Carbohydrate Polymers 92 (2013) 976–981

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Multi stage peroxide and activated peroxide bleaching of kenaf bast pulp

Farhad Zeinaly[a,*], Jalal Shakhes[b], Nooshin Zeinali[c]

[a] Young Researchers Club, Gorgan Branch, Islamic Azad University, Gorgan, Iran
[b] Department of Wood & Paper Science Faculty of Forest and Wood Technology, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran
[c] Department of Chemistry, Islamic Azad University, Gorgan Branch, Gorgan, Iran

ARTICLE INFO

Article history:
Received 15 August 2012
Received in revised form 17 October 2012
Accepted 19 October 2012
Available online 26 October 2012

Keywords:
Hydrogen peroxide
TAED activator
Chemical oxygen demand (COD)
Brightness
Viscosity

ABSTRACT

Soda-anthraquinone kenaf bast pulp (12.5 kappa number and 32% ISO brightness) has been bleached with multi stage peroxide bleaching process. Bleaching process was carried out in different sequences of peroxide stage without and with activator (tetraacetylethylenediamine, TAED) to about 80% ISO brightness. Full bleached pulp production with high brightness and viscosity and also, low chemical oxygen demand (COD) and no adsorbable organic halogens (AOX) in effluent are the aims of this study. The effects of temperature, retention time, chemical charges, TAED/peroxide ratio and alkalinity have been studied in order to maximize the brightness gain at the lowest viscosity loss. H_2O_2 was activated as bleaching agent under milder conditions, such as low alkalinity or low temperature, by TAED activator. Therefore, TAED charge caused to an improvement in viscosity, pulp yield and effluent COD load. Pre-treatment with EDTA for 30 min and in acidic condition gave 2–4% gain in ISO brightness.

1. Introduction

Nonwood fiber is an alternative for wood fiber in pulp and paper production, especially in those countries with no industrial forests. Thus, the investigation of preparing, pulping, bleaching and paper making processes and also fiber properties of these substituted materials is necessary (Zeinaly, 2009).

Kenaf (*Hibiscus cannabinus* L.) is a short-day annual herbaceous plant that belongs to the Malvaceae family. Stem contains two distinctive fiber types: the bast or the outer bark fibers (3–4 mm long and slender, comparable to softwood fibers), and the inner core of short woody fibers (0.5–0.7 mm long, comparable to hardwood fibers) (Francois, Donovan, & Maas, 1992; Nkaa, Ogbonnaya, & Onyike, 2007).

Because nonwoods are diverse and have a wide range of different characteristics, pulping and bleaching processes are specific for each of them. In the case of kenaf stalk, it is more intricate because the kenaf bast and core fibers have different natures and structures, and each will exhibit different behavior during pulping. Thus, research on kenaf pulping and bleaching is mainly directed to the pulp and paper characteristics of either the kenaf core or bast in separate preparation systems (Nezamoleslami, Suzuki, & Kadoya, 1997; Zeinaly, 2009).

Kenaf bast fiber is a long fiber that has been noted by the Iranian pulp and paper industries, because the local wood fiber resource is hardwood a short fiber which produces weak pulp. Currently softwood long fiber is imported and added to hardwood pulp in a ratio of about 20% to improve the final paper mechanical properties (Mazandaran Paper and Wood Industries Co.).

One of the most important phases in pulp production is the bleaching process, which, in addition to its high investment and process cost, is the highest water consuming process and thus the highest effluent producer. The industry's goal is to carry out the bleaching process with the lowest water emission and to also lower the total production cost while still maintaining acceptable bleached pulp properties.

As summarized by Singh (1991), pulp bleaching operations in the early part of past millennium were primarily centered on chlorine. Changes of environmental regulations and societal pressures have dramatically altered the bleaching landscape. The early 1990s saw two competing bleaching technologies; a variety of researchers proposed the replacement of chlorine with Totally Chlorine Free (TCF) bleaching chemicals (i.e., Z, P, A, etc.) whereas Elemental Chlorine Free (ECF) was championed by many others (Anderson & Amini, 1996; Fuhrmann, Rautonen, & Liias, 2000; Senior, Hamilton, Ragauskas, Sealey, & Froass, 1998). In the U.S.A., EPA's promulgated Cluster Rules approved the use of ECF bleaching technologies, while other parts of the globe saw increased industrial application of TCF bleaching technologies. Usable stages and sequences of TCF bleaching are peroxide (P), activated peroxide (Pa), oxygen (O), peracetic acid (Paa) and ozone (Z). Furthermore, sometimes an acid washing

---

[*] Corresponding author. Tel.: +98 912 5657146; fax: +98 171 2245964.
E-mail addresses: farhad.zeinaly@yahoo.com (F. Zeinaly), jalalshakhes@yahoo.com (J. Shakhes), zeinali.nooshin@gmail.com (N. Zeinali).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.10.043

or chelation stage (Q) is used to remove the metal ions from the pulps.

