Bleaching

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Chlorine dioxide bleaching of nineteen non-wood plant pulps

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Abstract: Bleaching of unbleached and oxygen delignified pulps from nineteen non-wood plants has been evaluated in elemental chlorine free bleaching. Chlorine dioxide charge (κ factor 0.15, 0.20 and 0.25) and temperature (70 and 85 °C) in the delignification stage (D) were varied. Chlorine dioxide (ClO_2) charge and temperature exhibited lower κ number and higher brightness after alkaline extraction (EP) stage. High temperature ClO_2 delignification (D_{HT}) exhibited higher final pulp brightness. The final brightness of wheat straw pulp reached to 90 % after $D_0/D_{HT}(EP)D_1$ bleaching, while banana pseudo stem pulp showed the worst bleachability. Residual hexeneuronic acid contents in final pulp from most of the non-wood plants were lower and exhibited 1–2 % higher pulp brightness in D_{HT} process than D_0 process. Oxygen delignified pulp and D_{HT} process discharged lower COD load.

Keywords: brightness; elemental chlorine free bleaching; hexeneuronic acid; κ number; non-wood pulps.

Introduction

Most of the forest deficient countries like Bangladesh are recommended to use non-wood fibers in pulp and paper manufacturing due to limited wood supply. Despite wood is the main raw material for paper pulp manufacturing, non-wood lignocellulosic fibers from cereal straw and other sources are widely used in many developing countries (Hart 2020). The global production of paper and cardboard stood at approximately 419.7 million metric tons in 2017. The market value of paper and pulp glob-

ally is expected to experience an increase within the five-year period comprised between 2019 and 2024, from an estimate of 63.3 billion U.S. dollars, to around 79.6 billion U.S. dollars by 2024 (Garside 2019). This increasing trend is mainly from developing countries like China. The GDP growth in Bangladesh is above 6 % since last 15 years, consequently increasing the living standard of people. The per capita paper and board consumption in Bangladesh is about 5 kg, which is much lower than the advanced countries (250 kg/capita), and the Asian average (≈ 45 kg/capita) (FAO 2017; <https://paperonweb.com/Bangladesh.htm>). The major drawback for pulp and paper production here is that it has very limited forest resources and more than half of the demand is fulfilled by import. Thus the country needs alternative fibrous raw materials. In this regard, many researches have been working on alternative raw materials for pulping (Akhtaruzzaman et al. 1991, Ferdous et al. 2020, 2020a, Jahan et al. 2007, 2007a, 2012, Matin et al. 2015).

Studies have shown that the soda anthraquinone (AQ) pulping is the widely accepted process for efficient conversion of non-woods into pulp without with faster delignification (Hart and Rudie 2014). The major part of delignification occurs during the pulping process and rest is removed further in bleaching stages. Pulp bleaching is a chemical process to brighten the pulp through the removal of lignin. It is the most expensive and polluting step in pulp industry as extensive bleaching is required by pulps produced by chemical pulping. It is accomplished with various compounds containing chlorine or oxygen and alkali extractions in several stages. During bleaching lignin is reacted with elemental chlorine and its derivatives to produce fragmented chlorolignins (Kumar et al. 2007). Alkali used in extraction stage dissolves these fragmented non-cellulosic chlorolignin compounds. The major groups of chlorolignin compounds found in pulp mill effluent are chlorophenols, chlorocatechols, chlorotannins, chlorinated resin and fatty acids etc. (Kaur et al. 2018). The reduction of chlorine compounds in pulp bleaching reduces chlorinated organics in the effluent (Kaur et al. 2018, Nie et al. 2013, 2014). Many attempts have been studied in reducing ClO_2 consumption (Bajpai et al. 2006, Shin and Mera 1994, Jahan et al. 2013, 2017, Haque et al.

