oxygen of 0.75 (Nie et al. 2015).

RESULTS AND DISCUSSIONS

Chlorine Dioxide Bleaching of the Bagasse Pulp
The unbleached bagasse pulp was bleached by chlorine dioxide. It was obtained at a temperature of 60 °C, an initial pH of 3.5, and a chlorine dioxide dosage of 10 kg/odt, 30 kg/odt, and 50 kg/odt. As shown in Fig. 1, the lignin decreased 45% and the brightness increased 30.4% ISO at a chlorine dioxide dosage of 50 kg/odt within the first 5 min.

As the reaction continued, the lignin decreased and brightness increased more slowly. Similar results were obtained at different levels of chlorine dioxide dosage. The viscosity decreased lightly, which meant that a small amount of cellulose was degraded during the chlorine dioxide bleaching. Hart and Hsieh (1993) suggested that chlorine dioxide could easily react with some components of the unbleached pulp under acidic conditions, which occurred quickly at the beginning of the bleaching. Kolar et al. (1983) reported that more than 60% of the chlorine dioxide was converted into hypochlorous acid during the bleaching.

The hypochlorous acid reacts with lignin rapidly and creates phenolic hydroxyl groups (Ni 1992). Generally, the chlorine dioxide tended to react with phenolic lignin structures; the lignin fragments deposited on the surface of the fiber reacted with hypochlorous acids, so the bleaching efficiency was improved by the formation of hypochlorous acids. Other functional groups of the fiber surface formed during the bleaching reaction with the electron donor, which also affected the whole efficiency of the bleaching.

ATR-FTIR Analysis of the Fiber Surface
The surface chemistry of the sampled pulp (at 0 min, 5 min, 15 min, and 30 min) during the chlorine dioxide bleaching was studied by ATR-FTIR and XPS. The ATR-FTIR spectroscopy was used to determine the changes of the chemical groups on the surfaces of the pulp samples. The ATR-FTIR spectra of the sampled pulps recorded in the range of 1750 cm$^{-1}$ to 1000 cm$^{-1}$ are shown in Fig. 2.
Fig. 1. Residual lignin (a), brightness (b), and viscosity (c) during the chlorine dioxide bleaching.
The bands at 1105 cm\(^{-1}\), 1130 cm\(^{-1}\), 1145 cm\(^{-1}\), 1152 cm\(^{-1}\), 1259 cm\(^{-1}\), 1270 cm\(^{-1}\), 1340 cm\(^{-1}\), 1426 cm\(^{-1}\), 1595 cm\(^{-1}\), 1615 cm\(^{-1}\), and 1652 cm\(^{-1}\), referred to as C-H, O-H, -OCH\(_3\), or CH\(_2\) bending frequencies, indicate that a large amount of lignin was contained in the pulp (Mohammed-Ziegler \textit{et al.} 2004; Kaparaju and Felby 2010; Xu \textit{et al.} 2011). The band at 1652 cm\(^{-1}\) is referred to as the C=O stretching in conjugated p-substituted aryl ketones (Xu \textit{et al.} 2011). The relative intensity of this band decreased during the bleaching, especially in the first 5 min. In the bagasse pulp, lignin is a phenolic random polymer and contains a large number of aromatic rings. The assignment at 1615 cm\(^{-1}\) is referred to as aromatic skeletal vibrations plus a C=O stretch, and it decreased after the chlorine dioxide treatment, which showed that most of the lignin was degraded and that most of the aromatic ring plus the C=O structure was destroyed (Pang \textit{et al.} 2012). The relative intensity of the band at 1595 cm\(^{-1}\), which was assigned to the aromatic skeletal vibrations, decreased during the bleaching, indicating the decrease in the lignin content. The relative intensity of the band at 1426 cm\(^{-1}\) decreased during the bleaching, which meant that some methoxyl groups were removed. The peaks at 1270 cm\(^{-1}\), 1259 cm\(^{-1}\), 1152 cm\(^{-1}\), 1145 cm\(^{-1}\), 1130 cm\(^{-1}\), and 1105 cm\(^{-1}\) decreased and gradually disappeared during the chlorine dioxide bleaching, which showed that the lignin content of the fiber surface was largely removed after the chlorine dioxide treatment.

