

# EFFECT OF INTRODUCING OZONE PRIOR TO ELEMENTAL CHLORINE FREE BLEACHING OF WHEAT STRAW PULP ON PULP, PAPER AND EFFLUENT PROPERTIES

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Ozone has been considered for the development of greener processes for hardwood and softwood pulps. This paper summarizes the results obtained using ozone bleaching on wheat straw pulp, followed by elemental chlorine free bleaching. This work evaluated the effect of introducing ozone bleaching on the optical properties of wheat straw pulp, along with the content of metal ions and hexenuronic acid in the pulp, pulp strength and morphological properties, as well as effluent properties. Introducing an ozone stage into the ECF bleaching sequence of wheat straw pulp improved pulp brightness by 2.5 units, pulp whiteness – by 4.0 units, while reducing the hexenuronic acid content by 21.6% and brightness reversion – by 34.8%, and allowed attaining physical strength and morphological properties comparable to those of the control. The introduction of the ozone treatment reduced the Fe, Cu and Mn content in the pulp by 6%, 11% and 31%, respectively. It also significantly reduced the COD in the bleaching filtrate by 41.2%, BOD – by 39.6%, colour level – by 57.9% and AOX – by 47.3%, compared to the control. The introduction of ozone prior to elemental chlorine free bleaching of wheat straw pulp was demonstrated to improve effluent quality, while yielding comparable pulp and paper properties.

**Keywords:** elemental chlorine free bleaching, ozone bleaching, wheat straw pulp, viscosity, brightness, kappa number

## INTRODUCTION

Ozone bleaching is now well established for hardwood and softwood pulps, being considered as one of the best available technology from the environmental point of view. Presently, about 24 wood based mills worldwide are producing about 8 million tons of ozone bleached pulp.<sup>1</sup> Unfortunately, none of the agro based mills is reported to use ozone as bleaching chemical in their bleaching sequence. The reason may be the lower physical strength properties of agro residue pulps, as compared to those of wood pulps. Ozone is a very strong oxidizing agent, which reacts with all the chemical constituents present in the cellulosic pulp. Though the reaction of ozone is more selective towards lignin, as compared to carbohydrates, the formation of intermediate radicals during ozone bleaching resulted in the deterioration of carbohydrates.<sup>2,3</sup> The formation of radicals during the ozone bleaching of pulps not only promotes an unwanted attack on carbohydrates, but also decomposes the ozone and thereby increases its consumption. The reaction of ozone with the carbohydrate fraction of the pulp reduced pulp viscosity, which ultimately resulted in lower strength properties of paper.<sup>4</sup> Ozone bleaching of pulps, such as agro residue based raw material pulps, having lower physical strength properties is supposed to be more critical.

Higher degradation of carbohydrates during ozone bleaching of agro residue pulps may make the pulp unusable for papermaking. In the present study, the effect of introducing ozone in elemental chlorine free (ECF) bleaching of wheat straw pulp is investigated.

Until now, the majority of the research studies on ozone bleaching were performed on softwood or hardwood kraft pulps.<sup>5-9</sup> Very scanty literature is available on the ozone bleaching of non-wood pulps.<sup>10-12</sup> Earlier, the main parameters affecting the ozone bleaching of wheat straw pulp were determined using the Plackett–Burman design,<sup>13</sup> and the ozone bleaching conditions for wheat straw soda pulp were further optimized using response surface methodology.<sup>14</sup>

This paper describes the introduction of ozone in the ECF bleaching of wheat straw pulp on the optical properties, content of metal ions and hexenuronic acid, strength and morphological properties of the pulp, as well as on effluent properties. The results of the study will be relevant to the pulp and paper industry using ECF bleaching sequence without ozone. Present study will be more beneficial for agro based paper mills planning to improve product and effluent quality.

## **EXPERIMENTAL**

### **Material used**

For the study, wheat straw was collected from North India and was separated from grain using power driven threshing machines.