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2019, Nie et al. 2015). The studies showed that xylanase, oxygen, peracid or acid treatment improved subsequent ClO_2 bleaching. Hot acid treatment and high temperature chlorine dioxide delignification (D_{HT}) bleaching are thoroughly investigated by Ragnar and Lindström (2004) and showed that the D_{HT} had superior results of the investigated parameters. The delignification efficiency of ClO_2 in the D_0 stage depends on the reaction time and reaction temperature, while reducing the effluent load of bleaching chemicals and also improving the bleached pulp properties (Nie et al. 2015, Kumar et al. 2007).

The basic concept for the high temperature ClO_2 delignification (D_{HT}) stage is that the reaction rate of chlorine dioxide with remaining pulp lignin is faster at high temperature than that with hexenuronic acid (HexA). Thus, at the early stage of the reaction most of the chlorine dioxide reacts with lignin, but the HexA remains in the pulp and are eliminated later through pulp acid hydrolysis stages (Eiras et al. 2003). Ventorim et al. (2005) revealed that a partial acid hydrolysis of HexA occurred in D_{HT} treatment resulting into decrease in generation of chlorinated organic halides. Ventorim et al. (2005) also found that at a similar ClO_2 dose (kappa factor 0.20 at pH 3.0) in D_{HT} bleaching produced 46.3 % less AOX in the filtrate in relation to the D_0 . Brogdon (2009) stated in his review that hot A-stage removed 30 to 90 % of HexA entering into the bleach plant and some lignin as well. Most applications of hot A-stages are combined with the D_0 into a single operation, (A/ D_0) or “hot D_0 -Stage.” Such processes can be very effective at reducing the total ClO_2 needed for ECF bleaching of hardwood pulps (20 to 50 %).

Most of the D_{HT} bleaching studies used 95 °C for longer time, consequently reduced viscosity and a slight drop in final pulp brightness. The lower brightness obtained after D_{HT} is explained by the brightness reversion reactions caused by maintaining the pulp at high temperature/time in the complete absence of chlorine dioxide (Eiras et al. 2003). The hot acid treatment also formed new lignin phenolic hydroxyl groups, which may form new chromophores (Uchida et al. 1999). Many of the research were carried out on D_{HT} at initial stage of bleaching of hardwood pulp (Ragnar and Lindström 2004, Ventorim et al. 2005, Zhang et al. 2018, Tavast et al. 2011, Davies et al. 2009, Lachenal and Chirat 2000) but available literature on non-wood/agricultural residues pulps are scarce.

Therefore, chlorine dioxide bleaching (ClO_2) of unbleached and oxygen delignified pulps of 19 non-wood plants was carried out with varying ClO_2 charge (kappa factor 0.15, 0.2 and 0.25) and temperature (70 and 85 °C). The final pulp properties as well as the effluent quality were also studied.

Table 1: Chemical characteristics of crops residues (Ferdous et al. 2020).

Raw material	Lignin (%)	α -cellulose (%)	Pentosan (%)	Ash (%)
Wheat straw	25.1	37.0	18.0	9.12
Corn stalks	19.7	35.1	17.8	4.48
Mustard stalks	18.1	33.7	18.9	5.04
Eggplant stalks	28.4	35.0	14.3	1.66
Chia plant	23.2	30.5	13.2	2.58
Banana pseudo stem	24.1	40.2	13.4	6.85
Banana leaf	20.7	41.4	13.3	6.97
Banana peduncle	20.4	45.2	14.8	1.77
Bagasse	20.4	39.3	16.9	0.67
Bamboo	26.9	46.9	18.4	3.27
Okra plant	18.7	29.6	15.1	0.77
Kaun plant	19.3	35.9	17.6	7.3
Kash	19.8	43.3	22.3	1.07
Rice straw	22.9	38.7	18.0	15.1