Due to environmental impacts, there has been an increase in the use of hydrogen peroxide as a total or partial substitute for chlorine-based bleaching agents with ECF and TCF sequences. But, in order to achieve satisfactory brightness while using only hydrogen peroxide, the bleaching stages must have intense conditions of temperature, retention time, chemicals charge, etc. (Anderson & Amini, 1996; Khristova, Tomkinson, & Lloyd Jones, 2003). Hydrogen peroxide is a common and efficient bleaching agent in mechanical or chemical pulp bleaching. Hydrogen peroxide in milder conditions (40–70 °C temperature) acts as a bleaching agent with limited lignin removal for mechanical high yield pulps without significant yield loss. In intense conditions (70–90 °C temperature), hydrogen peroxide is a lignin removal bleaching agent (Zeinaly, Dehghani, & Mirmehdi, 2009).

The hydrogen peroxide (H_2O_2) bleaching reaction is attributed to the oxidative action of the hydroperoxide ion (HOO^-) which is produced by the dissociation of hydrogen peroxide in alkaline conditions according to Eq. (1) (Singh, 1991; Sixta, 2006):

$$H_2O_2 + OH^- \rightarrow H_2O + HOO^- \quad (1)$$

Thus, alkali is needed to activate hydrogen peroxide by forming the reactive hydroperoxide anion species. However, a high concentration of hydroperoxide anions causes decomposition of hydrogen peroxide, especially at elevated temperatures (Eq. (2)). Therefore, it is common practice to add sodium silicate as a stabilizing and buffering agent, and the pH value has to be controlled by the rate of adding alkali to the bleach liquor (Zeinaly, Shakhes, Shakeri, & Zeinaly, 2011).

$$HOO^- + HOOH \rightarrow (\text{energy})HO_2^{\bullet} + HO^{\bullet} + OH^- \quad (2)$$

Bleaching at intense conditions has disadvantages in terms of throughput and yield and may involve significant capital investment, additional energy and chemical costs. It may also have negative impact on pulp quality, such as polysaccharide chains cleavage caused by high temperature; and high alkalinity peroxide stages may also be an issue. Therefore, the use of a bleaching activator such as tetra acetyl ethylene diamine (TAED) is a solution to increased hydrogen peroxide effectiveness on pulp bleaching and thus alleviating the need for such aggressive reaction conditions (Khristova, Tomkinson, Valchev, Dimitrov, & Lloyd Jones, 2002). This occurs by the generation of oxidants which are stronger than hydrogen peroxide. The TAED reaction with peroxide, depending on the bleaching stage pH, will produce either peracetic acid or peracetate anion (Bajpai, 2005; Coucharriere, Mortha, Lachenal, Briois, & Larnicol, 2002) (Eqs. (3) and (4)).

$$\text{TAED} + HOO^- \rightarrow \text{TriAED} + CH_3COOO^- \quad (3)$$

$$\text{TriAED} + HOO^- \rightarrow \text{DAED} + CH_3COOO^- \quad (4)$$

The optimum pH of TAED-assisted alkaline peroxide delignification is lower than that used in conventional alkaline peroxide stages (Bajpai, 2005). Chemical properties and flexibility of TAED make it possible to activate peroxide under conditions for which the peroxide alone is ineffective as a bleaching agent, such as low alkalinity or low temperature (Khristova et al., 2002). The use of TAED can be safely incorporated into ECF and TCF bleaching sequences for different types of pulp (Turner & Mathews, 1998) TAED can be used at low amounts, under alkaline conditions, to boost the brightening performance of peroxide and perform rapid bleaching (Khristova et al., 2003).

In this paper, the bleaching characteristics of kenaf bast fibers under various bleaching conditions and bleached pulp properties are investigated. Also, multistage peroxide bleaching with TAED activator is introduced as a TCF process for full bleaching of low-kappa kenaf bast soda-AQ pulp.

2. Materials and methods

2.1. Materials

Unbleached pulp was prepared from kenaf bast using soda-AQ pulping. The unbleached pulp had a yield of 48%, 32% ISO brightness, 61 centipoises viscosity and 12.5 kappa number. A 2.5 l rotary laboratorial digester with 6 bomb and indirect electrical heater was used for pulping. Cooking conditions are shown in Table 1. All chemical reagents used for pulping, bleaching and testing were analytical grade.

2.2. Methods

2.2.1. Chelation stage

Pulp chelation was the first stage of bleaching sequences in all treatments. Chelation conditions were 3% pulp consistency, 3.5–4 pH, 70 °C, 30 min and 0.3% DTPA on OD fiber. Then the pulp suspension was thickened to about 25% consistency in a Büchner funnel with a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect fines.

2.2.2. Alkali peroxide bleaching stages

Alkali peroxide bleaching stages were conducted in polyethylene bags using the following conditions: 2–4% H_2O_2, 1–3% NaOH, 0–3% sodium silicate (water glass), 0–0.5% Epsom salt ($MgSO_4{\cdot}7H_2O$), 0–0.2% DTPA, 8–10% pulp consistency, 0–0.3 TAED/peroxide molar ratio, 75–85 °C, and 30–60 min residence time (Table 2) (all chemical charges are expressed based on oven dried pulp).