### **Physical and chemical analysis of wheat straw**

Bulk density of the wheat straw was determined as per Tappi Useful Method UM 23 (2015), generally used to determine the bulk density of wood chips. The sample of wheat straw was prepared for chemical analysis as per Tappi T 264 cm-07. Different chemical constituents of wheat straw, such as cellulose, hemicelluloses, holocellulose, acid insoluble lignin and acetone extractives, were analyzed following the test methods of Updegraff (1969),<sup>15</sup> Deschatelets (1986),<sup>16</sup> Wise (1946),<sup>17</sup> along with Tappi T 222 om-11 and Tappi T 204 cm-07, respectively. The ash content, acid insolubles, silica content, 1% sodium hydroxide solubility and hot water solubility were determined using Tappi T 211 om-12, Tappi T 244 cm-11, Tappi T 245 cm-07, Tappi T 212 om-12 and Tappi T 207 cm-08, respectively.

### **Pulping of wheat straw**

Following pulping conditions were kept for producing unbleached pulp of about 14 kappa number in the lab autoclave digester using soda pulping process: active alkali dose as NaOH – 16.0%, anthraquinone dose – 0.05%, material to liquor ratio – 1:4, pulping time at maximum temperature – 20 min, maximum pulping temperature – 166 °C, H factor – 225. After completion of pulping the digested material was disintegrated and washed with hot water to remove the dissolved substances. Prior to further processing the pulp was screened using 0.15 mm slotted screen in a laboratory Somerville type pulp fractionator as per Tappi test method T 275 sp-12.

### **Oxygen delignification of pulp**

Single stage oxygen delignification (ODL) of the screened pulp was carried out in a pressurized reactor with stirring during the reaction. The following conditions were maintained during the ODL stage: sodium hydroxide dose of 1.5% per o.d. pulp, oxygen dose of 1.5% per o.d. pulp, pulp consistency of 10%, time of 60 min and temperature of 85 °C.

### **Ozone treatment of pulp**

Before the ozone treatment, the pulp was preacidified to a pH of about 2.0, using 2 mol/L sulfuric acid at a pulp consistency of about 5%, then centrifuged to a consistency of about 30%, before being fluffed. The ozone stage bleaching of the pulp was performed in a reactor with continuous ozone gas injection through small apertures at the bottom and under stirring to ensure proper interaction of the ozone gas with the fluffed pulp. The following conditions were maintained during the ozone bleaching of pulp: consistency of 30%, pH of 2.0, temperature of 50 °C, time of 3 min, ozone gas flow rate of 1.5 L/min, ozone gas concentration of 0.045 g/L.

The residual ozone left after the reaction and the ozone dose applied to the pulp were measured by the iodometric wet chemistry method.<sup>18</sup> An alkali treatment was done on the pulp, after the ozone treatment, in low density polyethylene bags, using the following conditions: temperature of 75 °C, consistency of 10%, time of 30 min and sodium hydroxide dose of 1.5% per o.d. pulp. Alkali extraction of the pulp was then carried out. The pulp was washed thoroughly prior to determining its kappa number, brightness and viscosity.

### **Bleaching of pulp**

Elemental chlorine free bleaching of oxygen delignified and ozone treated wheat straw pulps was carried out following a D<sub>0</sub>E<sub>OP</sub>D<sub>1</sub> sequence using the conditions summarized in Table 1. The different stages were performed in sealed polythene bags placed in a thermostat-controlled water bath.

### **Analysis of pulp parameters**

Different properties of the wheat straw pulp, such as kappa number, viscosity, brightness, whiteness, hexenuronic acid (HexA) and freeness, were analyzed following Tappi test methods T 236 om-06, T 230 om-08, T 525 om-12, T 560 om-05, T 560 om-05 and T 227 om-09, respectively.

