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Effect of hot chlorine dioxide delignification on AOX in bagasse pulp wastewater

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Abstract This work describes the effect of the hot chlorine dioxide delignification (D_{HT}) on the properties of bagasse fiber and the formation of AOX. The bagasse pulp was subjected to both D_{HT} and normal temperature chlorine dioxide delignification (D_0), and the AOX contents in the effluent were determined respectively. The GC–MS results showed that the main components of the D_0 stage wastewater were chlorinated hydrocarbons and chlorinated diphenyls. In contrast, those AOXs in the D_{HT} stage wastewater were very few. The GC–MS, ATR-FTIR, and XPS results showed the D_{HT} process is more effective in the removal of the residual phenolic lignin and the hemicellulose-linked HexA compared with D_0. Furthermore, in comparison, the AOX content could be reduced by 50% with D_{HT}. The fully bleached pulp obtained via $D_{HT}E_pD$ process has a higher brightness than that obtained by D_0E_pD, which provides a reliable theoretical basis for industrial application.

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Introduction

Paper mill wastewater contains toxic compounds that include endocrine disruption complex mixtures and other genotoxic agents (Balabanič et al. 2017). The key to sustainable development involves reducing environmental pollution and this can be achieved by handling and controlling parameters such as chemical oxygen demand (COD), ammonia-nitrogen (NH_4-N) and adsorbable organic halides (AOX) in industrial effluent (Zhang et al. 2012). Some of the AOXs are toxic and extremely harmful compounds that are mainly produced from the chlorine bleaching of fibers. To date, the fiber delignification technology has mainly focused on elemental chlorine-free (ECF), totally chlorine-free (TCF), and waste-free bleaching methods in order to reduce or check the formation and release of AOX. Currently, ECF is the most widely used bleaching technique owing to the regulations dictating the type of bleaching agent, equipment, and technology that can be employed. The main chemical in ECF bleaching technology is chlorine dioxide. Even though the normal chlorine dioxide delignification process is highly selective, it results in the production of several types of AOX. In this process, free chlorine is generated from chlorine dioxide, which reacts with

the residual lignin and hexenuronic acid (HexA) to produce AOX (Nie et al. 2014). Tarvo et al. have found that the formation of AOX is a result of the decomposition of organic chlorinated compounds (OX) in the chlorine dioxide delignification of kraft pulp with the passage of time (Tarvo 2010b). Bjorklund et al. have reported that there are two types of AOX; the unstable AOX that are obtained from HexA in the pulp and the stable AOX species that are related to the Klason lignin content of the pulp (Björklund et al. 2004). The recent studies involving means of AOX control have suggested adopting reduction technology together with the chlorine dioxide delignification process, mainly via control of the invalid decomposition of chlorine dioxide in the bleaching process (Ventorim 2005) and removal of the AOX precursors via pretreatment (Cadena et al. 2011; Nie et al. 2015; Sharma et al. 2014; Yao et al. 2017). Another strategy involves follow-up treatment to the bleaching effluent to reduce the amount of AOX. These methods mainly include Fenton up-flow anaerobic treatment, UV degradation, bioremediation, activated carbon adsorption, ultrafiltration, reverse osmosis, electrodialysis etc. (Chaparro and Pires 2015; Deshmukh et al. 2009; Osman et al. 2013; Savant et al. 2006; Tiku et al. 2010). Mjm et al. have evaluated the dehalogenation of the hydroxide ions and found that eliminating the washing steps between D_0 and alkaline extraction (E_p) reduces 65% of AOX (Magara et al. 2006; Mjm et al. 2001). By the addition of sodium sulfide in the alkaline extraction section of the ECF bleaching technique, AOX can be reduced to ca. 40–50%. These methods are mainly achieved by reducing the phenolic hydroxyl groups in the pulp (Nie et al. 2016). The bleaching effluent first undergoes anaerobic treatment, followed by aerobic microbial degradation to remove 82% of the AOX content (Singh and Thakur 2006). However, Gomes et al. have found that while biological treatment proved ineffective toward AOX removal in bleached wastewater, AOX undergoes reduction if the pulp materials are subjected to moderate acid hydrolysis before delignification or hot chlorine dioxide delignification (Gomes et al. 2007).

The reaction conditions of hot chlorine dioxide delignification are typically severe. Juutilainen et al. set a pH of 8.5–10 in order to prevent the formation of hypochlorous acid and promote the oxidative degradation of HexA, but the results have been

unsatisfactory (Juutilainen et al. 1999). Eiras et al. have optimized the conditions of hot chlorine dioxide delignification and were able to improve the delignification efficiency and selectivity. After optimization of the hot chlorine dioxide delignification process, ca. 7% of the operational costs are conserved, and the properties of the fibers are also improved (Eiras and Maria 2002). Hot chlorine dioxide bleaching can thus control the formation of AOX. When the eucalyptus pulp is subjected to oxygen delignification after hot chlorine dioxide delignification, AOX can be reduced by 40–50% than under normal temperature chlorine dioxide delignification conditions (Ventorim 2005). Chlorine dioxide and lignin are more susceptible to oxidation during hot chlorine dioxide delignification, while the formation of lignin chloride is inhibited (Magara et al. 2006). In addition, the residual HexA and lignin are also degraded under the hot and acidic conditions (Magara et al. 2006). The hot chlorine dioxide delignification process which operates with high efficiency also helps in reduction in the dosage of chlorine dioxide (Jiang et al. 2006; Petit-Breuilh et al. 2004). Above all, if the D_{HT} is used in the first stage of ECF bleaching by replacing D_0, the amount of chemicals utilized in the process can be reduced in addition to the AOX content and other chlorinated species present in bleaching wastewater, thus improving the environment.

In this work, the effect of D_{HT} on the fiber structure of bagasse has been studied. By using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) combined with X-ray photoelectron spectroscopy (XPS), the lignin characteristics of pulp fiber before and after the D_{HT} have been analyzed and compared with the D_0 process. The effect of the D_{HT} on AOX was studied using gas chromatography-mass spectrometry (GC–MS) and an AOX analyzer.