The chemicals were mixed in a beaker using the following order: water, sodium silicate, sodium hydroxide, Epsom salt, DTPA, TAED, and finally hydrogen peroxide. The prepared bleach liquor was then added to the pulp, which had been heated to the reaction temperature, and good mixing was provided by kneading. The polyethylene bag was sealed and placed into a water bath for the desired retention time at the set temperature. Initial and final pH values of every stage were measured.

After each stage, there was no liquor drain and pulp washing, and the chemical for the next stage to be run was simply charged to the pulp. The pulp consistency was decreased stage by stage due to some water being added along with chemical charge.

2.2.3. Testing methods

After completion of the bleaching time, the suspension pH was decreased to 4.5–5.5 by adding sulfuric acid to stop the bleach reactions and also to prevent alkali darkening. The pulp sample was cooled to room temperature with cold running water and diluted to a 1–2% suspension using deionized water. The well-mixed pulp suspension was then filtered on a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines. The resultant filtrate was further filtered with a Whatman medium-fast filter paper in a Büchner funnel, to remove the residual fines, and then used for calculating the COD load of bleaching effluent, according to the standard method (5220, B). Finally, the brightness, kappa and viscosity of bleached pulps were measured according to the TAPPI standard methods.

2.3. Calculation

There was a close relationship between kappa number and viscosity reduction during pulp bleaching, as both decreased undue

Table 1
Pulping conditions.

Active alkali %	AQ dose %	Max temp. °C	Time to max temp. min	Cooking time min	Liquid to mass weight ratio
20	0.1	170	50	60	7:1

Table 2
Bleaching stages condition.

Stage	H_2O_2%	NaOH %	Alkali ratio	Na_2SiO_3%	$MgSO_4$%	DTPA %	TAED molar ratio	Cons. %	Time min
Q	–	–	–	–	–	0.3	–	3	30
P_1	4	3	0.75	3	0.5	0.2	–	10	60
$P_{2\text{-}30}$[a]	3	1.8	0.6	–	–	–	–	9	30
$P_{2\text{-}60}$	3	1.8	0.6	–	–	–	–	9	60
P_3	2	1	0.5	–	–	–	–	8	30
$Pa_{2\text{-}30}$	3	1.8	0.6	–	–	–	0.3	9	30
$Pa_{2\text{-}60}$	3	1.8	0.6	–	–	–	0.3	9	60
Pa_3	2	1	0.5	–	–	–	0.3	8	30
A_3	–	–	–	–	–	–	0.3[b]	8	30

[a] $P_{2\text{-}30}$ shows the second peroxide stage with 30-min stage duration and so for the rest.
[b] TAED charge for A3 stage was equal to Pa3 stage (because A3 had no peroxide charge).

more intense conditions and with an increasing number of bleaching reactions. Kappa number reduction, an index of residual lignin in pulp, is favorable. However, pulp viscosity reduction caused by carbohydrate decomposition and polysaccharide chain cleavage is not. To reorganize the proportions of these factors, another index called "selectivity factor" (Eq. (5)) shows the amount of fall in pulp viscosity per a kappa unit decrease. Higher selectivity factor is equal to lower carbohydrate decomposition and/or higher lignin removal.

$$\text{Selectivity} = \frac{1 - K_f/K_i}{1 - \mu_f/\mu_i} \qquad (5)$$

where K_f is the kappa number after bleaching, K_i is the initial kappa number, μ_f is the pulp viscosity after bleaching and μ_i is the initial viscosity.

3. Results and discussion

The bleaching process was conducted in 3–4 sequences for 120–180 min. Initial Q stage for metal ion chelating in about 3.5–4 pH (set by sulfuric acid use) was conducted for half of the treatments. After the Q stage, bleaching stages were performed on the pulp suspension. The initial and final pH values in every bleaching stage were measured and are shown in Table 3.

Pulp suspension chelating led to improve brightness gain of 2–3.7% ISO brightness units (Fig. 4) in all bleaching treatments. The maximum range of brightness increase was between the $QP_1P_{2\text{-}30}P_3$ and $P_1P_{2\text{-}30}P_3$ sequences at 85 °C temperature as a result of more peroxide or hydroperoxide ion decomposition by transition metals at higher temperatures and in alkaline condition (Eqs. (6) and (7)) (Suess, 2010). When we added chelation stage to $P_1P_{2\text{-}30}P_3$ sequence, the brightness improvement reached its maximum level.

$$2\,M^{n+} + H_2O_2 \rightarrow 2\,M^{(n-1)+} + O_2 + 2H^+ \qquad (6)$$

$$2\,M^{(n-1)+} + H_2O_2 + 2H^+ \rightarrow 2\,M^{n+} + 2H_2O \qquad (7)$$

TAED activator causes the creation of stronger oxidant agents in bleaching media such as peracetic acid or anion peracetate, through reaction with peroxide or hydroperoxide ion in alkali condition (Eqs. (8) and (9)). Also, the reaction between TAED and hydroxyl ion (OH^-) has produced acetic acid in an alkali environment, which is a strong oxidant agent, and thus has improved pulp bleaching efficiency (Eqs. (10) and (11)) (Coucharriere et al., 2002).