Materials and methods

Materials

Pulps from non-wood plants were prepared separately at the laboratory by soda-anthraquinone (AQ) process. These 19 non-wood plants had a lot of variation in chemical, anatomical and morphological properties (Ferdous et al. 2020). The chemical characteristics of some of these non-woods were published elsewhere and presented in Table 1 (Ferdous et al. 2020). As for example, jute fiber was characterized with high cellulose, low lignin and longer fiber length (Jahan et al. 2007a). Rice, wheat and kaun straws had high percentage of fines generated from parenchymatic cell (Ferdous et al. 2020a). Therefore, optimum conditions were varied among the raw materials. Bleaching experiment was performed only for the pulp obtained at optimum conditions. The cooking experiment was conducted in an electrically heated thermostatically controlled digester of 20 litre capacity. 1 kg non-wood was used for all experiments. All non-wood plants were cooked under the conditions given in Table 2. Based on our previous studies, the AQ charge and material to liquor ratio were kept constant at 0.1 % and 1:6, respectively (Ferdous et al. 2020a).

Oxygen delignification

Oxygen delignification (OD) was carried out in thermostatically controlled digester, rotating at 1 rpm. OD conditions

Table 2: Pulping conditions and pulp properties of unbleached and oxygen delignified pulps from nineteen non-wood plants.

Raw material	Cooking conditions			Kappa number			Viscosity (mPa.s)			Brightness (%)			HexA (µmol/g)		
	Alkali charge (%)	Max temperature (°C)	Time at max temp (h)	Un-bleached	O ₂ -delignified		Un-bleached	O ₂ -delignified		Un-bleached	O ₂ -delignified		Un-bleached	O ₂ -delignified	
Bamboo	18	170	2	26.82	7.31		16.13	14.98		19.81	14.98		13.11	45.74	13.34
Banana pseudo stem	18	170	2	23.57	12.03		19.08	18.51		11.32	18.51		10.91	15.93	10.67
Banana leaf	20	170	2	33.28	17.41		20.89	20.79		16.09	20.79		28.32	23.66	28.65
Banana peduncle	20	170	2	28.8	22.6		21.39	19.59		14.32	19.59		20.34	27.86	20.76
Cassava stalks	20	170	3	31.4	10.32		12.81	12.56		16.22	12.56		24.28	24.78	24.76
Chia stalks	20	170	3	27.65	12.11		10.96	10.22		15.62	10.22		53.65	22.55	53.24
Cotton stalks	20	170	3	31.19	8.01		11.78	11.61		11.15	11.61		76.73	30.57	61.23
Dhaincha	18	170	2	14.1	6.9		14.69	13.26		29.59	13.26		53.32	53.42	53.14
Eggplant stalks	18	170	3	28.79	13.68		12.81	12.56		21.71	12.56		26.64	30.5	27.22
Jute fiber	18	170	2	11.98	7.62		13.21	12.48		28.95	12.48		79.41	56.99	67.34
Jute stick	20	170	2	18.26	6.26		14.85	13.13		27.47	13.13		77.60	47.69	70.36
Kaun straw	14	150	2	10.07	6.56		15.49	14.23		32.26	14.23		32.32	41.51	33.43
Mulberry stalks	20	170	3	21.35	6.86		12.65	11.09		22.86	11.09		60.65	44.92	61.04
Mustard stalks	20	170	3	18.6	10.45		13.51	12.73		23.12	12.73		37.03	41.59	38.22
Okra stalks	20	170	3	30.68	22.31		21.57	21.01		13.02	21.01		22.00	15.28	25.32
Pineapple leaves	14	170	2	19.3	6.1		12.65	11.79		19.44	11.79		8.87	32.25	8.23
Red lentil stalks	20	170	3	18.26	5.42		12.69	11.55		24.75	11.55		21.90	39.50	22.23
Rice straw	14	150	2	13.16	5.17		16.04	15.31		37.93	15.31		7.66	50.05	7.67
Wheat straw	14	150	2	12.32	5.56		16.75	16.05		29.37	16.05		10.66	35.70	10.33

were 110 °C, retention time 60 min, pulp consistency 10 %, NaOH 2 %, MgSO_4 0.3 % and O_2 -pressure 3.5 kg.cm⁻².