Materials and methods

Chemicals and raw materials

The bleached pulp and chlorine dioxide were taken from the pulp mill of Guangxi China. The kappa number, brightness, viscosity and HexA content of unbleached pulp were 8.7, 43.24%ISO, 1095 ml/g and 15.31 µmol/g, respectively. Chlorine dioxide solution was stored in a brown bottle and the concentration of

available chlorine was 21.16 g/L. All other chemicals used in this study were purchased from Zhiyuan chemical reagent company (Tianjin, China), and all of chemicals are analytical grade.

Hot chlorine dioxide delignification

The bagasse pulp (60 g bone dry) with deionized water was mixed in plastic bags and the pulp consistency was keep at 10% during the delignification process. Chlorine dioxide was added to the pulp slurry when the reaction temperature reached the demand of D_{HT} treatment. The chlorine dioxide bleached pulps were completely washed and the E_p and D_1 stages were performed at 10% consistency in plastic bags. Other parameters were shown in Table 1. The pulp were kneaded every 5 min during the bleaching until the end. Collected bleach wastewater to be tested and the pulps were washed with distilled after delignification. The bleached pulp were placed in a lab with constant temperature and constant humidity for 24 h and then subjected to characterization.

Analysis methods

Determination of pulp characteristics and bleaching effluent

The brightness, the kappa number, the viscosity and HexA content of bagasse pulp were determined according to the standard of Tappi (T 560 om-05), Tappi (T 236 om-99) Tappi (T230 om-04) and Tappi (T282 sp-07) respectively.

The AOX measurements were employed by Multi X 2500 halide analyzer (Jena, Germany). The basic

Table 1 Process parameters of $D_0E_pD_1$ and $D_{HT}E_pD_1$ of bagasse pulp

Bleaching stage	A	D_0	D_{HT}	E_p	D_1
ClO_2 (kg)/odt pulp	–	24	24	–	6
Temperature (°C)	90	60–65	85–95	65–70	70 ± 1
H_2O_2 (kg/t)	–	–	–	0.6	–
NaOH (kg/t)	–	–	–	10	–
pH	3	3–4	3–4	11–12	3–4
Consistency (%)	10	10	10	10	10
Time (min)	90	60	120	120	120

method and process as follows: bleaching effluent first through the activated carbon column, the organic chloride of the bleaching effluent then adsorbed by the activated carbon column. Sodium nitrate was used in washing the adsorbed inorganic chloride of the activated carbon column, and then the activated carbon column burned in the combustion furnace. Content of AOX calculated though the micro coulomb titration method (Nie et al. 2014).

ATR-FTIR spectra analysis

ATR-FTIR spectra (4000–450 cm^{-1}) were recorded by employing ZnSe crystal ATR (USA) and NEXUS 470 FTIR spectrometer (Canada). Spectra were obtained with 4 cm^{-1} resolution and 256 scans were carried out for sample spectra (Nie et al. 2015).

XPS spectra analysis

The hand sheets were dried after fully washed (basis weight: 80 g/m^2). After drying, samples were put into the Soxhlet and extracted for 4–6 h 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 X-ray photoelectron spectroscopy (XPS) measurement (Nie et al. 2015). XPS spectra were collected on a Kratos Axis Ultra DLD multitechnique X-ray photoelectron spectrometer (UK) using a monochromatic Al Kα X-ray source (hv = 1486.6 eV). All XPS spectra were recorded using an aperture slot of 700 × 300 μm, survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra were recorded with a pass energy of 40 eV. Oxygen and carbon atoms ratio (O/C) were calculated by a low resolution X-ray photoelectron spectroscopy.

GC–MS analysis

GC–MS analyses were performed using Agilent 6890 series apparatus GC systems (Agilent Technologies, Santa Clara, USA) coupled to a quadrupole mass spectrometer (model HP 5973) equipped with an elastic quartz capillary column HP-5MS (30 m × 0.25 mm i.d., film thickness 0.25 μm) (Yao et al. 2016). For GC–MS detection electron ionization with ionization energy of 70 eV was used over a scan range of 40–450 atomic mass units. The voltage of the

detector was 1.75 kV. Helium was the carrier gas, at a flow rate of 1.2 ml/min. Injector and transfer line temperatures were set at 230 and 280 °C, respectively; the temperature of the ion source was 230 °C. Column temperature was initially kept at 80 °C for 2 min, then gradually increased to 240 °C at 9 °C/min and finally held isothermally for 2 min. The samples (1 μL) were injected with 1:20 split ratio.

Results and discussion

Effect of hot chlorine dioxide delignification on the properties of bagasse fiber and AOX content

In order to study the effect of hot chlorine dioxide delignification on the whiteness, viscosity, and yield of bagasse fibers, and the AOX content of the bleaching effluent, the D_0E_pD and $D_{HT}E_pD$ bagasse bleaching processes were carried out. It is evident from Fig. 1a that the brightness of D_0 treated pulps was much higher than those treated by D_{HT} process using an identical amount of chlorine dioxide. This is due to the degradation of hemicellulose during D_{HT} treatment, which breaks down the bonds of the lignin-carbohydrate complex (LCC). This increases the extraction of the lignin, leading to the migration of more lignin to the surface of the fiber, which is consistent with the results described by McDonough et al. (Mcdonough et al. 2009). After alkaline extraction (E_p), the residual lignin, chromophore, and chromogenic groups were dissociated from the surface of the fiber. The lignin content of the reaction during D_{HT} was found to be higher than observed the D_0 treatment. Therefore, after the alkaline extraction the brightness of the D_{HT} treated pulp were much higher than that of the D_0 treated pulp. Following alkaline extraction, the chlorine dioxide delignification (D) is mainly to remove the small amount of residual lignin in the fiber. The final brightness of the $D_{HT}E_pD$ fully bleached pulp was higher than the D_0E_pD fully bleaching pulp by 1.86% ISO, as shown in Fig. 1a. Compared with D_0 treated pulps, the damage of the D_{HT} treated bagasse fiber was greater and their viscosity had reduced to 187 mL g^{-1}, as illustrated in Fig. 1b. This phenomenon occurs because when the content of residual lignin and HexA in the pulp is decreased, HOCl oxidizes the cellulose present in the reaction system (Zhou et al. 2008). It has been reported

that carbohydrate degradation might occur if the time of the D_{HT} treatment is prolonged (Lachenal and Chirat 1998). The yield of the D_{HT} treated pulp may be expected to decrease under such circumstances, but the yield loss of the $D_{HT}E_pD$ fully bleached pulp is not obvious; the yield was only 1.61% lower than that of the pulp bleached fully by the D_0E_pD treatment, as illustrated in Fig. 1c.