Table 1  
Conditions of D<sub>0</sub>E<sub>OP</sub>D<sub>1</sub> sequence

Particulars	D <sub>0</sub> stage	E <sub>OP</sub> stage	D <sub>1</sub> stage
Temperature (°C)	55	80	75
Time (min)	45	120	180
Consistency (%)	10	10	10
Sodium hydroxide (%)	-	1.3 <sup>#</sup> /0.7 <sup>*</sup>	-
Hydrogen peroxide (%)	-	0.5	-
Chlorine dioxide (%)	0.88 <sup>#</sup> /0.46 <sup>*</sup>	-	0.5

<sup>#</sup>Dose of chemicals used for bleaching oxygen delignified pulp; <sup>\*</sup>Dose of chemicals used for bleaching ozone treated pulp

The brightness reversion tendency of the bleached pulps was evaluated in terms of post colour (P.C.) number calculated from the brightness value measured before and after aging. Standard accelerated aging of pulps was carried out by placing pulp sheets at 105 °C for 4 h as per Tappi UM 200. The P.C. number of the pulp was calculated using the equation described by Giertz,<sup>19</sup> as given below:

$$\text{P. C. number} = \left[ \frac{(1 - R_2)^2}{2R_2} - \frac{(1 - R_1)^2}{2R_2} \right] 100 \quad (1)$$

where R<sub>1</sub> is the brightness before the aging test and R<sub>2</sub> is the brightness afterwards.

The content of transition metals (Fe, Cu, Mn, Zn and Mg) in the pulp was determined using a NovAA 300 spectrophotometer manufactured by Analytik Jena AG after the acid digestion of the samples, according to Tappi test method T 266 om-06. The morphological properties of the pulp fibers were measured using an L&W fiber tester as per Tappi test method T 271 om-07.

Paper handsheets were prepared from the refined and unrefined pulps, as per TAPPI T 205 sp-06 using a British type handsheet former. Refining the pulps were carried out in a PFI mill (Hamjern Maskin A/S, Hamar, Norway; PFI mill no. 616), applying 100 revolutions as per Tappi test method T 248 sp-08. Prior to analyzing the physical strength properties, as per Tappi test method T 220 sp-06, the handsheets were conditioned at 27±2 °C and 65±5% relative humidity as per ISO: 187.

#### Analysis of effluent parameters

The filtrates (effluent) generated in each stage of bleaching (D<sub>0</sub>, E<sub>OP</sub> and D<sub>1</sub> stages) were mixed in the corresponding volumetric proportions. The combined effluent was characterized with regard to chemical oxygen demand (COD), biological oxygen demand (BOD), as well as colour and adsorbable organic halide (AOX), using test methods IS: 3025 (Part-58), IS: 3025 (Part-44), APHA: 2120 C and ISO: 9562:2004, respectively.

## RESULTS AND DISCUSSION

### Physical and chemical properties of wheat straw

The physical and chemical properties of the wheat straw used in the present study, determined on oven dried material basis, are given in Table 2. Wheat straw has 64.5 kg/m<sup>3</sup> bulk density, which is marginally higher than the reported values of 52-53 kg/m<sup>3</sup> for chopped wheat straw.<sup>20</sup> Bulk density is an important characteristic of raw materials, which directly influences the transportation cost and the storage area.<sup>21,22</sup> Wheat straw has 2.3% acetone extractives and 9.9% water soluble extractives, which are comparable with earlier reported values for wheat straw and hardwood species, but lower than the values reported for softwood species.<sup>23,24</sup> Acetone removes mainly resin material, including the fatty and resin acids, sterols, waxes and fats present in the raw material. Subsequently, hot water is used to extract tannins, gums, sugars, starches and colouring matter. Hot water soluble extractives of wheat straw mainly contain free fatty acids, waxes, sterols, triglycerides, diglycerides, sterol esters, resin acid and phenolic compounds.<sup>25</sup> Wheat straw was found to contain 36.6% cellulose, 28.1% hemicelluloses, 16.4% lignin and 7.1% inorganics, which is comparable with the values reported earlier by other researchers for wheat straw obtained from different places.<sup>26,27</sup>

