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Oxidative Delignification and Bleaching of Alkaline Sulphite-Anthraquinone Wheat Straw Pulp

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In this study, the oxidative delignification and bleaching of alkaline sulphite-anthraquinone (AS/AQ) wheat straw pulp is reported. Oxygen, oxone and hydrogen peroxide were used to achieve targeted brightness > 80 % ISO without compromising the other pulp properties *i.e.*, burst, tensile and tear index, kappa number, CED viscosity, hexenuronic acid, accelerated ageing and percentage yield of bleached pulp. The effect of various reaction parameters such as alkali, pulp consistency, temperature, time and bleaching agent dosage were optimized for each stage of bleaching.

Key Words: Oxidative delignification, Oxone, Hexenuronic acid, Kappa number, Accelerated ageing, Wheat straw pulp.

INTRODUCTION

Pulp and paper science is presenting new and innovative technologies since its origin. Stringent environmental regulations arising in the past few decades, have given a new dimension to products and technologies which can comply with the regulations and be eco-friendly. The limitation of meeting environmental standards puts pressure on economics and profitability of a company; so it becomes a great challenge to strive for feasible environmental-economical processes.

Pulping and bleaching operations are the backbone of cellulose industry. Economically feasible total chlorine free pulping and bleaching technology is the ultimate goal. Chlorine if present in the pulping and bleaching processes can release organochlorines which are hazardous for the environment. Various environmentally safe bleaching approaches such as elemental chlorine free (ECF) and total chlorine free (TCF) processes are extensively being studied for wood and non-wood pulp varieties[1-5].

Total chlorine free bleaching sequences developed so far comprise multi-stages such as OQ(OP), OQ(OP)P[3] for bleaching of alkaline sulphite/anthraquinone (AS/AQ) wheat straw pulp, $OpQP_o$ for soda-AQ wheat straw pulp[4], AZEYP for wheat straw kraft pulp[6], XOAZRP for wheat straw pulp[7], *etc*. As a single TCF agent has not been found to effectively fully bleach the pulp without comprising pulp properties such as, viscosity, sugar contents and strength properties, multistage sequences are preferred for selective removal of lignin while protecting cellulosic content, the building block of paper.

This work focuses on the development of total chlorine free (TCF) delignifying-bleaching sequences for AS/AQ wheat straw pulp. In this study, depolymerization of lignin fragments for bleaching was carried out in successive stages of oxygen and oxone treatment in alkaline media with intermediate water washing. Application of oxone (Ox) for extended delignification and bleaching of wheat straw pulp was particularly investigated. The pulp was then further bleached with hydrogen peroxide to gain targeted brightness of 80 + % ISO.

EXPERIMENTAL

Alkaline sulphite-anthraquinone (AS/AQ) wheat straw pulp was prepared in Packages Limited, Pakistan. The straw pulp sample was acidified (A) with 2.0 % of 4N H_2SO_4 on o.d. pulp basis at 25 °C for 15 min and then distilled water washed to neutral pH to remove metal contents.

Oxygen delignification (O): 500.0 g of oven dried (o.d.) acid treated straw pulp was fed in to a closed loop revolving digester at 10.0 % fiber consistency with the addition of 0.3 % of $MgCO_3$ and 2.0 % solution of NaOH on oven dry pulp. The homogenized reaction mixture was then charged with different doses of oxygen to delignify the pulp. The reaction was continued for 60.0 ± 10 min at 100 °C in a revolving digester with subsequent water washing to neutral pH. The pulp sample was then dewatered at high fiber consistency (> 35.0 %), sealed and shipped to University of Tasmania, Australia. Here the pulp was stored at 4 °C until further experimentation.

Extended delignification and bleaching: Different oxidative TCF chemicals (oxone, hydrogen peroxide) were employed for AO-treated pulp at varying conditions of temperature, time, consistency and chemical doses. The reaction was carried out in polythene zip-lock bags kept in a temperature controlled water bath set at specified reaction temperature conditions. After each bleaching stage, the pulp was washed with distilled water at neutral pH.

Various pulp properties such as brightness[8], tear[9], tensile[10] and burst index[11], kappa number[12], cupricethylenediamine (CED) viscosity[13], were studied by using test methods specified by International Standards Organization (ISO) and Technical Association for Pulp and Paper Industry (TAPPI).