Under the typical conditions of the amount of chlorine dioxide added, the AOX content of the effluent following the D_0 treatment is twice as much as the D_{HT} treatment, as shown in Fig. 1d. Some studies have shown that chlorine dioxide and lignin are mainly oxidized on D_{HT} treatment and the chlorination reaction of lignin is inhibited (Magara et al. 2006). In addition, the residual HexA and lignin in the pulp decrease under hot and acidic conditions during the D_{HT} process (Magara et al. 2006).

The AOX content of D_0 and D_{HT} after E_p account for 19 and 28% of the total present in the effluent, respectively. While E_p treatment does not produce AOX, the presence of the latter is mainly attributed to the residual amount in the treated fiber after the D_0 and D_{HT} treatments. This part of the AOX is dissolved under alkaline conditions. In addition, the use of hydrogen peroxide on the AOX dehalogenation effect to reduce the AOX content (Magara et al. 2006; Mjm et al. 2001). Therefore, the conditions of alkali extraction (alkali content, time, temperature, pulp consistency) and other factors affect the role of alkali extraction, and also influence the AOX content of the wastewater.

The D treatment produces less AOX than either D_0 or D_{HT}. The AOX content of the D_0 and D_{HT} after the D treatment is 0.13 kg/adt pulp and 0.11 kg/adt pulp, respectively. In addition, analysis of the AOX content of the bleaching effluents showed that AOX was reduced during acid hydrolysis followed by chlorine dioxide (A/D_0). And A/D_0 technologies have proven very useful for bleaching of bagasse pulp. Levels of AOX in the pre-bleaching effluents increased in the order $D_{HT}E_pD < A/D_0E_pD < D_0E_pD$ are presented in Fig. 2. The pre-bleaching AOX load represented from 63% (D) to 66% (A/D) of the whole effluent AOX load. The $D_{HT}E_p$ and A/DE_p treatments produced effluents with AOX loads 29 and 27% less than that of the DE_p, respectively. However, the A/D treatment produced effluent with an AOX load only slight greater than that of the D_{HT} treatment, showing that
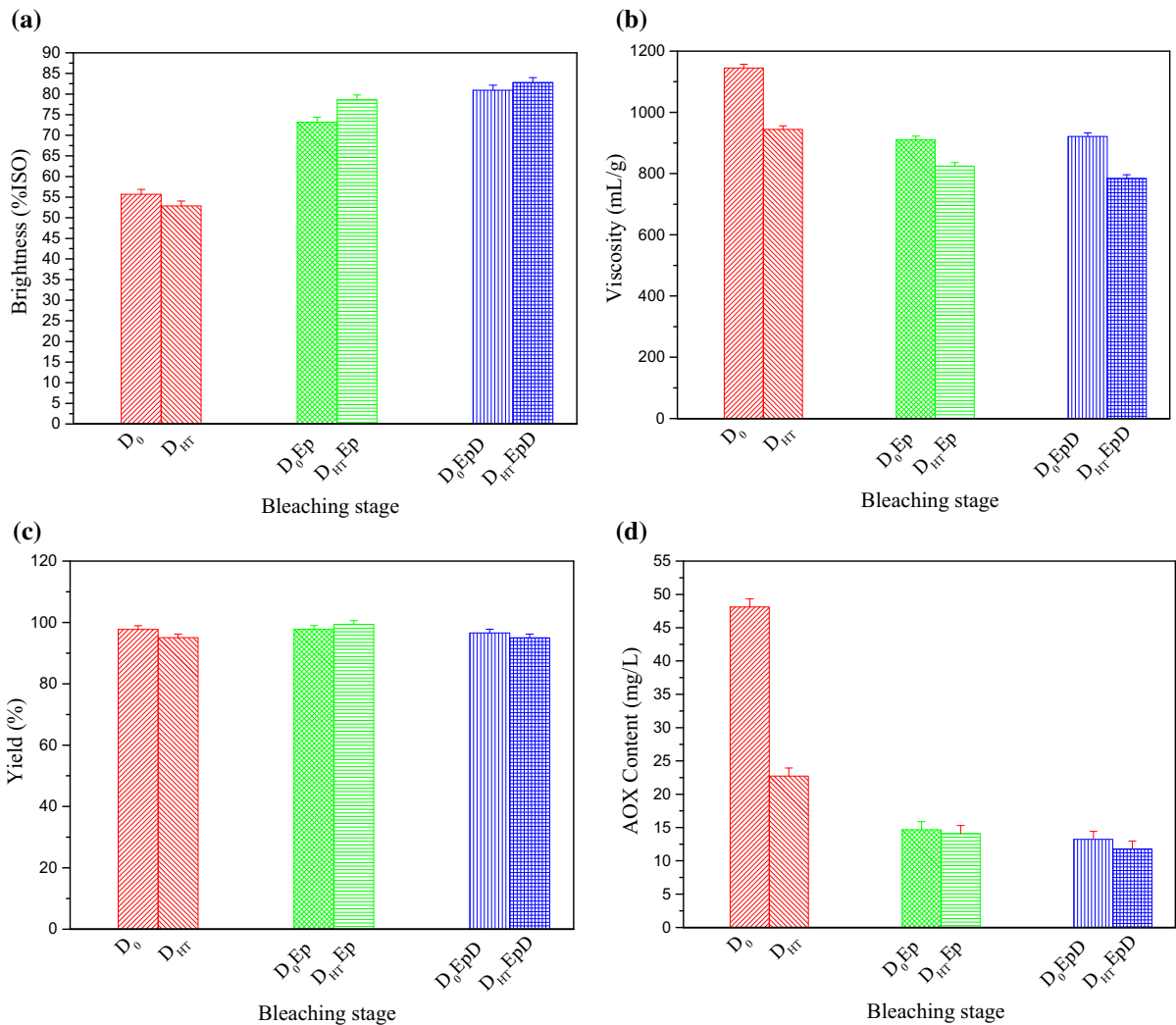
Fig. 1 Influence of different bleaching stage on brightness (**a**), viscosity (**b**), yield (**c**) and AOX content (**d**)
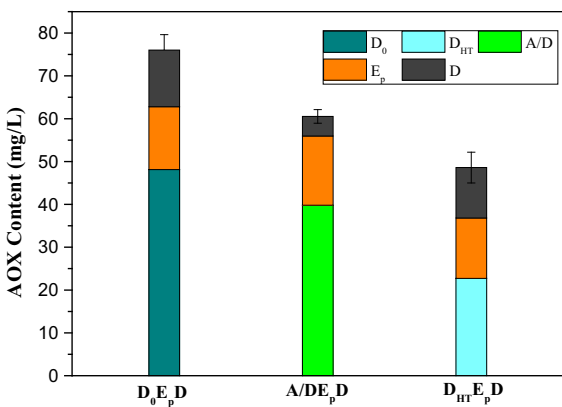