Table 2  
Physical and chemical properties of wheat straw

Particulars	Results
Bulk density (kg/m <sup>3</sup> )	64.5 ± 1.9
1% NaOH solubility (%)	28.2 ± 0.8
Hot water solubility (%)	11.1 ± 0.7
Acetone extractives (%)	2.3 ± 0.2
Water soluble extractives (%)	9.9 ± 0.6
Hemicelluloses (%)	28.1 ± 0.3
Cellulose (%)	36.6 ± 0.8
Lignin (%)	16.4 ± 0.3
Holocellulose (%)	64.4 ± 1.0
Ash (%)	7.1 ± 0.2
Acid insolubles (%)	4.6 ± 0.3
Silica (%)	4.1 ± 0.2

Table 3  
Bleaching of pulp using ECF sequence D<sub>0</sub>E<sub>OP</sub>D<sub>1</sub> with and without ozone

Particulars	Results	
	ECF (control)	ECF (with ozone)
<i>ODL stage</i>		
Kappa no.	8.9	
Brightness (%ISO)	47.1	
Viscosity (mPas)	12.9	
<i>Z stage</i>		
Kappa no.	-	4.7
Brightness (%ISO)	-	61.5
Viscosity (mPas)	-	10.8
<i>D<sub>o</sub> stage</i>		
Final pH	2.2 ± 0.1	2.2±0.1
Residual ClO <sub>2</sub> (ppm)	16.7 ± 0.7	13.6±0.5
<i>E<sub>OP</sub> stage</i>		
Final pH	10.6 ± 0.1	10.5±0.1
Residual H <sub>2</sub> O <sub>2</sub> (ppm)	34.0 ± 2.0	66.0±2.0
Brightness (%ISO)	82.3 ± 0.2	84.2±0.1
Kappa number	2.3 ± 0.1	1.5±0.1
<i>D<sub>1</sub> stage</i>		
Final pH	3.7 ± 0.1	3.8±0.1
Residual ClO <sub>2</sub> (ppm)	19.0 ± 2.0	26.3±2.5
Brightness (%ISO)	84.5 ± 0.2	87.0±0.2
P.C. number	0.46 ± 0.04	0.30±0.01
CIE whiteness	79.4 ± 0.3	83.4±0.3
Viscosity (mPas)	10.3 ± 0.1	9.7±0.1

Pulps produced from agricultural residues, except sugarcane bagasse, are difficult to bleach to a high brightness (+85% ISO) level. Wheat straw pulp was reported to reach 84.8% ISO brightness, using 10 different conventional and elemental chlorine free (ECF) bleaching sequences.<sup>28</sup> Oxygen delignified wheat straw pulp was bleached to 84.5% ISO brightness by the ECF bleaching sequence (D<sub>0</sub>E<sub>OP</sub>D<sub>1</sub>), using optimized bleaching chemicals and conditions. Based on earlier studies and the results of the present study, it appears that wheat straw pulp has a brightness ceiling at about 85% ISO brightness level, when using ECF bleaching sequences without ozone. With the introduction of ozone, prior to the ECF bleaching sequence, pulp brightness was increased by 2.5 units to 87.0% ISO. The whiteness of the pulp was also improved by 4.0 units from 79.4 to 83.4 CIE units. The improvement in the pulp brightness and whiteness of the ECF bleached pulps after introducing ozone in the previous stage may be due to the additional removal of HexA and metal ions in the ozone stage. The metal ions present in the pulp form strongly coloured complexes with the lignin structures and cause a significant decrease in pulp brightness, while the presence of a high amount of HexA also reduces the brightness

of pulp.<sup>29,30</sup> When introducing ozone prior to ECF bleaching, the viscosity of the final bleached pulp was marginally reduced to 9.7 mPas from 10.3 mPas. The ozone treated pulp required less chlorine based bleaching chemicals and attained higher brightness, compared to the pulp bleached without using ozone. The improved bleachability of the ozone treated pulp may be due to the better removal of metal ions, compared to that from the pulp bleached without ozone.