$$\text{TAED} + HOO^- \rightarrow \text{TriAED} + CH_3COOO^- \qquad (8)$$

$$\text{TriAED} + HOO^- \rightarrow \text{DAED} + CH_3COOO^- \qquad (9)$$

$$\text{TAED} + OH^- \rightarrow \text{TriAED} + CH_3COO^- \qquad (10)$$

$$\text{TriAED} + OH^- \rightarrow \text{DAED} + CH_3COO^- \qquad (11)$$

Reaction of TAED and hydrogen peroxide in alkali conditions produced acids and released proton (H^+) in bleaching environment which caused a decrease in the pH value (Table 3). The pH decrease depended on final pH of the prior stage, TAED dose, alkali/peroxide ratio, chemical charges, temperature, residual peroxide of the prior stage, etc. As it shown in Table 3, the pH of bleaching sequences with no activator in stages was higher than 10 but, when the TAED activator was used the pH fell to about 8–5.

Chelation agents prevented hydrogen peroxide of being decomposed by transition metal ions, thus hydroperoxide ion increased in the reaction environment and its high concentration led to more bleaching reactions and high hydroxyl ion (OH^-) consumption. Thus, the pH falling rate in bleaching sequences with Q stage was more than those of without the chelation stage (Table 3).

The effect of bleaching temperature on the pH value was positive. At higher temperature, the hydroxyl ion (OH^-) preparation and concentration were higher resulting in increased bleaching reactions, hydroperoxide production, and peroxide and alkali consumption. Thus, the difference between initial and final pH was much more noticeable at higher temperatures (Table 3). Alkali is needed to activate hydrogen peroxide by forming the reactive hydroperoxide anion species. On the other hand, too high of a concentration of hydroperoxide anions causes decomposition of hydrogen peroxide, especially at elevated temperatures. Therefore, it is a common practice to add sodium silicate as a stabilizing and buffering agent (Zeinaly, Dehghani, & Mirmehdi, 2009).

When the TAED activator was used in the bleaching stages, the pH of suspension decreased immediately (Table 3). Results indicated that the use of TAED without bleach chemicals charge (A stages) led to higher pH reduction compared to the consumption of TAED, peroxide and alkali charge mixture in Pa stages. The reason is that the alkali charge tends to neutralize acidic pH.

The optimum pH of TAED-assisted alkaline peroxide delignification is lower than that used in conventional alkaline peroxide stages. TAED also reacts with peroxide under neutral and even acidic conditions while under such conditions peroxide alone is ineffective as a delignifying agent (Turner & Mathews, 1998).

Pulp yield data indicated that, when the bleaching conditions became more intense, the yield loss of pulp increased. Thus, the bleaching yield decreased by increasing pH value, chemical charge, temperature, and retention time. Also, the use of the activator in the bleaching sequence resulted in increased pulp yield (Fig. 1).

Table 3
pH changes of bleaching sequences.

Bleaching sequences	Time (min)	Temp. (°C)	Initial pH P_1 stage	Final pH P_1 stage	Initial pH P_{-2} stage	Final pH P_{-2} stage	Initial pH last stage	Final pH last stage
$QP_1P_{2\text{-}30}P_3$	150	85	11.15	10.56	12.04	11.19	12.45	11.30
$QP_1P_{2\text{-}60}P_3$	180	85	11.22	10.51	11.91	10.88	12.28	11.00
$QP_1Pa_{2\text{-}30}Pa_3$	150	85	11.36	10.70	6.81	5.18	5.57	5.19
$QP_1Pa_{2\text{-}60}Pa_3$	180	85	11.15	10.61	6.80	5.07	5.46	5.14
$QP_1P_{2\text{-}30}A_3$	150	85	10.98	10.59	11.92	11.15	7.91	6.12
$QP_1P_{2\text{-}60}A_3$	180	85	11.19	10.56	12.00	10.72	7.57	5.94
$QP_1Pa_{2\text{-}30}A_3$	150	85	11.17	10.58	6.78	5.16	5.00	4.81
$QP_1Pa_{2\text{-}60}A_3$	180	85	11.25	10.64	6.80	5.08	4.97	4.75
$P_1P_{2\text{-}30}P_3$	120	85	11.92	10.89	12.42	11.53	12.63	11.70
$P_1P_{2\text{-}60}P_3$	150	85	12.00	10.94	12.35	11.31	12.51	11.48
$P_1Pa_{2\text{-}30}Pa_3$	120	85	12.04	10.88	7.64	6.11	6.04	5.62
$P_1Pa_{2\text{-}60}Pa_3$	150	85	11.89	10.95	7.77	5.95	5.92	5.60
$P_1P_{2\text{-}30}A_3$	120	85	11.95	10.91	12.38	11.46	8.12	6.68
$P_1P_{2\text{-}60}A_3$	150	85	12.00	10.87	12.40	11.27	8.00	6.45
$P_1Pa_{2\text{-}30}A_3$	120	85	11.98	10.90	7.75	6.14	5.82	5.36
$P_1Pa_{2\text{-}60}A_3$	150	85	12.02	11.00	7.68	5.93	5.54	5.19
$QP_1P_{2\text{-}30}P_3$	150	75	10.79	10.26	11.45	11.00	12.35	11.16
$QP_1P_{2\text{-}60}P_3$	180	75	10.88	10.19	11.51	10.81	12.26	11.01
$QP_1Pa_{2\text{-}30}Pa_3$	150	75	10.92	10.17	6.52	5.17	5.49	5.11
$QP_1Pa_{2\text{-}60}Pa_3$	180	75	10.85	10.22	6.49	5.04	5.41	5.05
$QP_1P_{2\text{-}30}A_3$	150	75	10.82	10.11	11.54	11.04	7.82	6.04
$QP_1P_{2\text{-}60}A_3$	180	75	10.76	10.23	11.52	10.79	7.65	5.90
$QP_1Pa_{2\text{-}30}A_3$	150	75	10.75	10.08	6.47	5.15	5.04	4.86
$QP_1Pa_{2\text{-}60}A_3$	180	75	10.80	10.14	6.50	5.06	4.95	4.80
$P_1P_{2\text{-}30}P_3$	120	75	11.06	10.75	11.97	11.26	7.97	6.42
$P_1P_{2\text{-}60}P_3$	150	75	11.04	10.77	11.95	11.05	7.86	6.35
$P_1Pa_{2\text{-}30}Pa_3$	120	75	10.96	10.69	7.22	5.87	5.94	5.62
$P_1Pa_{2\text{-}60}Pa_3$	150	75	10.95	10.71	7.19	5.71	5.85	5.57
$P_1P_{2\text{-}30}A_3$	120	75	11.14	10.68	11.93	11.22	7.95	6.39
$P_1P_{2\text{-}60}A_3$	150	75	11.05	10.70	11.95	11.07	7.83	6.36
$P_1Pa_{2\text{-}30}A_3$	120	75	11.12	10.65	7.16	5.85	5.69	5.22
$P_1Pa_{2\text{-}60}A_3$	150	75	11.08	10.70	7.19	5.70	5.56	5.16