Brightness reversion (%) was determined by accelerated aging the pulp sample at 105 °C in an oven for 72 h ± 10.0 min. Reversion per cent was then calculated by comparing the average results before and after the dry heat treatment in the oven.

Hexenuronic acid (HexA) was measured by hydrolyzing 0.05 g pulp sample in 10.0 mL of mercuric chloride (0.6 %) and sodium acetate (0.7 %) solution at 65 °C for 0.5 h[14]. The HexA contents of solution were then calculated by measuring UV absorption at two wavelengths (260 nm and 290 nm) as:

$$C_{HexA} = 0.287 \times [(A_{260} - A_{290}) \times V/w] \text{ [Ref. 14]}$$

where, 0.287 is the calibration factor for dual wavelength measurement, V = volume of hydrolyzed solution (mL), w = oven dry pulp (g).

RESULTS AND DISCUSSION

The purpose of acidification prior to delignification and bleaching is to remove metal ions from wheat straw pulp. The presence of metals not only reduces the bleachability, but also increases the bleach chemical consumption of the pulp.

Effect of oxygen delignification (O): Oxygen is one of the typical delignifying chemicals. Acidified (A) AS/AQ wheat straw pulp was treated with oxygen at two different gauge pressures (75 psi and 100 psi). The result in the Fig. 1 show that increasing the pressure from 75 psi to 100 psi for pulp delignification increases the brightness by 3 % ISO units.

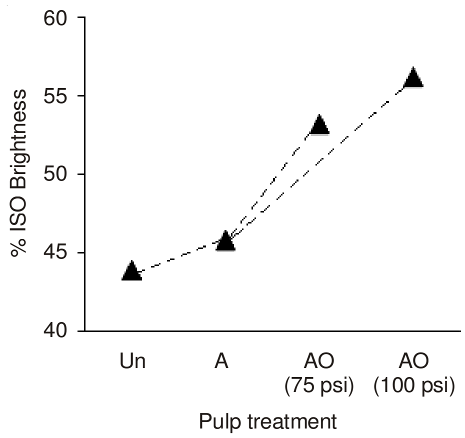


Fig. 1. Effect of various chemical treatments on % ISO brightness (Un is Unbleached untreated pulp, A is acidified-washed pulp, AO is acid treated oxygen delignified pulp)

Increased brightness values can also be achieved by extended delignification with oxygen but this results in degradation of carbohydrates, low pulp yield (%) and increased capital cost for oxygen charge on pulp. These effects disfavour extended oxygen treatment[15]. Therefore, oxygen delignification treatment was carried out up to 100 psi gauge pressure.

When other physical and chemical properties of oxygen delignified (AO) pulp studied; it was found that increasing oxygen charge from 75 psi to 100 psi gauge pressure reduced the pulp strength. No significant difference was observed in burst and tears index values but a significant drop in tensile index was observed. Thus any treatment beyond 100 psi was expected to further reduce the pulp strength. Other pulp properties such as kappa number, CED viscosity and % yield show similar results (Table-1). Therefore, 100 psi gauge pressure was selected for further experimentation.

TABLE-1
VARIOUS PROPERTIES OF AS/AQ WHEAT STRAW PULP AT DIFFERENT TREATMENT STAGES

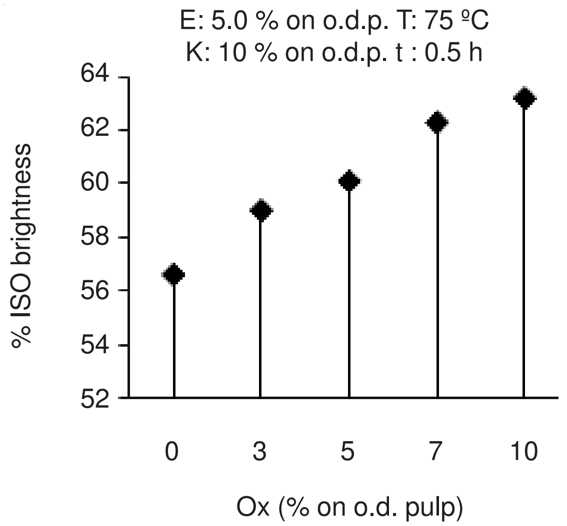
Parameters	Un	A	AO (O at 75 psi)	AO (O at 100 psi)
Burst index (K Pa m²/g)	2.8	2.8	2.9	2.7
Tensile index (Nm/g)	61.3	55.19	60.6	39.5
Tear index (mN m²/g)	3.8	5.6	5.0	5.2
Yield (%)	–	96.6	93.1	93.42
Kappa number	12.4	10.8	6.7	6.6
CED viscosity (cP)	13.10	13.28	13.00	12.98