Brightness reversion (P.C. number) of the pulp bleached after the ozone treatment was reduced by 34.8%, as compared to ECF bleached pulp without ozone. The reason behind the reduction in brightness reversion may lie in the presence of a lower amount of HexA in the pulp bleached using the ECF sequence with ozone, compared to the pulp bleached without ozone. Other researchers also reported that pulps with higher HexA content are more prone to brightness reversion,<sup>31</sup> and the use of ozone in prebleaching reduced the brightness reversion by removal of HexA.<sup>7</sup>

### Metal ions in pulp

The effect of introducing ozone in the ECF bleaching of wheat straw pulp on the content of metal ions was evaluated by analysing five main metal ions present in the pulp, *i.e.* magnesium (Mg), iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu). Metal ion contents in the final wheat straw pulps bleached with and without ozone are shown in Figure 1. The ECF bleached wheat straw pulp exhibited 87 ppm of Mg, 216 ppm of Fe, 22 ppm of Zn, 6 ppm of Mn and 4 ppm of Cu. Out of the five metals analysed, three metals, namely Fe, Cu and Mn, are reported to be the most harmful for pulp bleaching with respect to brightness development, cellulose degradation and chemical consumption.<sup>32,33</sup> The transition metal ions present in the pulp were reduced substantially in the ozone bleaching stage due to the extremely low pH (about 2.0) maintained during the treatment. Introducing the ozone stage prior to the ECF bleaching of wheat straw pulp further reduced the Fe, Cu and Mn content in the pulp by 6%, 11% and 31%, respectively. These metal ions come primarily from the raw material and secondarily from contamination caused by the process water and corrosion of the equipment. The presence of these metal ions leads to the decomposition of bleaching chemicals and the formation of non-selective species, which leads to the degradation of polysaccharide chains and thereby loss of pulp viscosity.<sup>34,35</sup>

### Hexenuronic acid in pulp

The content of hexenuronic acid (HexA) present in the unbleached pulps of different raw materials used for making pulp and paper is listed in Table 4. HexA groups are formed in the xylan chains during kraft pulping. These acid groups cause increased consumption of bleaching chemicals, decreased brightness, greater brightness reversion and poorer metal removal.<sup>36</sup> Wheat straw has HexA content of 13.6  $\mu\text{mol/g}$ , which is higher than that of sugarcane bagasse and rice straw, but lower than that of bamboo, eucalyptus and casuarina. Casuarina has the highest HexA content – of 54  $\mu\text{mol/g}$ , and sugarcane bagasse the lowest – of 6.6  $\mu\text{mol/g}$ . The presence of HexA has an influence on the kappa number of pulp, as permanganate attacks HexA, which therefore contributes to the kappa number of the pulps. The contribution of the HexA content to the kappa number is of 2-7 units, depending on the type of the pulp.<sup>37</sup> HexA groups consume approximately 8.6 equivalents of potassium permanganate per mole of HexA present in the pulp.<sup>38</sup> The HexA present in the pulp also reacted with the bleaching chemicals, such as ozone and chlorine dioxide. The reaction rate of ozone with HexA was reported to reach 134 mmol/kg/min, as compared to 56.8 mmol/kg/min, in the case of lignin in oxygen delignified eucalyptus pulp.<sup>39</sup>

Table 4  
Hexenuronic acid present in unbleached pulps of different raw materials

Particulars	Hexenuronic acid content ( $\mu\text{mol/g}$ )
Sugarcane bagasse	6.6 $\pm$ 0.6
Rice straw	10.8 $\pm$ 0.4
Wheat straw	13.6 $\pm$ 0.5
Bamboo	18.2 $\pm$ 0.9
Eucalyptus	41.5 $\pm$ 2.3
Casuarina	54.0 $\pm$ 2.5