Bleaching in alkali media causes the polysaccharides DP to degrade, which occurs by hydroxyl ions attack on the reducing-end of polymer chains, a peeling reaction, and also by hydroxyl ions attacks on oxygen of ether bonds and cleavages (glycosidic cleavages). But, these degrading reactions often occur at high temperatures (150–190 °C) (Hon & Shiraishi, 2000). Although the alkaline hydrolysis of cellulose is a relatively slow reaction resulting in small weight loss, its impact on pulp viscosity in alkaline pulping is appreciable. But alkaline hydrolysis of hemicellulose extracts them from pulp and results in yield loss. Although the use of TAED at any stage of bleaching sequences caused pH to fall to neutral or somewhat acidic pH, the yield loss was reduced (Table 3 and Fig. 1).

The COD amounts in the bleaching effluent had a direct relation to yield loss, and whatever decreases the yield causes an increase in the COD load. The yield loss increase led to an increase in organic component of the bleach liquor, the main function of the COD load (Fig. 2).

Peroxide bleaching activation with TAED in 1 or 2 stages gave a higher yield and lower filtrate COD in bleached pulp production from kenaf bast fibers. These results directly depend on the solubility of organic materials in the bleach liquor. The activated peroxide stages, in addition to increasing pulp yield, reduce the COD load of the filtrate. Bleaching sequences with a third stage of A (TAED charge) had better results than the others.

As shown in Fig. 3, the selectivity factor increased by pulp chelation stage use in the bleaching sequences, which can be justified by hydroperoxide ion protection and the distractive effect reduction of hydroxyl ion on carbohydrate chins.

Fig. 3 shows the bleaching selectivity factor in different sequences at both 75 and 85 °C temperatures and with or without initial chelation stage (Q stage). As the results indicate, the

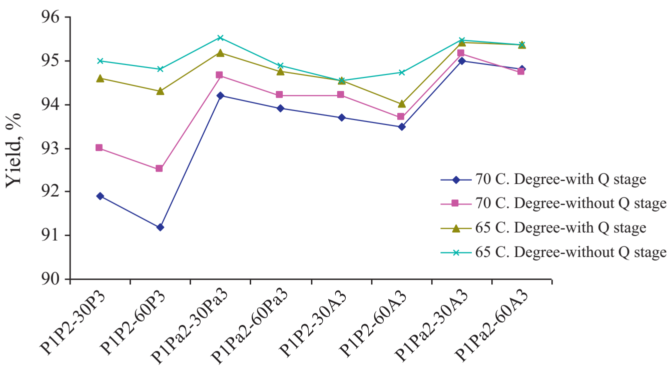

Fig. 1. Pulp yield of bleaching sequences.

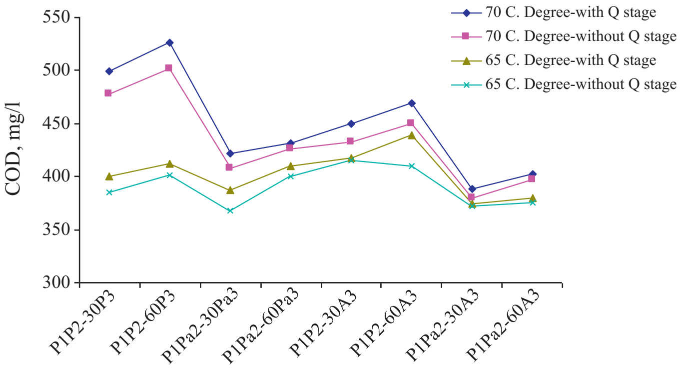

Fig. 2. COD load of bleaching effluent.