Extended delignification and bleaching with oxone (Ox): Oxone is a versatile oxidizing agent, a triple salt of potassium peroxymono sulphuric acid ($KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) which is non-toxic in nature[16].

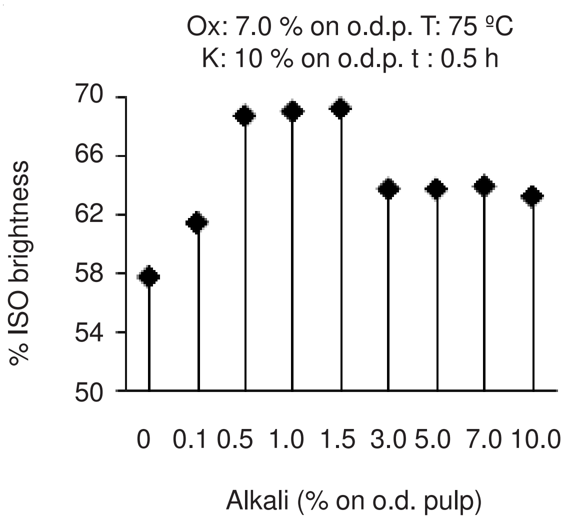
The effects of different reaction conditions (chemical doses, temperature, time and consistency) were investigated with the aim of achieving an optimum brightness with oxone treatment of the pulp. Fig. 2(a) shows that increasing the concentration of oxone charge from 3.0-5.0 % on oven dry pulp increases the brightness by only *ca.* 1.0 % while increasing the oxone charge from 5.0-7.0 % on o.d. pulp increases pulp by 2.0 units of % ISO. Any further increase resulted in only a small increase in brightness. Thus 7.0 % oxone solution on oven dry pulp was selected to optimize the other reaction conditions (Fig. 2a).

The effect of alkaline dose was investigated at 7.0 % optimum oxone dosage. 0.5 % alkali was enough to increase the ISO brightness to 68.8 %. An increase from 0.5-1.5 % alkali only resulted in a small brightness increase. Any further increase in alkali dose was found to lower the brightness (Fig. 2b). Thus mild alkaline treatment at 0.5 % on oven dry pulp was selected as the optimal dose to remove the lignin. The effectiveness of alkaline extraction during peroxyacids' treatment was also demonstrated by Springer; as it washes away the depolymerized fragments of lignin[17].

Consistency, the concentration of the pulp suspension in water, is a very important reaction parameter in pulping and bleaching experiments. Results in Fig. 2(c) show that increasing the reaction mixture from 5 to 15 % consistency on oven dry pulp increased the pulp brightness. However, in medium consistency range (10-15 % on o.d.p) the change in brightness is very small. Thus any value within the medium consistency range can be optimal for further bleaching trials. For this work 15 % was chosen for further experiments.



(a)