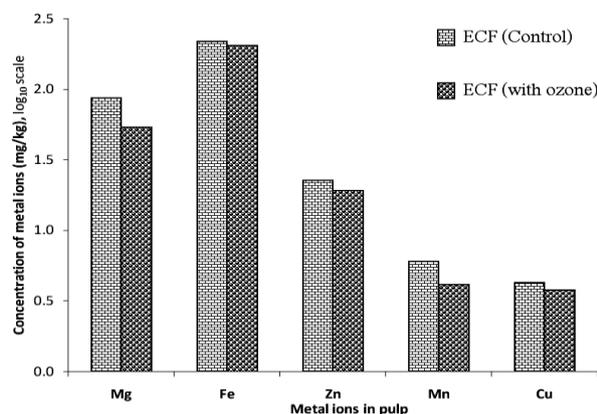


Figure 1: Effect of introducing ozone on metal ions in bleached pulp

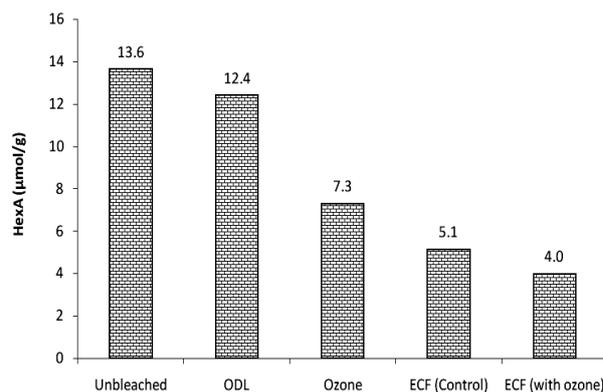


Figure 2: Hexenuronic acid content in wheat straw pulp at different stages

The content of HexA in wheat straw pulp at different stages is illustrated in Figure 2. The ODL stage was the least effective in reducing the HexA from the pulp (causing a decrease of 9.0%), whereas the ozone stage reduced it by 41.1%. The ECF bleaching of ODL pulp and ozone treated pulps reduced the HexA content by 62.3% and 68.0%, respectively. The additional reduction in HexA content in the ozone treated ECF bleached wheat straw pulp has contributed to an improvement in pulp brightness and whiteness, as well as to a reduction in brightness reversion. Shatalov and Pereira<sup>40</sup> also reported a reduction of about 67% in hexenuronic acids recorded during bleaching of giant reed kraft pulp.

### Physical strength properties

The physical strength properties of refined and unrefined ECF bleached wheat straw pulps (with and without ozone) are given in Table 5. For the unrefined pulps, the freeness reached 385 CSF and 360 CSF for the ECF bleached pulp without ozone (control) and the ECF bleached pulp with ozone, respectively. The paper handsheets made from the unrefined control pulp exhibited 43.5 mN/g tensile index, 3.6 kN/g burst index, 7.0 mN.m<sup>2</sup>/g tear index and 27 double fold numbers. These physical strength properties were improved upon refining, except the tear index. There was no noticeable difference in the physical strength properties of the control and the ECF bleached pulp with ozone. Mishra *et al.*<sup>41</sup> reported marginal (4.3%) reduction in the tear index of eucalyptus pulp after introducing ozone in elemental chlorine free bleaching.