Fig. 2 Effect of different pre-bleaching stages on AOX content

the D_{HT} and A/D stage reduces effluent AOX. Another research showed that the hot acid hydrolysis followed by chlorine dioxide bleaching of eucalyptus pulp, AOX could be reduced by 10–20% (Gomes et al. 2007). The main reason for reduction of AOX formation was that hemicellulose could be removed by mild hot acid treatment (Yao et al. 2017). Thus, the AOX content can be reduced by a follow-up D treatment. On considering the properties of the bagasse fiber and the environmental pollution caused by the bleaching effluent, it is can be seen that the D_{HT} replacement the D_0 be used in bagasse ECF bleaching will be better.

Effect of hot chlorine dioxide delignification on the bagasse fiber structure

In order to study the structural changes in the bagasse fiber when subjected to different treatments, ATR-FTIR spectra were obtained, as shown in Fig. 3. For the bagasse fiber, the broad band around 3500–3200 cm^{-1} was due to O–H stretching vibrations of cellulose, hemicellulose, and lignin bonding. The band at around 3300–2750 cm^{-1} was assigned to the C–H stretching vibration of methyl groups (CH$_3$) and methylene groups (CH$_2$) in bagasse fiber. The absorption peak at around 1900–1600 cm^{-1} was attributed to the aromatic skeletal vibrations and C=O stretching. The band at around 1429–1421 cm^{-1} was assigned to the OCH$_3$ in-plane bending vibration of the syringyl and guaiacyl units in lignin. The band at around 1375–1365 cm^{-1} was attributed to the C–H stretching vibration in phenolic lignin while those around 1342–1254 cm^{-1} were seen due to the skeletal vibrations of the benzene ring in lignin (Candido et al. 2017; Reis et al. 2017). The different spectral bands, their vibrational assignment, and relative intensity are listed in Table 1.

The absorbance of the lignin bands at 3328.24 cm^{-1} increased, demonstrating a higher amount of free phenolic structures in D$_{HT}$ treated pulp than present in the raw bagasse. This phenomenon could be explained by the fact that the β-O-4 linkages in the lignin molecule were broken when subjected to D$_{HT}$ treatment (Lachenal and Chirat 1998). The peaks at 1161.06, 1050.48, and 996.54 cm^{-1} obviously increased in the D$_{HT}$ treated
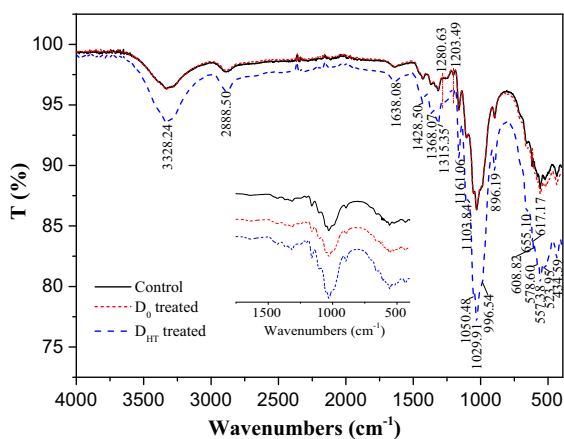

Fig. 3 ATR-FTIR spectra of the bagasse fibers

pulps, as the residual HexA of the hemicellulose side chain decreased under hot and acidic conditions during the D$_{HT}$ process (Magara et al. 2006). Bands at 1638.08, 1428.55, 1368.07, and 1315.35 cm^{-1} increased in intensity after D$_{HT}$ treatment, indicating an increase in the carbonyl and methoxy containing aromatic moieties in lignin. These moieties were exposed to the fiber surface owing to the HexA and lignin continuous degradation of bagasse fiber (Nie et al. 2015; Tarvo 2010a). The bands at 897–893 cm^{-1} were characteristic absorption peaks of carbohydrates (Reis et al. 2017), and on comparison with the untreated and D$_0$ treated pulps, the D$_{HT}$ treated pulp had a higher relative intensity of this band at 896.19 cm^{-1}. These results showed that the β-glycosidic and C–H bonds were cleaved and the carbohydrates were partially degraded during the D$_{HT}$ treatment (Table 2).

XPS has often been employed for the analyses of chemical elements present on the fiber surface based on the chemical shift of the electron binding energy. XPS analysis was conducted to determine the atomic oxygen to carbon ratios (O/C) and lignin mass% of bagasse fiber before and after the D$_{HT}$ treatment, as shown in Table 3. The O/C ratio obtained for control pulp was 0.54, and this value increased after delignification. This suggests that the surface of the pulp treated via chlorine dioxide delignification had more lignin than control pulp. Compared with the typical chlorine dioxide delignification process, the O/C ratio of the D$_{HT}$ treated bagasse fiber surface showed larger increase, indicating that D$_{HT}$ treatment is more effective than D.