Evaluation of pulp

The kappa number (T 236 om-99), viscosity (T 230 om-99), brightness (T 452 om-92) and HexA (T 282 pm-07) of the resulting pulps from the unbleached and oxygen delignified state were determined in accordance with Tappi Test Methods. Three replicates of all experiments were done, and average reading was taken.

$D_0(\text{EP})D_1$ and $D_{\text{HT}}(\text{EP})D_1$ bleaching

Unbleached and oxygen delignified pulps were bleached by $D_0(\text{EP})D_1$ and $D_{\text{HT}}(\text{EP})D_1$ bleaching sequences (where D represents chlorine dioxide and (EP) represents peroxide reinforced alkaline extraction). The chlorine dioxide charge in D_0 and D_{HT} stages were varied by kappa factor 0.15, 0.2 and 0.25. The temperature was 70 °C in D_0 stage for 45 min. Pulp consistency was 10 %. The pH was adjusted to 2.5 by adding dilute H_2SO_4 . In the D_{HT} stage, bleaching temperature was 85 °C and all other parameters remained same. In the alkaline extraction stage, temperature was 70 °C for 60 min in a water solution of 2 % NaOH and 0.5 % H_2O_2 (on od pulp) were used. After (EP) stage, kappa number, viscosity and brightness were determined in accordance with Tappi Test Methods as above.

In the D_1 stage, pH was adjusted to get end pH 4.5. The ClO_2 charge in the D_1 stage was fixed to 1 %. The brightness, viscosity and HexA of the bleached pulp and COD in the mixed effluent collected from D_0 , EP and D_1 stages were determined in accordance with PAPTAC Methods H.3.

Results and discussion

Pulps from 19 non-wood plants were prebleached by oxygen delignification under identical conditions. Entering kappa number was varied from 10.1 in kaun straw pulp to 33.3 banana leaf pulp. The oxygen delignification degree varied among the raw material from 21.5 % to 72.7 %. The lowest and highest delignification degrees on oxygen delignification were observed for banana peduncle and bamboo pulps, where entering kappa number was 28.8 and 26.8, respectively. The oxygen delignification should be limited up to 50 % delignification to maintain pulp viscosity. Oxygen delignification increased pulp brightness from 6 % to 28 % depending on non-wood pulps. Un-

bleached brightness of jute fiber pulp was 28.95 %, which increased to 56.99 % on oxygen delignification. On the other hand, oxygen delignification of wheat straw pulp increased to 35.7 % for 29.37 % in the unbleached state.

Pulp viscosity loss during oxygen delignification is caused by cellulose chain cleavage resulting from attack by oxygen-based radicals generated through reactions with lignin. As shown in Table 2, there were no significant changes of pulp viscosities after oxygen prebleaching. The pulp viscosities decreased by 2 % to 12 %. The maximum viscosity drop was 12 % for mulberry stalks pulp, where delignification degree was 67 %. The HexA content in 19 non-wood plants pulps was varied from 7.66 to 79.41 $\mu\text{mol/g}$ pulp. The lowest HexA content was in rice straw pulp and the highest in jute fiber pulp. Oxygen delignification did not change HexA content (Table 2).

In alkaline pulping process, 4-O-methyl- α -D-glucuronic acid groups react with alkali and form hexenuronic acids through beta elimination of the methoxyl (Teleman et al. 1995). Thus, HexA is a product of alkaline cooking, and their amount in the pulp depends on the amount of 4-O-methyl- α -D-glucuronic acid originally present in the raw material and alkaline cooking condition. Oxygen delignification is a part of extended alkaline cooking. Therefore, HexA content in oxygen delignified pulp did not decrease, even in some cases increase.