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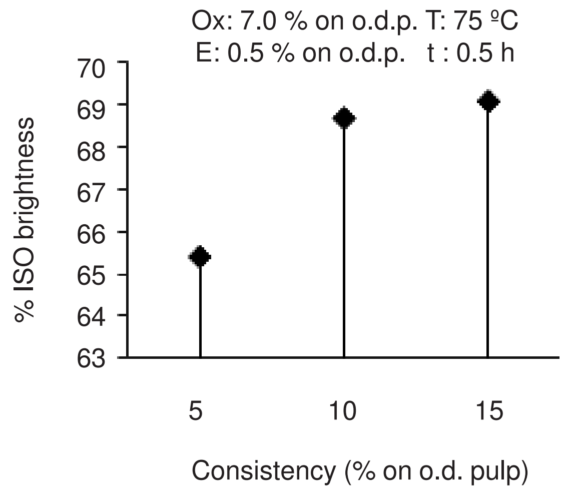
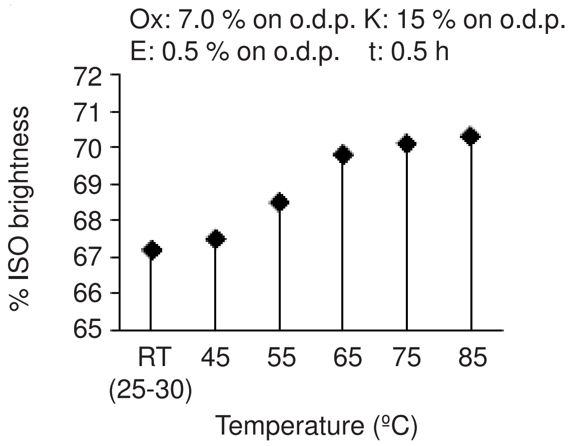
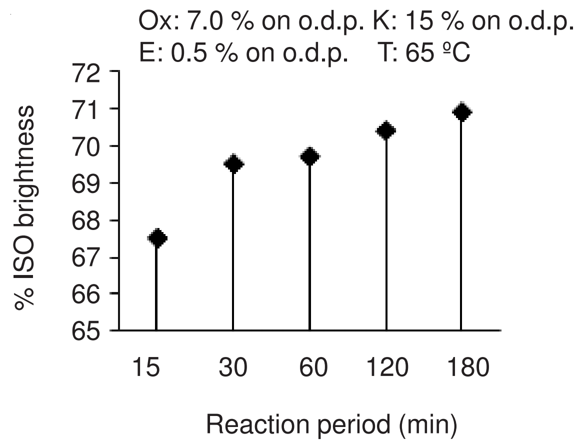


(c)



(d)



(e)

Fig. 2. Effect of different reaction conditions on oxone bleaching

The effect of temperature variations on oxone treatment of AS/AQ wheat straw pulp was studied. The results in Fig. 2(d) show that although increasing the temperature from ambient (25-30 °C) to 65 °C resulted in a slight increase in brightness; no further improvement in brightness occurred when the temperature was increased to 85 °C. Thus 65 °C was selected to be optimal reaction temperature. Also it has been reported that the selectivity of oxone towards delignification increases at high temperature[18].

The effect of various reaction periods for oxone treatment of pulp shows that brightness values gradually increase with increasing time, but the total brightness gain is only a little greater than 1 % ISO unit beyond 0.5 h, treatment period, even though the reaction period increased to 3 h (Fig. 2e). Selecting a low reaction period is also supported by the work of Breuilh *et al.*[18] as longer reaction times decrease the selectivity of peroxymonosulphuric acid towards hexenuronic acid removal.

The results thus demonstrated that oxone is a powerful oxidizing agent to improve brightness that can be used as a replacement for chlorinated bleaching chemicals. Similar advantages are also reported by Springer[17] for the use of potassium peroxymonosulphate as it requires mild reaction conditions with low energy and low capital requirements to produce high pulp yield (%).

Bleaching with hydrogen peroxide: After extended delignification, the AOOx treated pulp was bleached with hydrogen peroxide to achieve a target brightness greater than 80 % ISO. Various reaction conditions were studied to optimize peroxide bleaching stage.

