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 (ClO$_2$) charge and temperature exhibited lower kappa 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 hexenuronic 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; hexenuronic acid; kappa 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 globally 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 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. 2012, Open Access. © 2020 Ferdous et al., published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 International License.)
The studies showed that xylanase, oxygen, peracid or acid treatment improved subsequent ClO₂ bleaching. Hot acid treatment and high temperature chlorine dioxide delignification (Dₜ) bleaching are thoroughly investigated by Ragnar and Lindström (2004) and showed that the Dₜ 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 ClO₂ delignification (Dₜ0) stage is that the reaction rate of chlorine dioxide with remaining pulp lignin is faster at high temperature than that with hexeneuronic 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 Dₜ0 treatment resulting in decrease in generation of chlorinated organic halides. Ventorim et al. (2005) also found that at a similar ClO₂ dose (kappa factor 0.20 at pH 3.0) in Dₜ0 bleaching produced 46.3% less AOX in the filtrate in relation to the D₀. 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 D₀ into a single operation, (A/D₀) or “hot D₀-Stage.” Such processes can be very effective at reducing the total ClO₂ needed for ECF bleaching of hardwood pulps (20 to 50%).

Most of the Dₜ0 bleaching studies used 95 °C for longer time, consequently reduced viscosity and a slight drop in final pulp brightness. The lower brightness obtained after Dₜ0/E 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 Dₜ0 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 (ClO₂) of unbleached and oxygen delignified pulps of 19 non-wood plants was carried out with varying ClO₂ 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.

### 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

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**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    |
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 | O₂-delignified | Un-bleached | O₂-delignified | Un-bleached | O₂-delignified |
| Bamboo               | 18                 | 170          | 2                 | 26.82         | 7.31          | 16.13        | 14.98          | 19.81        | 45.74          | 13.11       | 13.34         |
| Banana pseudo stem   | 18                 | 170          | 2                 | 23.57         | 12.03         | 19.08        | 18.51          | 11.32        | 15.93          | 10.91       | 10.67         |
| Banana leaf          | 20                 | 170          | 2                 | 33.28         | 17.41         | 20.89        | 20.79          | 16.09        | 23.66          | 28.32       | 28.65         |
| Banana peduncle      | 20                 | 170          | 2                 | 28.8          | 22.6          | 21.39        | 19.59          | 14.32        | 27.86          | 20.34       | 20.76         |
| Cassava stalks       | 20                 | 170          | 2                 | 31.4          | 10.32         | 12.81        | 12.56          | 16.22        | 24.78          | 24.28       | 24.76         |
| Chia stalks          | 20                 | 170          | 3                 | 27.65         | 12.11         | 10.96        | 10.22          | 15.62        | 22.55          | 53.65       | 53.24         |
| Cotton stalks        | 20                 | 170          | 3                 | 31.19         | 8.01          | 11.78        | 11.61          | 11.15        | 30.57          | 76.73       | 61.23         |
| Dhaincha             | 18                 | 170          | 2                 | 14.1          | 6.9           | 14.69        | 13.26          | 29.59        | 53.42          | 53.32       | 53.14         |
| Eggplant stalks      | 18                 | 170          | 3                 | 28.79         | 13.68         | 12.81        | 12.56          | 21.71        | 30.5           | 26.64       | 27.22         |
| Jute fiber           | 18                 | 170          | 2                 | 11.98         | 7.62          | 13.21        | 12.48          | 28.95        | 56.99          | 79.41       | 67.34         |
| Jute stick           | 20                 | 170          | 2                 | 18.26         | 6.26          | 14.85        | 13.13          | 27.47        | 47.69          | 77.60       | 70.36         |
| Kaun straw           | 14                 | 150          | 2                 | 10.07         | 6.56          | 15.49        | 14.23          | 32.26        | 41.51          | 32.32       | 33.43         |
| Mulberry stalks      | 20                 | 170          | 3                 | 21.35         | 6.86          | 12.65        | 11.09          | 22.86        | 44.92          | 60.65       | 61.04         |
| Mustard stalks       | 20                 | 170          | 3                 | 18.6          | 10.45         | 13.51        | 12.73          | 23.12        | 41.59          | 37.03       | 38.22         |
| Okra stalks          | 20                 | 170          | 3                 | 30.68         | 22.31         | 21.57        | 21.01          | 13.02        | 15.28          | 22.00       | 25.32         |
| Pineapple leaves     | 14                 | 170          | 2                 | 19.3          | 6.1           | 12.65        | 11.79          | 19.44        | 32.25          | 8.87        | 8.23          |
| Red lentil stalks    | 20                 | 170          | 3                 | 18.26         | 5.42          | 12.69        | 11.55          | 24.75        | 39.50          | 21.90       | 22.23         |
| Rice straw           | 14                 | 150          | 2                 | 13.16         | 5.17          | 16.04        | 15.31          | 37.93        | 50.05          | 7.66        | 7.67          |
| Wheat straw          | 14                 | 150          | 2                 | 12.32         | 5.56          | 16.75        | 16.05          | 29.37        | 35.70          | 10.66       | 10.33         |
were 110 °C, retention time 60 min, pulp consistency 10 %, NaOH 2 %, MgSO4 0.3 % and O2-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.