$D_{\text{HT}}(\text{EP})$ and $D_0(\text{EP})$ pulp properties

The effect of kappa factor on (EP) kappa number, brightness and viscosity of 19 non-wood pulps are shown in Table S1. First ClO_2 stage is denoted as D_0 and D_{HT} at 70 °C and 85 °C, respectively. As expected, increasing kappa factor resulted in decrease kappa number and viscosity and increase brightness regardless D_0 or D_{HT} processes. D_{HT} bleaching is more efficient than D_0 and support chlorine dioxide dose reduction during bleaching (Table S1). The delignification to a lower kappa number is one of the factors to get high pulp brightness. The oxygen delignified pulp showed lower kappa number after (EP) stage. The kappa numbers after (EP) stage in D_{HT} bleaching were always lower than the corresponding D_0 bleaching. Kaur et al. (2019a) also showed that the kappa number of rice straw pulp after extraction stage was lower for D_{HT} than D_0 with the same ClO_2 dose. This is related to the acid leaching of lignin as described and reported by (Ikeda et al. 1999, Ikeda et al. 1999a). The highest and lowest (EP) kappa numbers were observed for okra plant and wheat straw, respectively. From the 19 non-wood plant pulps few are shown in Figure 1. As shown in Figure 1, for the pulp

Figure 1: Effect of D_{HT} delignification on kappa number after (EP) stage.

bleaching with kappa factor 0.2, (EP) kappa number were 11.76 and 7.78 in D_0 bleaching, which decreased to 9.61 and 5.15 in D_{HT} for unbleached and oxygen delignified pulp, respectively. The (EP) kappa number for wheat straw pulps decreased from 1.83 and 0.98 in D_0 bleaching to 1.38 and 0.63 in D_{HT} bleaching. The higher kappa number decreased in the D_{HT} (EP) stage as compared to the D_0 (EP) can be explained by the higher removal of HexA (Lachenal and Chirat 2000). This can also be explained by the degradation of hemicellulose during D_{HT} treatment, which breaks down the bonds of the lignin-carbohydrate complex (LCC) and increases the extraction of the lignin from the surface of the fiber, which is described by Zhang and coworkers (2018). But according to Ikeda et al. (1999), the temperatures were not high enough to cleave the C-O or C-C bonds that link lignin to carbohydrates in LCC. McDonough et al. (2009) speculated that proportion of HexA contributing to the pulp's kappa number entering the D_0 stage affected bleachability of a red oak pulp that underwent a hot acid hydrolysis.

Pulp brightness after D_0 (EP)/ D_{HT} (EP) stage is also shown in Table S1. Oxygen delignified pulp showed better pulp brightness than the unbleached pulp regardless D_0 or D_{HT} bleaching. The (EP) brightness of D_{HT} treated pulps was better than those treated by D_0 process using an identical kappa factor. Bamboo, dhaincha, jute fiber and jute fiber pulps showed improved brightness, while banana pseudo stem pulp showed the worst brightness. Primarily, unbleached pulp brightness can predict the pulp bleachability. At the starting, banana pseudo stem pulp brightness of was 11.32 % and 15.93 % for unbleached and oxygen delignified pulps, respectively (Table S1). Only (EP) brightness data of a few non-wood plant pulps are shown in Figure 2. The highest brightness advantage in D_{HT} stage than D_0 stage after (EP) stage was 3 % for dhaincha oxygen

Figure 2: Effect of D_{HT} delignification on brightness after (EP) stage.

delignified pulp. Ventorim et al. (2005) found the first chlorine dioxide stage at high temperature (D_{HT}) decreased the brightness by 2.5 % ISO and kappa number by 46 % (1.9 units) after extraction stage as compared to the conventional D stage. Their results were also supported by others (Ragnar and Lindström 2004, Eiras et al. 2003). The target of this study was to improve brightness and kappa number reduction at 85 °C for shorter bleaching time, which was achieved in this study.