The lignin content of the bagasse fiber can be calculated by O/C, and the true lignin content can be reflected by the further corrected (Gray et al. 2010). The lignin content of bagasse fiber treated with D$_0$ and after E$_p$ was determined to be 43.38 and 39.49%, respectively, while the actual lignin content was 14.29 and 12.45%, as summarized in Table 3. The lignin content of bagasse fiber treated with D$_{HT}$ and after E$_p$ was found to be 41.42 and 37.58%, and the actual lignin content was 13.34 and 11.59% respectively. Under the common dosage of chlorine dioxide, the lignin removal in the D$_{HT}$ process was higher than that in D$_0$ by 2%.

$$S_L = \frac{L}{L+S} = \frac{5 - 6(O/C)}{1.68 + 3.92(O/C)} \tag{1}$$

Table 2 Signals assignment of hand in ART-FTIR spectra and their relative intensity

Bands (cm^{-1})	Assignment	Relative intensity[a]		
		Control	D$_0$ treated	D$_{HT}$ treated
3500–3200	–OH stretching of hydrogen-bonding	0.98	0.98	0.96
3350–2700	C–H stretching vibration of alkyl groups in aliphatic bonds	0.99	0.99	0.99
1900–1600	–C=O stretching in conjugated *p*-substituted aryl ketones	1.00	1.00	0.99
1429–1421	Aromatic skeletal vibrations combined with –OCH$_3$ in-plane deformations	0.99	0.99	0.98
1375–1365	Aliphatic C–H stretching in CH$_3$ and phen-OH	0.98	0.98	0.97
1342–1254	Skeleton stretching of benzene ring	0.98	0.98	0.96
1161.06	C–O asymmetric band	0.96	0.96	0.93
1050.48	Hemicellulose absorptions to C–O stretching in C–O–C linkages	0.89	0.89	0.81
996.54	Arabinosyl side chains of hemicellulose	0.90	0.89	0.82
897–893	β-glycosidic C–H deformation from glycosidic bonds in carbohydrates	0.95	0.95	0.92

[a]The relative intensity was calculated as the ratio of intensity of the band to the intensity of band at 1510 cm^{-1}

Table 3 Measured and corrected surface atom ratios and lignin mass % for unbleached kraft pulps, estimated from XPS oxygen/carbon atom ratios

Samples	O (%)	C (%)	(O/C)[a] measured	Surface lignin (uncorrected)[b] mass %	(O/C)[c] corrected	Surface lignin (corrected)[d] mass %
Control	35.40	64.60	0.54	49.45	0.7163	17.35
D$_0$	36.13	63.87	0.57	43.38	0.7357	14.29
D$_{HT}$	36.75	63.25	0.58	41.42	0.7418	13.34
D$_0$E$_p$	37.20	62.80	0.59	39.49	0.7476	12.45
D$_{HT}$E$_p$	37.36	62.64	0.60	37.58	0.7532	11.59

[a]For sample, uncorrected, average and standard deviation for four or eight measurements of oxygen/carbon atom ratios

[b]Calculated from (O/C)measured and Eqs. 1 and 2

[c]Calculated from (O/C)measured and Eq. 3

[d]Calculated from (O/C)corrected and Eqs. 1 and 2

There S_L is the segment mole fraction of lignin in the surface, S is anhydroglucose or sugar units and L is lignin phenylpropane segments per unit volume in the sampled by XPS at the surface of the fibres.

$$Surface\ lignin\ (\%) = \frac{1.132 S_L}{1 + 0.132 S_L} \quad (2)$$

$$\frac{1}{(O/C)_{corrected}} = \left\{ \left[\frac{1 + (O/C)_{measured}}{1.833} \right] \times \left[\frac{1}{(O/C)_{measured}} + 1 \right] \right\} - 1 \quad (3)$$

In order to further study the effect of D$_{HT}$ on the fiber structure, the proportion of C1s on the fiber surface was analyzed. Appendix 1 (Fig. 6a–e) displays the high-resolution deconvolution of the C1s peak for the treated and untreated bagasse fiber. This deconvolution was performed to quantify the relative abundance of the different types of carbon atom. The deconvolution of the C1s peak associated with bagasse cellulose revealed the presence of four peaks. C1 represents C–C or C–H in bagasse fibers at 282.3 eV and C2 primarily represents a lignin bond, a phenolic hydroxyl group, and an alcoholic hydroxyl group (C–O–C or C–O–H) at 284.2 eV. While C3 refers predominantly to O–C–O or C=O in bagasse fibers at 285.6 eV, C4 is mainly the O=C–O carbon at 286.0 eV (Nie et al. 2015; Wang et al. 2011). The detection of C1 and C4 signals was attributed to the presence of aliphatic chains and aromatic ring-bearing molecules arising from the extracts, lignin, and hemicelluloses. While the D treatment resulted in a decrease in C1, the changes in C4 were minimal. The

D_{HT} treatment caused an increase in both C1 and C4, as summarized in Table 4. This showed that the aromatic ring structure is reduced in the fiber surface after normal chlorine dioxide delignification, the more phenolic lignin generated AOX through chlorinated reaction. As more lignin moved to the surface of the fiber, it lead to an increase in the phenolic hydroxyl and organic acid content after D_{HT} treatment. This may be explained by the facilitated oxidation reaction between chlorine dioxide and phenolic lignin and HexA degradation which produces organic acids during the D_{HT} treatment. These species are reduced after alkaline extraction. D_{HT} treatment resulted in an increase of C2 moieties but a decrease in C3, which indicates that the content of cellulose and hemicellulose in the bagasse fiber had relatively increased after chlorine dioxide delignification. However, some carbohydrates were degraded on D_{HT} treatment, therefore, the increase of C2 was relatively less.