### Morphological properties

The morphological properties of the ECF bleached wheat straw pulps (with and without ozone) are listed in Table 6. The ECF bleached wheat straw pulp without ozone exhibited 0.818 mm average fiber length, 17.5 µm mean width and 71.8 µg/m coarseness. The morphological properties of the ECF bleached wheat straw pulp with ozone were comparable with those of the control pulp. Moreover, the major morphological properties reported in this paper are comparable with those reported earlier by different researchers for wheat straw pulp, *i.e.* average fiber length of 0.66-1.18 mm and mean width of 13.6-19.32 µm.<sup>42-45</sup>

Table 5  
Physical strength properties

Particulars	ECF (control)		ECF (with ozone)	
	Unrefined	Refined	Unrefined	Refined
PFI revolution (no.)	0	100	0	100
Freeness (mL, CSF)	385 ±5	320 ±5	360 ±5	305 ±5
Tensile index (mN/g)	43.5 ±1.3	51.9 ±1.5	44.5 ±2.4	53.0 ±1.6
Burst index (kN/g)	3.6 ±0.2	4.9 ±0.2	3.9 ±0.1	4.9 ±0.1
Tear index (mN.m <sup>2</sup> /g)	7.0 ±0.3	6.7 ±0.2	7.0 ±0.3	6.8 ±0.3
Double fold (number)	27.0±2.0	62.0±8.2	26±2	60±3

Table 6  
Morphological properties

Particulars	ECF (control)	ECF (with ozone)
Mean length (mm)	0.818 ± 0.014	0.811 ± 0.014
Mean width (µm)	17.5 ± 0.14	17.4 ± 0.26
Coarseness (µg/m)	71.8 ± 1.1	69.0 ± 1.2
Mean kink angle (degree)	56.4 ± 1.3	57.2 ± 2.8
Mean kink index	2.88 ± 0.1	3.11 ± 0.5
Vessels/lakh fibers (no.)	965 ± 14.6	830 ± 12.3

Table 7  
Properties of the effluent generated during pulp bleaching

Particulars	ECF (control)	ECF (with ozone)
COD (mg/L)	1120 ± 20.5	659 ± 13.3
BOD (mg/L)	260 ± 4.2	157 ± 5.7
Colour (PCU)	406 ± 9.2	171 ± 4.2
AOX (mg/L)	11.0 ± 0.3	5.8 ± 0.2

### Effluent properties

The properties of the effluent generated during ECF bleaching of the pulps are given in Table 7. The combined effluent generated during bleaching of the control pulp recorded 1120 mg/L chemical oxygen demand (COD), 260 mg/L biochemical oxygen demand (BOD), 406 PCU colour level and 11.0 mg/L adsorbable organic halogens (AOX). The COD, BOD, colour level and AOX were reduced by 41.2%, 39.6%, 57.9% and 47.3%, respectively, upon the use of ozone prior to ECF bleaching due to the lower consumption of bleaching chemicals and the reduction in unwanted chemical reactions caused by the removal of metal ions prior to bleaching. Lundahl<sup>46</sup> reported that applying an ozone stage prior to ECF bleaching of eucalyptus hardwood pulp reduced the AOX by 50% and COD – by 39%, even without re-circulating the ozone stage filtrate in the brown stock washing system. The results of introducing the ozone stage in a mill scale operation demonstrate a 77.5% reduction in AOX generation per tonne of mixed hardwood pulp produced.<sup>47</sup>

### CONCLUSION

This study concludes that introducing an ozone stage prior to the ECF bleaching sequence of wheat straw pulp improved pulp brightness by 2.5 units and whiteness – by 4.0 units, while reducing the brightness reversion by 34.8%, when compared to the control. The reason behind the improvement in optical properties may be due to the additional removal of metal ions from the pulp, which ultimately reduced the formation of intermediate radicals during pulp bleaching. The introduction of the ozone stage prior to the ECF bleaching sequence of wheat straw pulp results in physical strength properties and morphological properties comparable with those of the control pulp. It also results in improved effluent quality. Introducing ozone in the ECF bleaching reduced the content of transition metal ions in the pulp by 38%, that of HexA – by 21.6%, also decreasing the COD in the bleaching filtrate by 41.2%, BOD – by 39.6%, colour level – by 57.9% and AOX – by 47.3%, compared to the control.

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