D0(EP)D1 and DHT(EP)D1 bleaching

Unbleached and oxygen delignified pulps were bleached by D0(EP)D1, and DHT(EP)D1 bleaching sequences (where D represents chlorine dioxide and (EP) represents peroxide reinforced alkaline extraction). The chlorine dioxide charge in D0 and DHT stages were varied by kappa factor 0.15, 0.2 and 0.25. The temperature was 70 °C in D0 stage for 45 min. Pulp consistency was 10 %. The pH was adjusted to 2.5 by adding dilute H2SO4. In the DHT 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 % H2O2 (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 D1 stage, pH was adjusted to get end pH 4.5. The ClO2 charge in the D1 stage was fixed to 1 %. The brightness, viscosity and HexA of the bleached pulp and COD in the mixed effluent collected from D0, EP and D1 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 μmol/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.

DHT(EP) and D0(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 ClO2 stage is denoted as D0 and DHT at 70 °C and 85 °C, respectively. As expected, increasing kappa factor resulted in decrease kappa number and viscosity and increase brightness regardless D0 or DHT processes. DHT bleaching is more efficient than D0 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 DHT bleaching were always lower than the corresponding D0 bleaching. Kaur et al. (2019a) also showed that the kappa number of rice straw pulp after extraction stage was lower for DHT than D0 with the same ClO2 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
bleaching with kappa factor 0.2. (EP) kappa number were 11.76 and 7.78 in D₀ bleaching, which decreased to 9.61 and 5.15 in D₇HT for unbleached and oxygen delignified pulp, respectively. The (EP) kappa number for wheat straw pulps decreased from 1.83 and 0.98 in D₀ bleaching to 1.38 and 0.63 in D₇HT bleaching. The higher kappa number decreased in the D₇HT(EP) stage as compared to the D₀(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 D₇HT 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 D₀ stage affected bleachability of a red oak pulp that underwent a hot acid hydrolysis.

Pulp brightness after D₀(EP)/D₇HT(EP) stage is also shown in Table S1. Oxygen delignified pulp showed better pulp brightness than the unbleached pulp regardless D₀ or D₇HT bleaching. The (EP) brightness of D₇HT treated pulps was better than those treated by D₀ 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 staring, 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 D₇HT stage than D₀ stage after (EP) stage was 3 % for dhaincha oxygen
delignified pulp. Ventorim et al. (2005) found the first chlorine dioxide stage at high temperature (D₇HT) 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 D₇HT bleaching. As for example, Figure 3 shows that the pulp viscosity of oxygen delignified banana leaf pulp decreased from 19.23 mPa.s in D₀ process to 18.93 mPa.s in D₇HT process only. No change of pulp viscosity was observed for chia pulp. But other studied showed that the D₇HT-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-
significant viscosity loss is related to the hot acid hydrolysis of the carbohydrates with the 2.5 pH conditions (Ventorim et al. 2005, 2008).

**D\textsubscript{HT} (EP)D\textsubscript{1} and D\textsubscript{0} (EP)D\textsubscript{1} pulp properties**

The impact of D\textsubscript{0} and D\textsubscript{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\textsubscript{0} process, which increased to 91.30 % in D\textsubscript{HT} process. As in initial and D\textsubscript{0}/D\textsubscript{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\textsubscript{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\textsubscript{0} process, while the same brightness was obtained at kappa factor of 0.15 in D\textsubscript{HT} process and saved 40 % ClO\textsubscript{2} in the first stage. Kumar et al. (2007) showed that the use of D\textsubscript{HT} reduced 15 % ClO\textsubscript{2} requirement and improved the brightness and brightness stability in comparison with the reference sequences D\textsubscript{0}.

The effect of the D\textsubscript{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\textsubscript{HT} bleached pulps was much less than the D\textsubscript{0} pulps. Banana pseudo stem, banana leaf, banana peduncle, chia plant and cassava plant pulps did not show significant differences in HexA contents between D\textsubscript{0} and D\textsubscript{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 μmol/g for D\textsubscript{HT} pulps and 2.39, 4.34 and 7.21 μmol/g for D\textsubscript{0} pulps from wheat straw, dhaincha and jute fiber pulps, respectively. This is cause of degradation of HexA in D\textsubscript{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\textsubscript{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 %.

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\textsubscript{0} and D\textsubscript{HT} processes were investigated. As shown in Table 3, the COD value of combined effluent from D\textsubscript{0}, (EP) and D\textsubscript{HT} (EP)D\textsubscript{1} bleaching was lower than D\textsubscript{HT} (EP)D\textsubscript{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) |
|-----------------------|-----------------|-------------------------|
|                       | D₀               | Dₜₜ           | D₀             | Dₜₜ           |
| Bamboo                | 652.9           | 443.9         | 479.0          | 323.7         |
| Banana pseudo stem    | 837.3           | 743.2         | 263.4          | 235.2         |
| Banana leaf           | 1105.0          | 1040.0        | 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         |
| Dhaichna              | 1138.4          | 1060.7        | 845.4          | 532.8         |
| Eggplant stalks        | 700.9           | 673.5         | 396.8          | 364.2         |
| Jute fiber             | 525.8           | 423.4         | 297.6          | 222.3         |
| Jute stick             | 728.8           | 631.4         | 652.1          | 522.6         |
| Kaun straw             | 1352.4          | 1090.0        | 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/Dₜₜ 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 Dₜₜ 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 Dₜₜ 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. Dₜₜ 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. Dₜₜ delignification produced pulp of lower kappa number and higher brightness than D₀ after extraction stage. HexA content in the final bleached pulp in Dₜₜ delignification was lower than those of D₀, resulted higher final brightness. Percentage of HexA removal in Dₜₜ process showed a linear relationship with final pulp brightness. The oxygen delignified pulp and Dₜₜ delignification discharged lower COD.

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