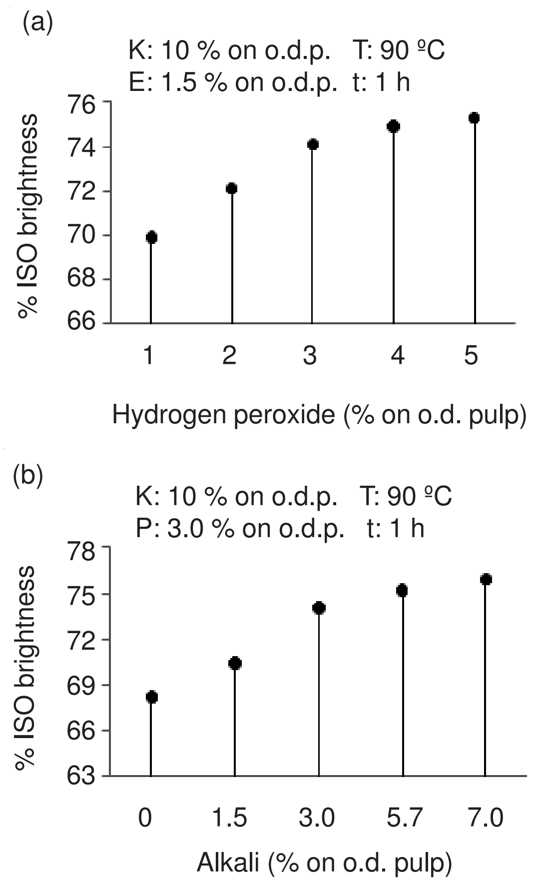
The effect of hydrogen peroxide (P) charge from 1.0-5.0 % on oven dry pulp was studied (Fig. 3a). Only a very small increase in brightness was achieved by increasing the dose beyond 3.0 % hydrogen peroxide treatment, hence, 3.0 % hydrogen peroxide treatment on oven dry pulp was selected to be optimal for bleaching.

Similar behaviour was observed while studying alkali charge (E) on peroxide bleaching trials (Fig. 3b) and 3.0 % alkali charge was selected as optimum charge.

Consistency results in Fig. 3(c) showed that *ca.* 1.0 % ISO unit increase occurred with each 5 % increase in pulp consistency up to 15.0 % on oven dry pulp during these beaching trials. Increasing pulp consistency from 15-20 % yielded almost equal results, so either of these two consistencies can be selected as optimal.

Next bleaching trials were conducted at varied temperature conditions and the results showed that temperature = 90 °C is effective for hydrogen peroxide bleaching.

Time period variations were observed to be very important during peroxide bleaching. A reaction time of 3 h was found to be effective to yield pulp with brightness of 81.29 %. After 3 h reaction period, no improvement in brightness was achieved with varying the other reaction conditions. Hence, the optimal bleaching conditions suggested various trials which are shown in the Table-2.