**XPS Analysis of the Fiber Surface**

X-ray photoelectron spectroscopy is an analytical technique that has been employed widely to analyze the chemical composition of a fiber’s surface (Yu \textit{et al.} 2002). The XPS method provided a qualitative analysis for the chemical elements of the fiber surface based on the chemical shift of the electron binding energy. The key points of the XPS method were oxygen and carbon analyses (Nie \textit{et al.} 2015). Assuming that all extractives were removed during extraction and that the surface consists of either lignin or carbohydrates, the content of surface lignin can be calculated by the (O/C) ratio of the fiber.
As reported by Kocaefe et al. (2013), the O/C ratio could directly indicate the oxygen content of the fiber surface. A higher O/C ratio means higher carbohydrate content on the fiber surface, while lower O/C ratio indicates higher lignin content (Kocaefe et al. 2013). As shown in Table 1, the O/C ratio obtained was 0.58 for the control pulp (0 min), and increased to 0.59, 0.60, and 0.63 for chlorine dioxide treated at 5 min, 15 min, and 30 min, respectively, which suggested that the lignin of the pulp surface gradually decreased as the bleaching progressed.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>O (%)</th>
<th>C (%)</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.54</td>
<td>63.46</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>37.02</td>
<td>62.98</td>
<td>0.59</td>
</tr>
<tr>
<td>15</td>
<td>37.33</td>
<td>62.67</td>
<td>0.60</td>
</tr>
<tr>
<td>30</td>
<td>38.53</td>
<td>61.47</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 1. The Atomic Composition and Surface Coverage of Lignin

Table 2. The C1s Peak Areas of the Bagasse Fibers

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>C1s Total = 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1 (%) (C=C or C-H)</td>
</tr>
<tr>
<td>0</td>
<td>22.92</td>
</tr>
<tr>
<td>5</td>
<td>19.68</td>
</tr>
<tr>
<td>15</td>
<td>20.02</td>
</tr>
<tr>
<td>30</td>
<td>17.07</td>
</tr>
</tbody>
</table>

These results were in accordance with the ATR-FTIR results. Generally speaking, the C1 (C-H or C-C) is considered to refer to only lignin (as the extractives were removed); C2 (C-O) and C3 (O-C=O or C=O) exist in the cellulose and hemicelluloses, and C2 can be seen for some lignin (low level), while C4 (O=C=O) represents carboxylic acids. The lignin content change was also confirmed by the decrease in the amount of C1 from 22.9% to 17.1% during the chlorine dioxide bleaching as shown in Table 2 and in Fig. 3, in the high-resolution XPS spectra of C1s.

High resolution XPS could identify the non-equivalent carbon functionalities of the fiber surface (Xu et al. 2011). It was observed that the chlorine dioxide treatment resulted in a decrease of C1 and increase of C2, which indicated that the residual lignin of the pulp was mostly removed by chlorine dioxide. The results of surface chemistry were similar with those of the earlier studies about chlorine dioxide bleaching. Backman and Gellerstedt (1993) found that the O/C ratio increased significantly during the oxidative treatment of a softwood kraft pulp. This ratio increased from 0.36 to 0.50 after bleaching of an elemental chlorine free (ECF) sequence. Zhong et al. (2010) reported that the surface lignin concentration of sisal fiber could be decreased up to 51% of the untreated fiber after chlorine dioxide treatment.
Fig. 3. The XPS spectra of the bagasse fibers during the bleaching (a) 0 min, (b) 5 min, (c) 15 min, (d) 30 min

Effects of Surface Chemistry

In wood fibers, the C1 peaks stand for the aromatic carbon and C2 peaks for aliphatic carbon. The C1/C2 ratios were considered as a reflection of the aromatic carbons content of lignin in the bleached samples (Kocaefe et al. 2013). Changes to the C1/C2 ratios of pulp samples during chlorine dioxide bleaching are shown in Fig. 4. It could be seen that the C1/C2 ratios of all three pulp samples decreased after bleaching for 5 min, 15 min, and 30 min. This was mainly because of the decrease in aromatic carbons from the lignin degradation caused by chlorine dioxide treatment, and the possible formation of new aliphatic carbons that might have noticeably deposited on the surface of the fiber. The (C1/C2) ratio was reduced remarkably after bleaching for 5 min and then continued to decrease to approximately 0.3 with a lower rate up to 30 min. This is similar to the decreasing content of lignin. It can be seen from Fig. 1(a) that the residual lignin was reduced by about 45% after bleaching for 5 min (chlorine dioxide dosage: 50 kg/odt), and then continued to decrease approximately 25% in the following 25 min. Due to the selective
oxidation of chlorine dioxide, cellulose and hemicellulose were not oxidized at the beginning of the chlorine dioxide bleaching stage.