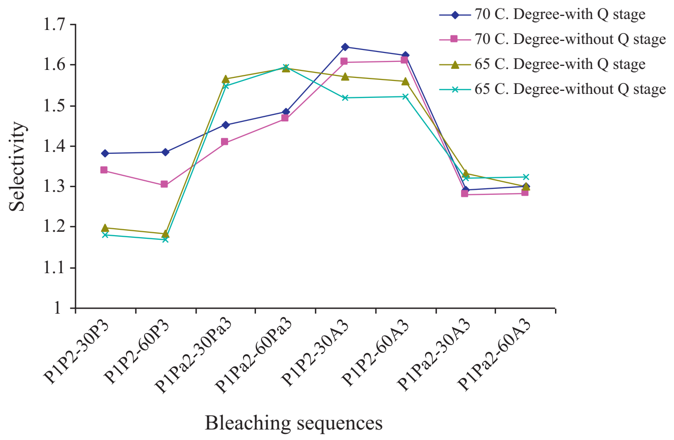

Fig. 3. Selectivity factor of bleaching sequences.

Table 4
Bleached pulp viscosity and kappa number.

Bleaching sequences	Time (min)	Temp. (°C)	κ no.	Viscosity (cP)
$QP_1P_{2\text{-}30}P_3$	150	85	4.0	31.00
$QP_1P_{2\text{-}60}P_3$	180	85	3.7	29.99
$QP_1Pa_{2\text{-}30}Pa_3$	150	85	4.9	35.47
$QP_1Pa_{2\text{-}60}Pa_3$	180	85	4.5	34.68
$QP_1P_{2\text{-}30}A_3$	150	85	3.0	32.81
$QP_1P_{2\text{-}60}A_3$	180	85	2.8	31.87
$QP_1Pa_{2\text{-}30}A_3$	150	85	6.2	37.20
$QP_1Pa_{2\text{-}60}A_3$	180	85	6.0	36.63
$P_1P_{2\text{-}30}P_3$	120	85	4.5	31.80
$P_1P_{2\text{-}60}P_3$	150	85	4.4	30.64
$P_1Pa_{2\text{-}30}Pa_3$	120	85	5.3	36.05
$P_1Pa_{2\text{-}60}Pa_3$	150	85	4.9	35.69
$P_1P_{2\text{-}30}A_3$	120	85	3.4	33.38
$P_1P_{2\text{-}60}A_3$	150	85	3.3	33.09
$P_1Pa_{2\text{-}30}A_3$	120	85	6.3	37.35
$P_1Pa_{2\text{-}60}A_3$	150	85	6.3	37.42
$QP_1P_{2\text{-}30}P_3$	150	75	6.8	37.78
$QP_1P_{2\text{-}60}P_3$	180	75	6.5	36.27
$QP_1Pa_{2\text{-}30}Pa_3$	150	75	5.7	39.80
$QP_1Pa_{2\text{-}60}Pa_3$	180	75	5.3	38.93
$QP_1P_{2\text{-}30}A_3$	150	75	5.0	37.71
$QP_1P_{2\text{-}60}A_3$	180	75	4.8	36.92
$QP_1Pa_{2\text{-}30}A_3$	150	75	7.2	41.60
$QP_1Pa_{2\text{-}60}A_3$	180	75	7.1	40.74
$P_1P_{2\text{-}30}P_3$	120	75	7.0	38.29
$P_1P_{2\text{-}60}P_3$	150	75	6.7	36.77
$P_1Pa_{2\text{-}30}Pa_3$	120	75	6.1	40.81
$P_1Pa_{2\text{-}60}Pa_3$	150	75	5.6	39.87
$P_1P_{2\text{-}30}A_3$	120	75	5.5	38.50
$P_1P_{2\text{-}60}A_3$	150	75	5.4	38.21
$P_1Pa_{2\text{-}30}A_3$	120	75	7.5	42.54
$P_1Pa_{2\text{-}60}A_3$	150	75	7.4	42.18

rate of bleaching process selectivity in all sequences and at both temperatures (75 and 85 °C) more or less increased when the initial Q stage had been used. This is related to hydroperoxide ion preservation from decomposition by neutralizing transition heavy metal ions, which results in increased removal of chromophores and lignin. Also, since hydroxyl ion is released from the alkali source, carbohydrates cleavage has increased at low hydroperoxide ion concentrations in the bleaching environment. Because hydroxyl ion was consumed by hydroperoxide ion during the bleaching reactions, its effects on carbohydrates decreased.

Therefore, the hydroperoxide ion growth and protection increased lignin removal, but carbohydrate cleavage which decreases viscosity was decreased with the result that the selectivity factor increased (see Eq. (5)). Also, the effect of Q stage on the selectivity factor was greater at higher temperatures (85 °C), because there is increased bleaching at this temperature range (Fig. 3). And, the decomposition processes for hydroperoxide ion or peroxide itself and also for carbohydrate and lignin polymers accelerate with increasing temperature.