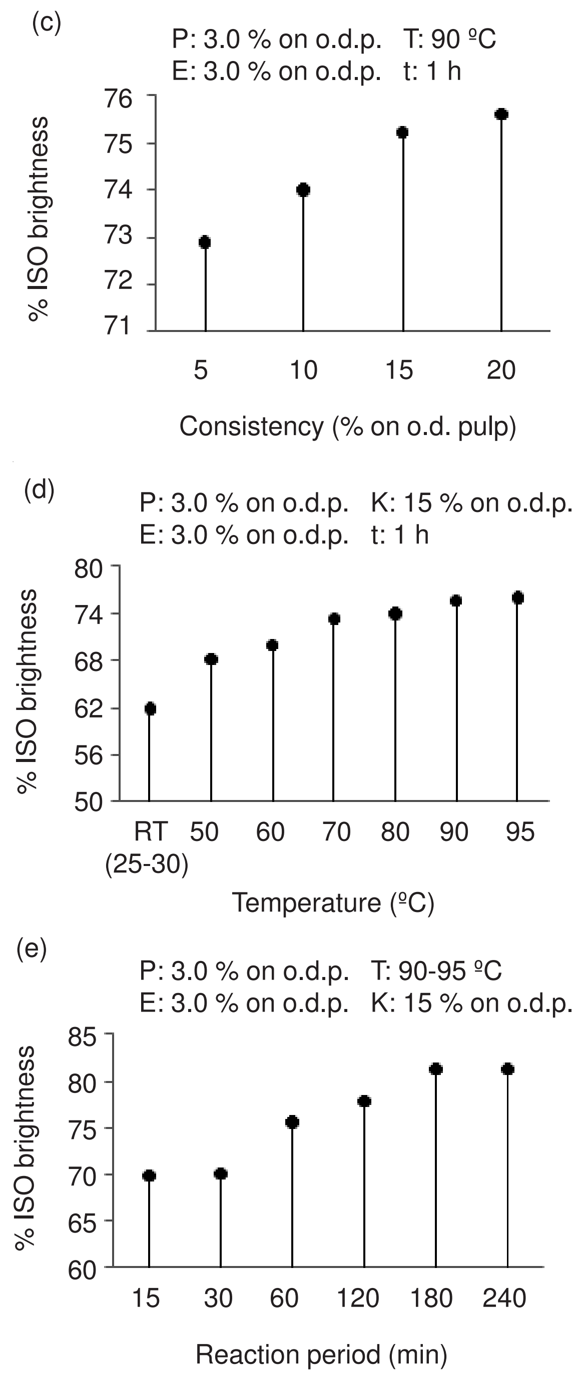


Fig. 3. Effect of different reaction conditions on hydrogen peroxide bleaching

TABLE-2
OPTIMAL BLEACH CONDITIONS AT VARIOUS STAGES OF AOOxP BLEACH SEQUENCE

Reaction parameters	Treatment stage		
	O	Ox	P
Consistency (% on o.d. pulp)	10	15	15
Bleaching agent (% on o.d. pulp)	–	7.0	3.0
Other chemicals (% on o.d. pulp)	2.0 % NaOH 0.3 % $MgCO_3$	0.5 % NaOH	3.0 % NaOH 0.2 % DTPA
Temperature (ºC)	100	65	90-95
Time (min)	60	30	180
Pressure (psi)	100	–	–

Multistage bleaching sequences are important for many reasons. They are usually employed to gain the maximum possible pulp brightness. These are also important to preserve pulp properties such as strength and viscosity. Employment of delignifying chemicals in any bleaching sequence is important to depolymerize the lignin content so that it can be easily washed away from the pulp. The shortest possible sequences are attractive for industrial applications. In an attempt to reduce the number of stages in the sequence: AOOxP presented in this paper, bleaching trials were also conducted without oxone. The AO treated pulp was bleached with hydrogen peroxide at varying doses; while the other reaction condition were maintained the same as those given in Table-2. Increasing the peroxide dose from 7.0 % on oven dry pulp in the AOP sequence yielded a 80.02 % ISO brightness (Fig. 4).

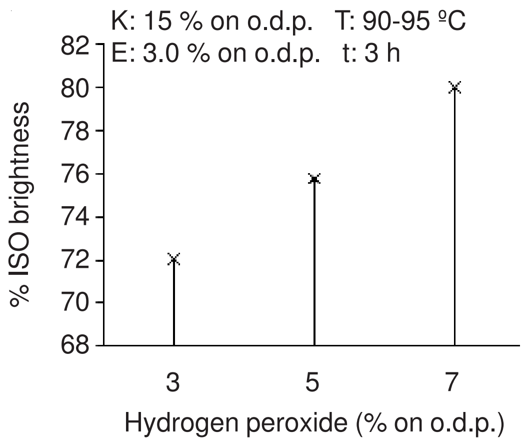


Fig. 4. Effect of hydrogen peroxide on pulp brightness in AOP bleach sequence

In the next attempt both oxygen delignification and oxone treatment stages were eliminated during bleaching trials and the A-treated pulp was directly bleached with varying doses of hydrogen peroxide at the optimized conditions given in Table-2. A maximum brightness gain of 76.90 % ISO was achieved at 10.0 % hydrogen peroxide treatment on oven dry pulp (Fig. 5).

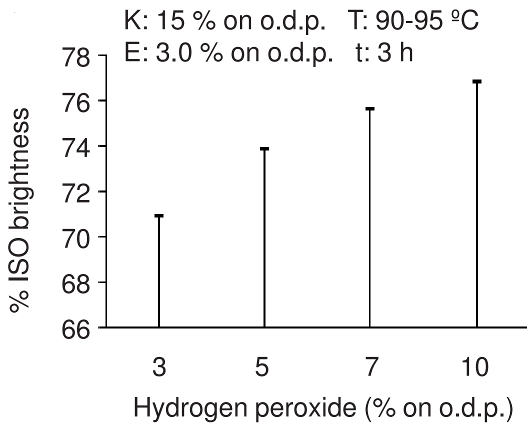


Fig. 5. Effect of hydrogen peroxide on pulp brightness in AP bleach sequence

Apparently, it can be suggested that the AOP bleach sequence is effective in achieving the 80 % ISO brightness target. Brightness is one prime parameter to design a bleach sequence; but other pulp properties that cannot be compromized are also of equal importance to finally decide on any bleach sequence. Therefore, the three bleach sequences: AOOxP, AOP, AP was further investigated for other pulp and paper properties.