Effect of D_{HT} on AOX components

AOX formation decreased upon D_{HT} treatment of bagasse fiber. In order to further analyze the AOX components present in bleached wastewater, the different organic chlorides were identified by GC–MS analyses of D_0 and D_{HT} treated bagasse fiber, as shown in Table 5. The total ion chromatogram (TIC) of the bleaching effluent with D_0 and D_{HT} treated bagasse fibre is shown in Appendix 2 (Fig. 7a, b). AOXs are comprised of at least four components: small molecule organic chlorides, macromolecular organic chlorides, chlorobenzene, and chlorophenol (Yao et al. 2017). D_0 stage bleaching effluent of sulfate bagasse pulp contains a large amount of chloroacetone and chlorophenols, including 1,1,3-trichloroacetone (C_3H_3ClO), 1,1,3,3-tetrachloro-2-propanone ($C_3H_2Cl_4O$), 2-Chloro-1,4-

benzenediol ($C_6H_5ClO_2$), 5-Chloro-1,3-benzenediol ($C_6H_5ClO_2$) and some amount of chlorinated hydrocarbons.

Malhotra, et al. have analyzed the DED bleaching wastewater of wheat straw pulp and found that it mainly contains p-chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 6-chloroguaiacol, 3,6-dichloroguaiacol, and 3,5-dichlorophenyl ether (Malhotra et al. 2013). Most of the AOX in the bleaching effluent of D_0 are macromolecular organochlorides, but only a few are organic compounds of low molecular weight.

The components such as chlorophenol and chloroacetone were removed from the bleaching wastewater after D_{HT} treatment, but 3-chloro-propionic acid ethyl ester and 2,2-dichloroethanol could still be detected. This is mainly due to the reaction between the organic acid and the hydroxyl moieties to generate esters during D_{HT}, resulting in the decrease in the chlorinated ketone content while the content of chlorinated ester increased. Studies have also shown that lignocellulose undergoes acid hydrolysis into small molecules which then undergo chlorination reactions (Zhou et al. 2008). The content of other components such as furfural and oligosaccharides increased as a result of the degradation of carbohydrates under hot and acidic conditions. This observation is consistent with the result of ATR-FTIR and XPS analyses and confirms that the hot chlorine dioxide delignification process is an effective means of reducing AOX.
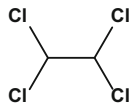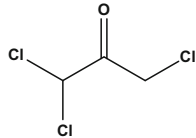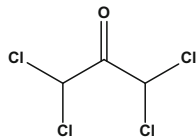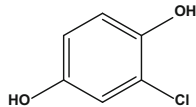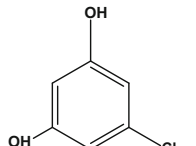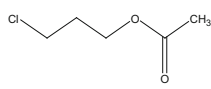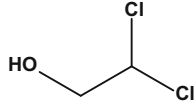
Mechanisms of decline in AOX formation as a result of hot chlorine dioxide delignification

Based on comprehensive analysis of the bagasse fiber and bleaching effluent before and after D_{HT} treatment,

Table 4 The C1s peak areas of the bagasse fibers

Samples	C1s total = 100			
	C1 (%) (C–C or C–H)	C2 (%) (C–O–C or C–O–H)	C3 (%) (O–C–O or C=O)	C4 (%) (O=C–O)
Control	11.11	27.66	46.43	14.81
D_0	7.42	50.77	27.63	14.18
D_{HT}	13.50	36.22	27.14	23.14
D_0E_p	10.03	46.87	27.11	15.99
$D_{HT}E_p$	16.12	44.36	21.12	18.40

Table 5 Major AOX species, peak time and chemical structure from bleaching wastewater of D_0 and D_{HT}

Intermediates		Retention time (min)	Chemical structure	Matching rate (%)
A	1,4-Dioxane	3.387		97
B	1,1,3-Trichloro-2-propanone	4.025		95
C	1,1,3,3-Tetrachloro-2-propanone	5.157		96
D	2-Chloro-1,4-benzenediol	9.970		94
E	5-Chloro-1,3-benzenediol	9.970		74
G	3-Chloropropyl acetate	3.153		88
F	2,2-Dichloro-ethanol	3.925		87

a mechanism of AOX reduction can be proposed, as shown in Fig. 4. There are three pathways of AOX generation, namely, the chlorination reactions of chlorine or hypochlorous acid and lignin as a main pathway of generating AOX (Nie et al. 2014), transformation of chlorine dioxide into chlorine free radicals during delignification, which subsequently react with HexA and generate AOX (Björklund et al. 2004; Nie et al. 2014; Petit-Breuilh et al. 2004), and, the organic chloride (OCl) oxidative decomposition to produce AOX during delignification (Tarvo 2010b).

The formation of AOX during delignification of chlorine dioxide has a linear relationship with the HexA content of the plant fiber (Björklund et al. 2004; Nie et al. 2015). However, it is not a simple linear relationship between HexA and AOX in the hot chlorine dioxide delignification process, which is

