The Effect of Hydrogen Peroxide Bleaching on the Properties of Hardwood Kraft Pulp Absorbed with Birchwood Xylan

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Abstract

Xylan can be applied to improve the strength properties of paper; however the optical properties, such as brightness, are decreased significantly. To solve that problem, an applicable bleaching process is therefore desired. The aim of this research was to investigate the impact of hydrogen peroxide bleaching on hardwood kraft pulp pretreated with birchwood xylan by measuring optical properties (whiteness, brightness, opacity) as well as physical properties (tensile index, tearing index, bulk) of handsheets made from the bleached pulp. Hydrogen peroxide bleaching, as a kind of totally chlorine free (TCF) bleaching method, is quite important industrially for chemical pulp. In our work, the process variables of peroxide bleaching including bleaching temperature, time, initial pH and $MgSO_4$ dosage were studied. The results showed that both good mechanical properties and optical properties could be achieved when the operating parameters were controlled properly and therefore hydrogen peroxide bleaching was proved to be a suitable method for bleaching hardwood kraft pulp with adsorption of birchwood xylan.

1. Introduction

Xylans are the most abundant of the hemicelluloses found in the cell walls of land plants, the content of which in softwoods and hardwoods are approximately 7–10% and 15–30%, respectively. Softwoods contain arabino-4-O-methylglucuronoxylan which is substituted on average by one 4-O-methyl-D-glucuronic acid group per 5 or 6 D-xylose units. Softwood xylan also contains one a-L-arabinose unit per 5–12 xylose units. In hardwoods the xylan is O-acetyl-4-O-methylglucuronoxylan. On average every tenth xylose unit is substituted by a 4-O-methylglucuronic acid residue and the amount of acetyl groups is 3.5–7 per ten xylose units[1,2].

Some researches have been conducted to study about the utilization of xylan as strength additives of paper. Spiegelberg evaluated the effect of hemicelluloses on the mechanical properties of individual pulp fibers and found xylan appeared to have the greatest effect on the strength properties[3]. The work of Tobias K□hnke

and Paul Gatenholm showed that tensile strength improvement of softwood pulps by xylan adsorption is more pronounced for once-dried fibers than for never-dried fibers[4]. Sch□nberg *et al.* investigated the importance of xylan for strength properties of bleached kraft pulp fibres by using enzymatic removal and chemical sorption experiments[5]. The research of Linder *et al.* concentrated on the mechanism of assembly of xylan onto cellulose surfaces[6]. However, with the amount of xylan adsorbed on fiber increasing, the optical properties of paper decreased remarkably and caused limitation for the use of xylan[7]. In order to acquire both enhanced strength and high brightness, an applicable bleaching process is thereby desired.

In recent years, environmental demands have directed bleaching conditions to elemental chlorine-free (ECF) or totally chlorine-free (TCF) bleaching sequences. Hydrogen peroxide bleaching gains more importance in industrial application, in particular, for chemical pulp bleaching[8]. Peroxide primarily works in alkaline conditions when the perhydroxyl ion, OOH^-, is formed as follows:

$$H_2O_2 + OH \longleftrightarrow OOH^- + H_2O \quad (1)$$

$$OOH^- + \text{chromophore} \longrightarrow \text{bleaching (chromophore destroyed)} \quad (2)$$

Alkaline peroxide bleaching can change the chemical, physical and optical properties of pulp significantly, accordingly adjusting the conditions of bleaching appears fairly essential to meet specific requirements of different paper products[9,10].

The primary objective of the study presented here was to evaluate the influence of hydrogen peroxide bleaching with different operating variables (bleaching temperature, time, initial pH and $MgSO_4$ dosage) upon hardwood kraft pulp with adsorbed birchwood xylan. The brightness, whiteness, opacity, bulk and tensile strength were examined to characterize the optical properties and physical properties of handsheets. According to the results, both good physical properties and optical properties could be obtained if the process parameters were controlled properly and hydrogen peroxide bleaching was therefore proved applicable for bleaching hardwood kraft pulp adsorbed with birchwood xylan.