As shown in Table S1, oxygen delignification reduced pulp viscosity insignificantly. The highest and lowest (EP) pulp viscosity was for banana leaf and chia pulp, respectively. There was no significant change in post extraction pulp viscosity after D_{HT} bleaching. As for example, Figure 3 shows that the pulp viscosity of oxygen delignified banana leaf pulp decreased from 19.23 mPa.s in D_0 process to 18.93 mPa.s in D_{HT} process only. No change of pulp viscosity was observed for chia pulp. But other studied showed that the $D_{HT}E$ treatment at 95 °C for resulted in significant drop in post extraction pulp viscosity as compared to the DE one (Ventorim et al. 2005, Ragnar 2003). Pulp exposed to high time/temperature reaction and acid pH may undergo slight carbohydrate hydrolysis. The sig-

Figure 3: Effect of D_{HT} delignification on viscosity after (EP) stage.

nificant viscosity loss is related to the hot acid hydrolysis of the carbohydrates with the 2.5 pH conditions (Ventorim et al. 2005, 2008).

$D_{HT}(EP)D_1$ and $D_0(EP)D_1$ pulp properties

The impact of D_0 and D_{HT} process on the final pulp brightness and viscosity of 19 non-wood plant pulps are shown in Table S2. A lot of variation of bleachability among these nineteen non-wood plant pulps was observed. Wheat straw pulp showed the highest final pulp brightness. At kappa factor 0.15, final pulp brightness of oxygen delignified was 90.17 % in D_0 process, which increased to 91.30 % in D_{HT} process. As in initial and $D_0/D_{HT}(EP)$ low brightness, there was no improvement of final pulp brightness for banana pseudo stem pulp. The final brightness reached to 44 % only at the highest ClO_2 charge. Dhaincha, eggplant plant, jute fiber and jute tick pulps also showed good bleachability. The oxygen delignified eggplant stalks pulp also showed good bleachability. At kappa factor 0.25, the final brightness of eggplant stalks oxygen delignified pulp reached to 82.24 % in D_0 process, while the same brightness was obtained at kappa factor of 0.15 in D_{HT} process and saved 40 % ClO_2 in the first stage. Kumar et al. (2007) showed that the use of D_{HT} reduced 15 % ClO_2 requirement and improved the brightness and brightness stability in comparison with the reference sequences D_0 .

The effect of the D_{HT} on the residual HexA of final pulps (oxygen delignified) was also studied and shown Figure 4. The residual HexA content in most of the D_{HT} bleached pulps was much less than the D_0 pulps. Banana pseudo stem, banana leaf, banana peduncle, chia plant and cassava plant pulps did not show significant differ-

Figure 4: Effect of D_{HT} delignification on HexA content in final bleached pulp.

ences in HexA contents between D_0 and D_{HT} in final pulps. This result reflected in final pulp brightness. At kappa factor, 0.2, the residual HexA contents were 1.02, 2.37, and 5.31 $\mu\text{mol/g}$ for D_{HT} pulps and 2.39, 4.34 and 7.21 $\mu\text{mol/g}$ for D_0 pulps from wheat straw, dhaincha and jute fiber pulps, respectively. This is cause of degradation of HexA in D_{HT} process (Colodette and Henricson 2012). HexA could not react with chlorine dioxide, but react with its intermediates such as hypochlorous acid and molecular chlorine (Tarvo et al. 2010, Lehtimaa et al. 2010), thereby influencing the bleachability and enhancing the consumption of chlorine dioxide. Percentage of HexA removal in D_{HT} process showed a linear relationship with final pulp brightness (Figure 5). The HexA removal in banana pseudo stem pulp was only 35 %, consequently showed the lowest pulp brightness (44 %) among these 19 non-wood pulps. On the other hand, the highest HexA removal was 96 % for dhaincha pulp, where final pulp brightness was 86 %.

Figure 5: Removal of HexA content D_{HT} delignification and final pulp brightness.