evident in the effect of high concentration of HexA on AOX, as shown in Fig. 5. As most of the HexA is prone to degradation under hot acidic conditions (Lachenal and Chirat 1998), the degradation products are less prone to chlorinated reactions, thus resulting in less AOX. Furthermore, the hot chlorine dioxide bleaching process can selectively remove the residual lignin in the fiber, and easily generate free phenol via breaking of lignin β-O-4 linkages, which rapidly produce organic acids via oxidation, resulting in a lesser degree of formation of OCl and AOX. Lignin is oxidized and cellulose degradation produces OCl, and HexA does not affect the formation of OCl under these conditions (Björklund et al. 2004). The chlorination of lignin was inhibited in the D_{HT} stage, but the degradation of cellulose is unavoidable. Overall, the pathway of generating AOX by the OCl is weakened.
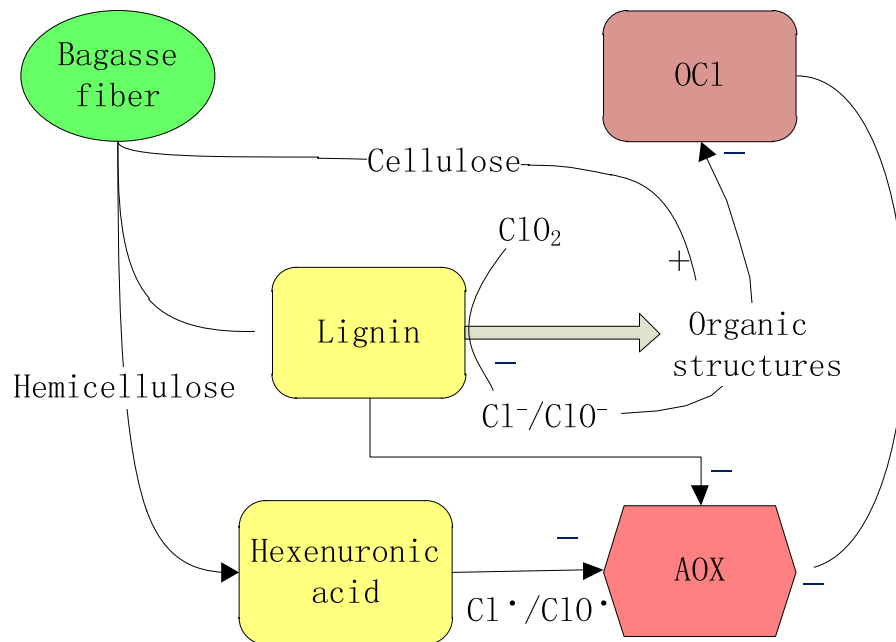
Fig. 4 Mechanisms of reduction of AOX (− represent subdued; + represent enhanced)
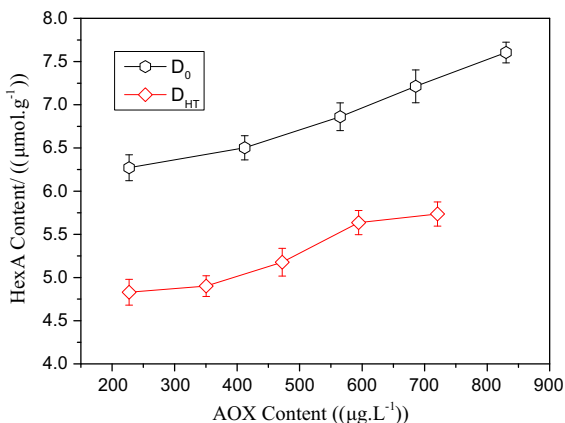

Fig. 5 Relationship between the AOX and HexA in D_0 and D_{HT}

Reducing the dosage of chlorine dioxide can also reduce the AOX content of the effluent (Nie et al. 2015). This reduction was more efficient at the D_{HT} stage; the chlorine dioxide demand was found to decrease by 24–33% and AOX content had reduced by 50% to obtain the same brightness, compared to the normal D stage. The lignin-HexA-xylan complex was formed during the pulp cooking. Hot chlorine dioxide delignification also results from the cleavage of the lignin-HexA-xylan complex (Jiang et al. 2006), which

enhances the degrading part of phenolic lignin (Lachenal and Chirat 1998) and thereby reduces the consumption of chlorine dioxide in the D_{HT} stage. Petit-Breuilh et al. pre-hydrolyzed the eucalyptus kraft pulp before ECF bleaching at 85–95 °C. The amount of chlorine dioxide was reduced by 42–77%, and the content of AOX and phenolic compounds in bleached effluent had also reduced (Petit-Breuilh et al. 2004).

Conclusions

In this work, the effect of precursors on AOX in hot chlorine dioxide delignification of bagasse pulp has been studied. The amount of AOX formed was found to depend on the dosage of the chlorine dioxide, HexA, organic chloride, and phenolic lignin concentration. This study also shows that the D_{HT} can degrade both phenolic lignin and HexA, and inhibit the production of organic chloride. Thus, considering the environmental aspects, the D_{HT} process for the removal of AOX is better than the D0. The AOX content of the bleaching effluent was found to have reduced by half after D_{HT} treatment.
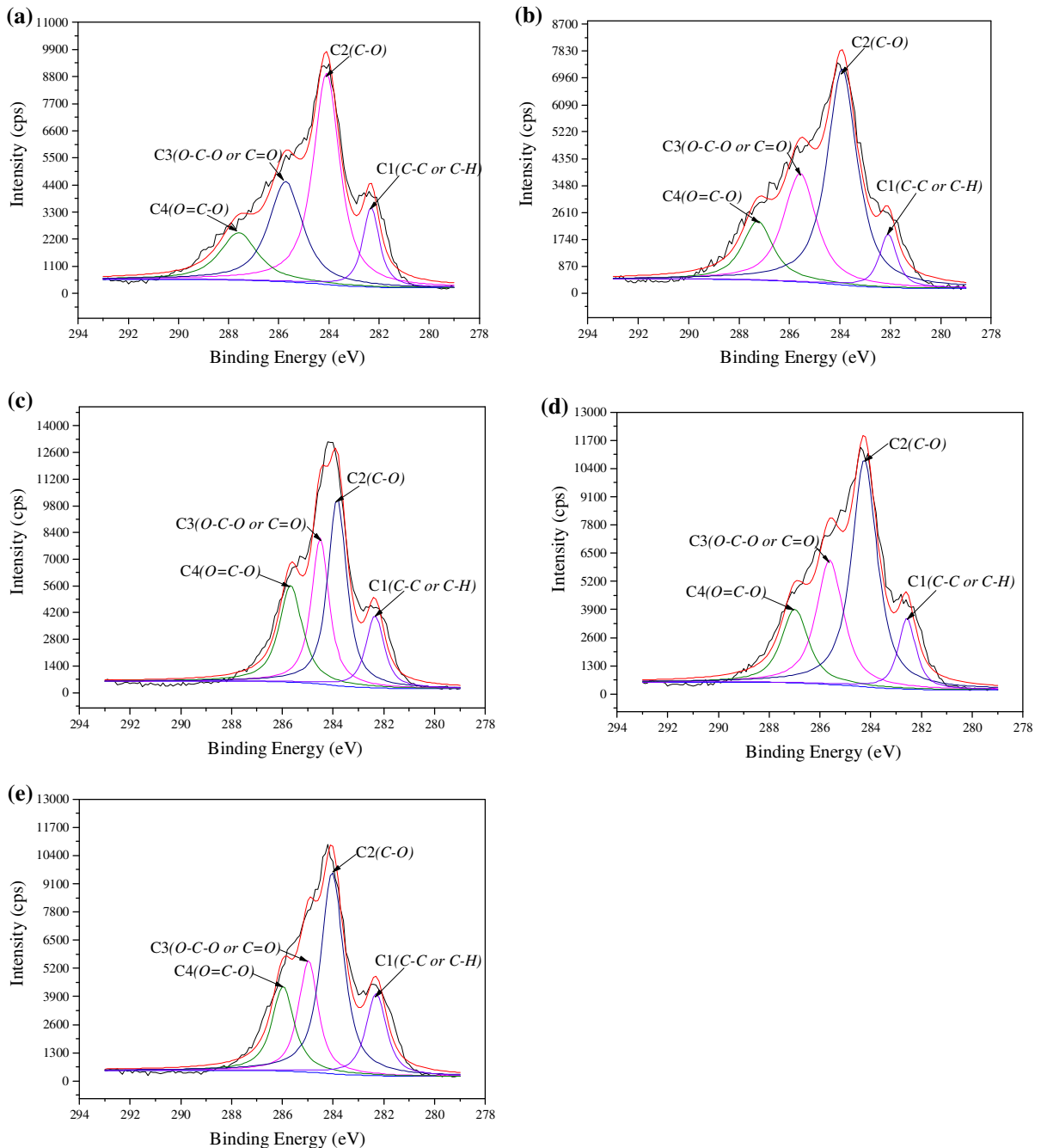
Appendix 1