The results in Table-3 showed that tensile index of all the hand sheets decreases during bleaching. Burst and tear index of hand sheets prepared after bleaching with AOOxP sequence improves while for the AOP and AP sequences these strength factors decrease during bleaching operations. Thus presence of oxone in the AOOxP bleach sequence seems to preserve or improve the strength of pulp fiber. This is also supported by the Springer in his work to highlight potential uses of peroxymonosulphate[17].

TABLE-3
VARIOUS PULP AND PAPER PROPERTIES OF UNBLEACHED AOOxP AND AOP BLEACHED AS/AQ WHEAT STRAW PULP

Parameters	Unbleached	AOOxP	AOP	AP
Brightness (% ISO)	43.9	81.29	80.02	76.9
Burst index (KPa m^2/g)	2.8	2.9	1.6	1.5
Tear (mN m^2/g)	3.8	4.0	3.4	3.2
Tensile index (Nm/g)	61.3	49.62	49.12	46.19
Kappa number	12.4	1.01	6.12	9.89
HexA (μmol/g)	30.44	0.88	15.29	21.32
CED viscosity (cP)	13.10	10.13	7.91	7.10
Yield (%)	–	80.66	75.19	76.27
Brightness reversion (%)	1.03*	0.18*	2.87*	4.24*

*Student t-test (Paired) showed statistically significant difference at 95 % confidence level in mean values of % ISO brightness before and after accelerated ageing at 105 ºC for 72 h ± 10 min.

The basic purpose of bleaching is to achieve high brightness. The brightness stability of the bleached product is of key importance with the passage of time and environmental exposure. Incomplete washing, generation of chromophores due to heat or other exposures and/or incomplete degradation of lignin polymer can lead to brightness reversion[19]. Thus, bleaching chemicals which have a higher capability to defragment the lignin polymer; followed by successive alkaline treatment to wash away lignin, result in less reversion. On the other hand, pulp bleaching with chemicals which are lignin preserving, to only brighten the pulp, are more vulnerable to the reversion phenomenon.

All the optimized bleached hand sheet samples (AOOxP, AOP and AP) were subjected to accelerated ageing. Samples were exposed to 105 ºC for 72 h ± 10 min and then brightness was measured. Results in Fig. 6 show that only a small decrease is observed (brightness reversion is 0.18 %) after ageing handsheet samples bleached with the AOOxP sequence. The AOP sequence was found to enhance the ageing process of the handsheets and this is even more pronounced when the AP sequence is used (Table-3). This shows that both delignifying chemicals, oxygen and oxone, are important to preserve bleaching stability. Thus AOP and AP bleach sequences are not suitable for commercial use. Various other studies also report that reversion was enhanced with hydrogen peroxide[20,21].

Generally, as the number of chemicals involved in a bleach sequence increases, the better the brightness stability[22]. Thus multistage sequences are important for better bleaching.

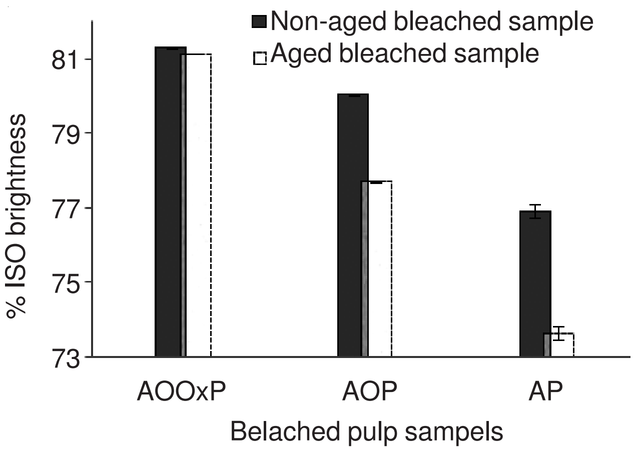


Fig. 6. Effect of ageing on brightness stability of hand sheets prepared at different bleach sequences (each bar represents an average of three independent measurements; the difference in non-aged and aged samples' brightness % ISO is statistically very significant)