Final pulp viscosity was also shown in Table S2. The final pulp viscosity was related to the entering viscosity of pulp of unbleached. Chia plant and lentil stalks showed the lowest final pulp viscosity of 5–7 mPa.s, where pulp viscosity entering into the bleaching system was 10–12 mPa.s. The pulp viscosity loss indicates cellulose degradation, ultimately reflected in papermaking properties.

COD in bleach effluent

The environmental impact of 19 non-wood plants pulps bleaching by D_0 and D_{HT} processes were investigated. As shown in Table 3, the COD value of combined effluent from D_0 , (EP) and D_1 stage in $D_{HT}(EP)D_1$ bleaching was lower than $D_0(EP)D_1$. Oxygen delignified pulp had

Table 3: COD values (mg/l) of bleach effluents from nineteen non-wood plant pulps.

Pulp	Unbleached (UB)		Oxygen delignified (OD)	
	D ₀	D _{HT}	D ₀	D _{HT}
Bamboo	652.9	443.9	479.0	323.7
Banana pseudo stem	837.3	743.2	263.4	235.2
Banana leaf	1105.0	1004.0	832.9	709.2
Banana peduncle	824.6	808.1	479.3	404.1
Cassava stalks	1023.0	1007.7	555.1	376.3
Chia stalks	715.0	610.1	677.4	414.0
Cotton stalks	752.9	520.7	479.0	323.7
Dhaincha	1138.4	1060.7	845.4	532.8
Eggplant stalks	700.9	673.5	398.6	364.2
Jute fiber	525.8	423.4	297.6	222.3
Jute stick	728.8	613.4	652.1	522.6
Kaun straw	1352.4	1090.00	942.2	733.8
Mulberry stalks	768.7	668.7	631.6	563.2
Mustard stalks	1187.0	984.0	1043.0	822.0
Okra stalks	1132.8	1092.4	930.6	798.4
Pineapple leaves	723.8	677.4	639.7	479.8
Red lentil stalks	827.9	762.1	461.0	376.3
Rice straw	696.7	669.9	328.2	267.9
Wheat straw	713.3	646.7	200.0	173.3

always lower COD load in effluent. The ClO₂ charge in D₀/D_{HT} stage of oxygen delignified was certainly lower as kappa number was lower, thus released less organic material from the pulp to the filtrate and resulted lower COD load. Similar results were also observed in ECF bleaching by Shin and Mera (1994). As an example of bamboo pulp, the D_{HT} process at kappa factor 0.2 decreased COD value from 652.92 mg/l to 443.9 mg/l for unbleached pulp and from 479.04 mg/l to 323.72 mg/l for oxygen delignified pulp. Similar COD value reduction in other reported data are available (Kaur et al. 2018, 2019). Kaur et al. (2019a) showed that D_{HT} based bleaching sequence reduced chlorophenols, chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringols and bromophenols were reduced by 9 %, 50 %, 34 %, 47 %, 17 % and 31 %, respectively, at the same chemical charge. D_{HT} based sequence also effectively reduced environmental parameters i.e. COD, BOD, TS, colour, lignin and AOX without compromising optical and strength properties Kaur et al. (2019a). Rolf et al. (2009) showed that the amount of dissolved organics, represented by COD was proportional to kappa number of unbleached pulp for wood and non-wood pulps. But at a given kappa number, the amount of COD was much higher for the non-wood pulp.

Conclusions

A lot of variation of bleachability among these nineteen non-wood plant pulps was observed. D_{HT} delignification produced pulp of lower kappa number and higher brightness than D₀ after extraction stage. HexA content in the final bleached pulp in D_{HT} delignification was lower than those of D₀, resulted higher final brightness. Percentage of HexA removal in D_{HT} process showed a linear relationship with final pulp brightness. The oxygen delignified pulp and D_{HT} delignification discharged lower COD.

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