See Fig. 6.

Fig. 6 The XPS spectrums of the bagasse fibers **a** control; **b** D_0 treated; **c** DHT treated; **d** $D_0 + E_p$ treated; **e** $D_{HT} + E_p$ treated
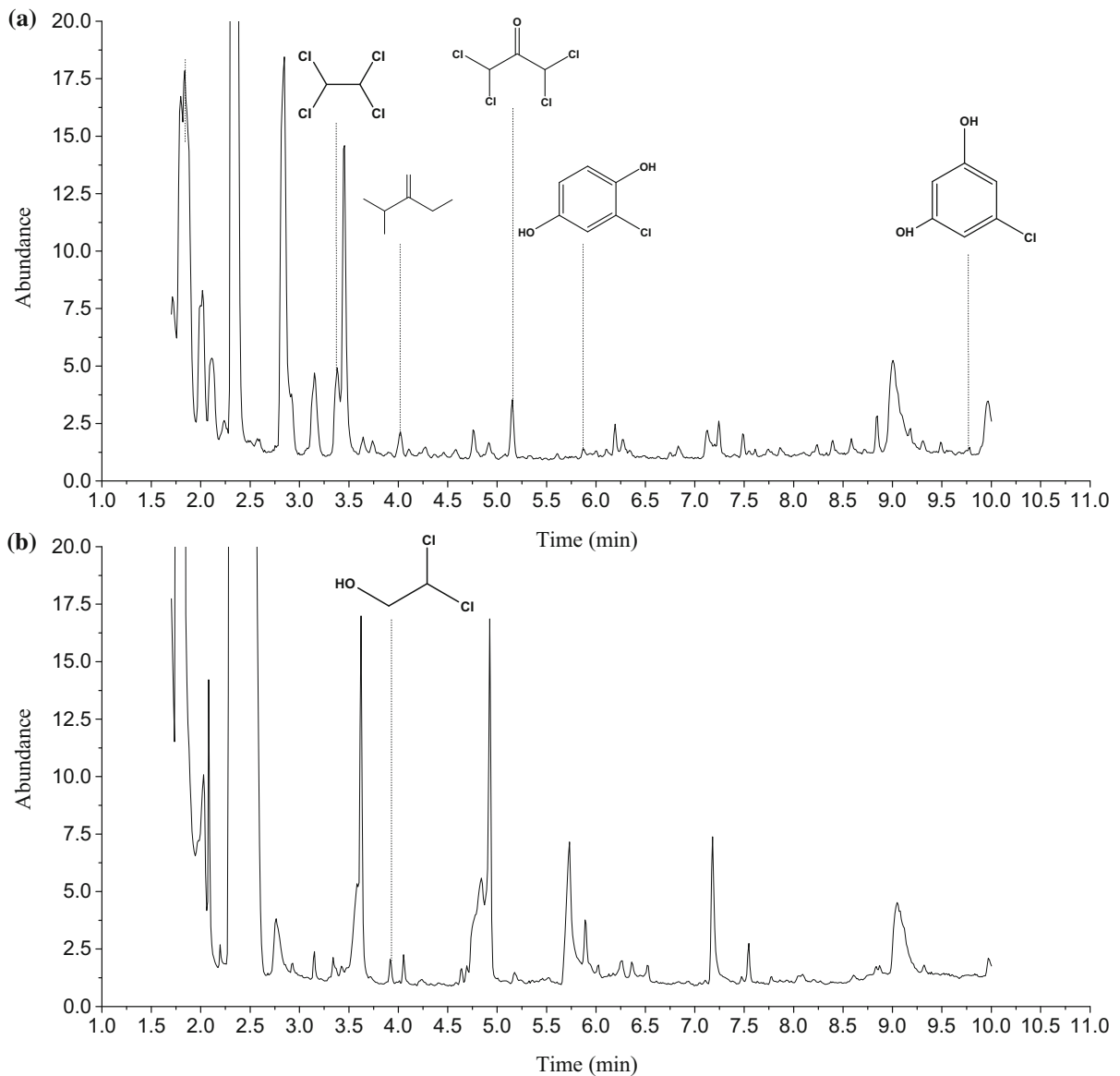
Appendix 2

See Fig. 7.

Fig. 7 TIC of bagasse pulp in effluent **a** D_0 stage and **b** DHT stage

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