Another important investigation for this study was to determine the kappa number. The lignin content, an important parameter for process control in both chemical pulping and bleaching[23], is estimated by the kappa number which involves the consumption of potassium permanganate in acidic media[24]. The lower the kappa number, the lower the lignin content in a pulp sample. Kappa number results showed that oxygen is effective to reduce the kappa number to about half of the original value (Table-1). Greater reduction in kappa number was observed in AOOxP sequence, where kappa number reduced to 1.01 showing a negligible amount of lignin present in pulp sample (Table-3). In the AOP sequence, kappa number reduced from 12.4 (unbleached kappa number) (Table-1) to 6.12 while in the AP sequence kappa number only lowered to 9.89 (Table-3). These values show that the AOP sequence partially depolymerizated the lignin while the AP sequence hardly depolymerizated the lignin. These results are in line with the results obtained during the ageing experiments. The presence of a high lignin content in the AOP and AP sequences increases the likelihood of ageing as compared to the AOOxP sequence in which most of the lignin was removed during pulp oxidation with oxygen and oxone.

Pulp CED (copper(II) ethylene diamine) viscosity represents the degree of polymerization of the cellulose in a pulp sample. The higher the viscosity, the greater the cellulose content of the pulp, which is necessary to build the structure of a hand sheet sample. A decrease in viscosity from 13.10 cP for unbleached pulp to 10.13 cP for AOOxP bleached pulp occurred, which falls within acceptable limits of viscosity for pulps. Further loss in viscosity was observed when the sample was bleached with AOP (7.91 cP) and AP (5.23 cP) sequences (Table-3). A considerable decrease in kappa number and a minor loss in pulp viscosity for AS/AQ wheat straw pulp bleached with AOOxP sequence reflects the selectivity of oxone towards lignin removal and cellulose protection respectively.

Varied pulping conditions effect the chemical conversion of pulp differently. HexA[25] is formed by the partial conversion of 4-*o*-methylglcouronic acid groups of xylan to 4-deoxy-4-hexenuronic acid groups (HexA) as shown in Fig. 7.

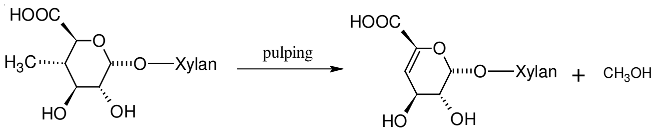


Fig. 7. Formation of HexA during pulping process[18]

Hexenuronic acid (HexA) if present in the bleached sample not only reduces brightness but also increases the chances of ageing[26]. Bleaching sequence AOOxP is effective in hydrolyzing the HexA content of the pulp. Thus the amount of HexA in the AOOxP bleached pulp remains almost negligible (0.880572 µmol/g) as compared to the AOP and AP sequences where HexA remains high as 15.29 µmol/g and 21.32 µmol/g respectively (Table-3). Elimination of HexA content during bleaching sequences also helps in improving the brightness stability which is indicative of the brightness reversion percentage values where chances of reversion reduces to 0.18 % for AOOxP bleached pulp (Table-3). The effectiveness of peroxymonosulphuric acid to remove HexA and lignin content at mild reaction conditions was also presented by Breuilh *et al.*[18].

Yield (%) data in Table-3 of the finally bleached pulp also favours a AOOxP bleach sequence where % yield of the final product is greater than 80 %.

Conclusion

Environmentally benign oxidative total chlorine free bleaching sequences were designed for AS/AQ wheat straw pulp. The results of kappa number and viscosity show comparatively low selectivity of the AOP and AP sequences towards lignocellulosic material of the pulp. The ageing data of these sequences also indicate increased risk of brightness reversion. In comparison to AOP and AP bleach sequences, AOOxP sequence yielded pulp with better properties. Thus it is concluded that oxone performs two roles: it reduces the residual lignin and brightens the pulp. Selectivity of the oxone in preservation of cellulosic content of pulp and complete removal of HexA during AOOxP sequence help retards brightness reversion. Thus oxone proves to be a powerful oxidizing agent to remove lignin and improve brightness as a replacement for chlorinated bleaching chemicals.

Bleaching nomenclature used in this paper

A = Acid wash/treatment
E = Alkaline extraction stage
O = Oxygen delignification
Ox = Potassium peroxymonosulphuric acid/ aq. solution of oxone
P = Hydrogen peroxide treatment
Q = Chelation
R = Reductive bleaching agent
X = Enzymatic treatment
Z = Ozone charge

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