As seen in Fig. 3, the initial Q treatment had a little effect on the selectivity factor in the bleaching sequences that had had activated peroxide stages or TAED charges. The reason is that, in these bleaching sequences, the pH falls to neutral and slightly acidic and peroxide decomposition by transition metal ions often occurs at high pH levels. Therefore, the Q stage does not have any important effect. Also, the use of the activator creates some effective ions, such as peracetic acid or peracetate anion, that are substitute of hydroperoxide ion and non sensitive to heavy metal ions. Thus, it can be said that, the Q stage application is not necessary for these bleaching sequences, and its application maybe just have a little effect on first bleaching stage (P_1) efficiency.

The temperature effect on the selectivity factor can be explained as follows: in bleaching sequences without TAED charge ($P_1P_{2\text{-}30}P_3$ and $P_1P_{2\text{-}60}P_3$), increasing temperature had a positive influence on the selectivity factor (Fig. 3). The reason is that, in alkali peroxide bleaching the rate of lignin removal increases with temperature increase. However, carbohydrate destruction which causes to viscosity loss occurs much frequently at higher temperatures (Table 4), but the rate of viscosity decrease was lower than the lignin removal value, so selectivity has increased. This result was also true for $P_1Pa_{2\text{-}60}A_3$ and $P_1Pa_{2\text{-}60}A_3$ bleaching sequences that had just one stage TAED addition (third stage: A_3), but the increased selectivity values were less than the bleaching sequences without TAED addition (Fig. 3).

The amount of the selectivity factor was decreased by the temperature increase in those sequences with a mixture of TAED activator and bleaching chemical charges at the second and/or third stages ($P_1Pa_{2\text{-}30}Pa_3$, $P_1Pa_{2\text{-}60}Pa_3$, $P_1Pa_{2\text{-}30}A_3$ and $P_1Pa_{2\text{-}60}A_3$) (Fig. 3). These results can be explained by the fact that activator adding led to the production of new oxidant agents (acetic acid and peracetic acid) acting as lignin removers in approximately neutral pH. The lignin removing capability of these oxidant agents remained almost constant across the ranges of 75–85 °C. Thus, the effect of temperature on these agents' bleaching and oxidation capability is low. In the other words, the temperature increase had caused carbohydrate chain cleavage resulting in viscosity decline and hence, simultaneously, selectivity factor decrease.

As Fig. 3 shows, the bleaching retention time had no significant effect on selectivity factor. Perhaps ineffectiveness of bleaching time on the ratio of Δ kappa to Δ viscosity in the same bleaching conditions was the cause.

Fig. 4 shows the brightness value of bleached pulps from different sequences affected by temperature, with or without the initial

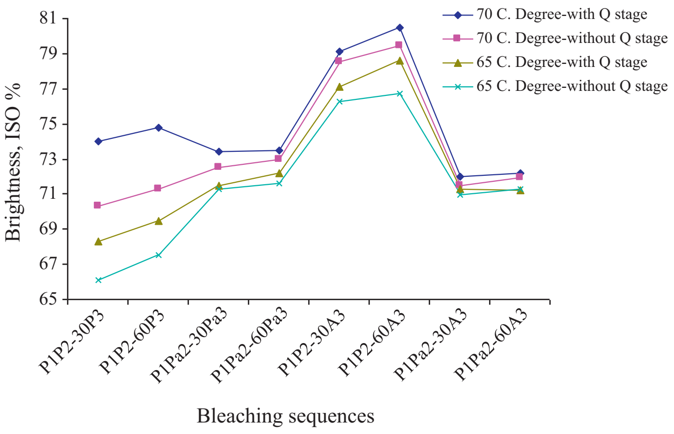

Fig. 4. Pulp brightness of bleaching sequences.

Q stage and retention time. As shown, the brightness degree in all sequences increased at high temperatures and retention time and also by the use of an initial Q stage.

Increasing retention time (150–180 min) in Pa_2 from 30 to 60 min had no significant effect on brightness values in the sequences of $P_1Pa_{2\text{-}30}Pa_3$, $P_1Pa_{2\text{-}60}Pa_3$, $P_1Pa_{2\text{-}30}A_3$ and $P_1Pa_{2\text{-}60}A_3$ (Fig. 4). Also, the Q stage had a little effect on pulp brightness values which had been bleached by the sequences containing activated peroxide (Pa) or activator stages (A). This is the result of no destructive effect from transition metals on oxidant elements in the activated peroxide stages. Therefore, these sequences with lower temperature and without initial Q stage have the same results and efficiency.

The highest brightness values were obtained by $P_1P_{2\text{-}60}A_3$ bleaching sequences, and the lowest values were from $P_1Pa_{2\text{-}30}A_3$ and $P_1P_{2\text{-}30}P_3$ at 85 and 75 °C, respectively (Fig. 4).