As is known, the interfacial interaction of polymers with liquid can clearly be affected by the acid-base properties of the polymers due to the formation of hydrogen bonds (Shen et al. 1998). Fowkes (1990) reported that the XPS was a useful technique for characterizing the acid-based properties of the fiber surface. The lower electron binding energies of the XPS spectra can be attributed to basic and electron-donating atoms (Fowkes 1990). Thus, C1 and C3 are classed as basic by the relation of C-H, C-C, O-C-O, and C=O groups, and C2 and C4 are suggested to be acidic in accordance with the OH, C-O, and O=C–O groups. Based on the acid-base theory of Fowkes, the acidity and basicity can be calculated from (C2 + C4) and (C1 + C3), respectively. The ratio of acidity to basicity (A/B) could be expressed as (C2 + C4) / (C1 + C3) (Kocaefe et al. 2013).

Changes in the A/B ratios of the pulp samples during chlorine dioxide bleaching are also shown in Fig. 4. The results indicated that the bleached pulps (at 5 min, 15 min, and 30 min) had higher A/B ratios than the untreated pulps (0 min), and the A/B ratios constantly increased as the bleaching time increased. This meant that the chlorine dioxide treatment caused an increase in the pulp acidity during this study. The pulp acidity might be correlated with the degradation of lignin and the cellulose layer left on the fiber surface. De Meijer et al. (2000) reported that the accepting component of surface free energy electron of wood fiber (1.1 mJ m⁻²) was lower than that of cellulose (1.67 mJ m⁻²). Therefore, higher A/B ratios indicated higher cellulose content and lower lignin content on the fiber surface after bleaching. In contrast, higher A/B ratios might also be associated with the degradation of the lignin-carbohydrate complex (LCC). The ether, ester, and glycosidic are the most frequent linkage types of the LCC (Fengel and Wegener 2011). The degradation of these three linkages because of bleaching might result in the generation of acidic functional groups of O=C–O, CH₃-OH, and OH. All these groups increased the acidity of chlorine dioxide-treated pulp surfaces. As the bleaching time continued to increase, more acidic function groups turned up on the fiber surface, and the A/B ratios constantly increased.

![Fig. 4. Ratio of aromatic carbons/alkiphatic carbons (C1/C2) and acidity/basicity (A/B) of bagasse pulp during chlorine dioxide bleaching](image-url)
CONCLUSIONS

1. Both ATR-FTIR and XPS spectroscopy were employed to effectively study the surface chemistry of the bagasse pulp during chlorine dioxide bleaching.

2. The results indicated that both the amount of residual lignin and the reactivity varied with various bleaching times. The lignin was degraded and the lignin amount decreased noticeably with increased bleaching time.

3. Some new aliphatic carbons were formed, which might have noticeably deposited on the surface of the fiber with the degraded lignin. The aliphatic carbons and lignin fragments reacted with the in-situ formed hypochlorous acids, and acidic functional groups appeared on the fiber surface, all which affected the bleaching efficiency.

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REFERENCES CITED


hydrogen peroxide," Bioresource Technology 216, 1098-1101. DOI:
10.1016/j.indcrop.2016.11.046
TMP suspensions," Journal of Wood Chemistry and Technology 20(1), 71-92. DOI:
10.1080/02773810009349625
(2011). "Fiber surface characterization of old newsprint pulp deinked by combining
hemicellulase with laccase-mediator system," Bioresource Technology 102(11),
6536-6540. DOI: 10.1016/j.biortech.2015.07.115
hemicelluloses and characterization of solid remainder," Bioresource Technology
185, 21-7. DOI: 10.1016/j.biortech.2015.02.052
hemicellulose by hot water to reduce adsorbable organic halogen formation in
chlorine dioxide bleaching of bagasse pulp." Industrial Crops and Products 96, 178-
185. DOI: 10.1016/j.indcrop.2016.11.046
non-wood pulps," Industrial Crops and Products 15(2), 123-130. DOI:
10.1016/s0926-6690(01)00102-9
fiber: Surface lignin and its influences on fiber surface characteristic and interfacial
DOI: 10.15376/biores.5.4.2431-2446

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DOI: 10.15376/biores.12.4.9302-9312