Brightness values were enhanced in $P_1P_{2\text{-}30}A_3$ and $P_1P_{2\text{-}60}A_3$ bleaching sequences, by just TAED activator charge in third stage (A_3). The reason is that TAED activator use in final stage activated the residual peroxide of previous stages and produced oxidant agents (acetic acid and peracetic acid) so that part of the previously unusable peroxide has converted to bleaching agents. Also, pH reduction in final stage prevented alkali darkening of bleached pulp, thus brightness increased (Fig. 4).

4. Conclusions

Results have indicated that, the achievement of printable paper appropriate brightness from kenaf bast soda pulp can be obtained by multi stages peroxide bleaching systems.

The pulp brightness increased about 5–8% ISO with the use of one activator stage (A_3) at the end of the bleaching sequences, compared to the others. But, adding the mixture of activator and bleach chemicals charge in one or two stages did not improve brightness values. The operation of sequences containing activated peroxide (Pa) and activator stages (A) with no initial Q stage and in lower temperatures will provide the same results because of their insensitivity to these factors.

In this research, $QP_1P_{2\text{-}30}A_3$ and $QP_1P_{2\text{-}60}A_3$ sequences were the best, not only increasing the brightness and also reducing the effluent COD load and pulp viscosity loss, even without the need for high temperatures and a Q stage.

References

Anderson, J. R., & Amini, B. (1996). The technology of chemical pulp bleaching. In D. W. Reeve, & C. W. Dence (Eds.), *Pulp bleaching – Principles and practices*. Atlanta: TAPPI Press.

Bajpai, P. (2005). Environmentally benign approaches for pulp bleaching. In *Developments in environmental management* (1st ed.). Amsterdam, Netherlands: Elsevier.

Coucharriere, C., Mortha, G., Lachenal, D., Briois, L., & Larnicol, P. (2002). Rationalization of the use of TAED during activated peroxide delignification and bleaching. Part I: Kinetic model. *Journal of Pulp and Paper Science*, *28*(10), 332–340.

Francois, L. E., Donovan, T. J., & Maas, E. V. (1992). Yield vegetative growth and fiber length of Kenaf grown on saline soil. *Agronomic Journal*, *84*, 592–598.

Fuhrmann, A., Rautonen, R., & Liias, P. (2000). TCF bleaching in closed and open systems. *PAPTAC International Pulp Bleaching Conference*, 207–214.

Hon, D. N. S., & Shiraishi, N. (2000). *Wood and cellulosic chemistry* (2nd ed.). 270 Madison Avenue, New York, USA: Marcel Dekker Inc.

Khristova, P., Tomkinson, J., & Lloyd Jones, G. (2003). Multistage peroxide bleaching of French hemp. *Industrial Crops and Products*, *18*, 101–110.

Khristova, P., Tomkinson, J., Valchev, I., Dimitrov, I., & Lloyd Jones, G. (2002). Totally chlorine free bleaching of flax pulp. *Bioresource Technology*, *85*, 79–85.

Nezamoleslami, A., Suzuki, K., & Kadoya, T. (1997). Preparation and properties of retted kenaf bast fiber pulp and evaluation as substitute for Manila hemp pulp. *Journal of Pack – Science Technology*, *6*(6), 339–347.

Nkaa, F. A., Ogbonnaya, C. I., & Onyike, N. B. (2007). Effect of differential irrigation on physical and histochemical properties of kenaf (*Hibiscus cannabinus* L.) grown in the field in Eastern Nigeria. *African Journal of Agricultural Research*, *2*(6), 252–260.

Senior, D., Hamilton, J., Ragauskas, A., Sealey, J., & Froass, P. (1998). Interaction of hydrogen peroxide and chlorine dioxide stages in ECF bleaching. *Tappi Journal*, *81*(6), 170–178.

Singh, R. P. (1991). *The bleaching of pulp* (3rd ed.). Atlanta, USA: TAPPI Press.

Sixta, H. (2006). *Handbook of pulp* (1st ed.). Morlenbach, Germany: Strauss GmbH.

Suess, H. U. (2010). *Pulp bleaching today* (1st ed.). Berlin/New York: Walter de Gruyter GmbH & Co. KG.

Turner, N. A., & Mathews, A. J. (1998). Enhanced delignification and bleaching using TAED activated peroxide. *TAPPI Pulping Conference Proceedings*, 1269–1276.

Zeinaly, F. (2009). *Investigation on the effects of using kenaf kraft and soda pulps on the recycled packing paper properties*. M. Sc. Thesis. Department of Pulp and Paper Industries, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran.

Zeinaly, F., Dehghani, M., & Mirmehdi, M. (2009). Bleaching of kenaf bast soda pulp with alkali peroxide. *Iranian Journal of Wood & Forest Science and Technology*, *16*(1), 105–113.

Zeinaly, F., Shakhes, J., Dehghani, M., & Shakeri, A. (2009). Hydrogen peroxide bleaching of CMP pulp using magnesium hydroxide. *Bioresources*, *4*(4), 1409–1416.

Zeinaly, F., Shakhes, J., Shakeri, A., & Zeinaly, N. (2011). Improving the bleaching process in CMP pulp from Mazandaran Wood & Paper Company. In *PAPTAC international mechanical pulping conference (IMPC'11)* (pp. 267–270).