2. Materials and Methods

2.1 Adsorption of Xylan on Kraft Pulp Fibers

A thoroughly washed (400 meshes), never-dried, non-beaten, industrially produced, bleached hardwood kraft pulp was used in our research. The physical and optical properties are presented in Table 2.1. 0.30% Poly-DADMAC (molecular

weight 400,000~500,000, Aldrich®, USA) based on oven dried pulp was added into pulp to promote the interaction of xylan with fibers. The pulp suspension was then washed to remove poly-DADMAC that did not adsorb on fibers. The xylan (from birchwood, SIGMA®, Germany) solution was pretreated at 90℃ for 15minutes and allowed to cool down to room temperature prior to mixing with pulp suspension for 20minutes. The characterizations of the kraft pulp adsorbed with xylan are also showed in Table.1.

Table. 1. The properties of untreated pulp ana xylan treated pulp

	Whiteness, %	Brightness, %	Opacity, %	Bulk, cm3/g	Tensile index	Tear index
Untreated	77.81	86.99	80.89	2.87	4.75	1.32
Xylan treated	59.13	78.26	84.71	2.94	6.15	1.52

2.2 Chelation Stage (Q Stage)

The chelation stage was performed at 70℃, 5% pulp consistency for 30 minutes, followed by a wash. For this stage, 0.30% DTPA (Diethylenetrianime pentaacetic acid, Samchun Pure Chemical Co., Ltd, Korea) based on oven dried pulp was added to the pre-warmed water and mixed well with pre-warmed pulp. The pulp was placed in a heat-proof polystyrene bag, sealed, and fully immersed in a pre-heated constant temperature water bath. The pulp was mixed every fifteen minutes for the duration of the experiment.

2.3 Hydrogen Peroxide Stage (P Stage)

All the hydrogen peroxide stages were processed at 10% pulp consistency with 2.0%odp hydrogen peroxide (Junsei Chemical Co., Ltd, Japan) in plastic bags placed in water bath. 3.0%odp Sodium silicate (Samchun Pure Chemical Co., Ltd, Korea) was used as hydrogen peroxide stabilizer. Before adding bleaching chemicals, the pulp was pre-warmed. During the bleaching experiment, the pulp was mixed every fifteen minutes. The bleaching time, temperature, initial pH and $MgSO_4$ (Junsei Chemical Co., Ltd, Japan) dosage varied according to different experiment designs. After bleaching, the pulp was washed to neutral pH.

2.4 Handsheets Forming and Measurements of Properties

Handsheets were made from the bleached pulp and conditioned. The optical properties including brightness, whiteness, opacity, and physical properties including bulk, tensile index, tearing index were measured according to TAPPI Test Method.

3. Results and Discussion

3.1 The effect of Bleaching Time and Temperature

All the hydrogen peroxide stages for researching the effect of bleaching time and temperature were performed with 0.05% $MgSO_4$ dosage and from initial pH 11.

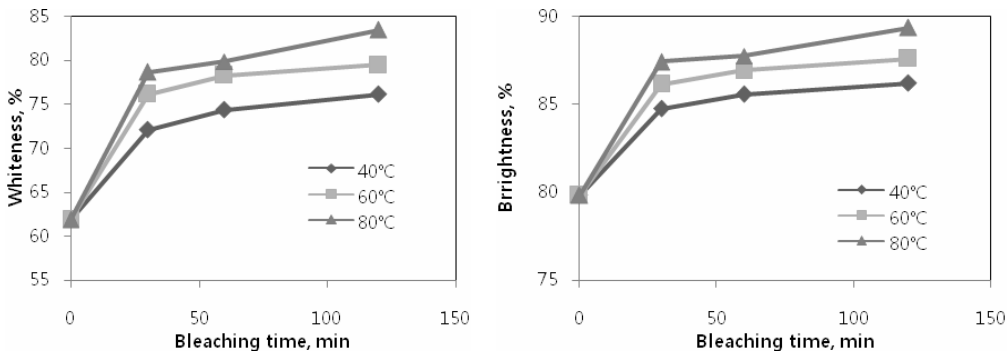

Fig. 1. The effect of bleaching time and temperature on whiteness and brightness.

Fig. 1 indicates that whiteness and brightness were enhanced, with increasing of bleaching time and temperature, as the effect of delignification was enforced. Besides, in the first 30 minutes, the tendency was much more evident than later.

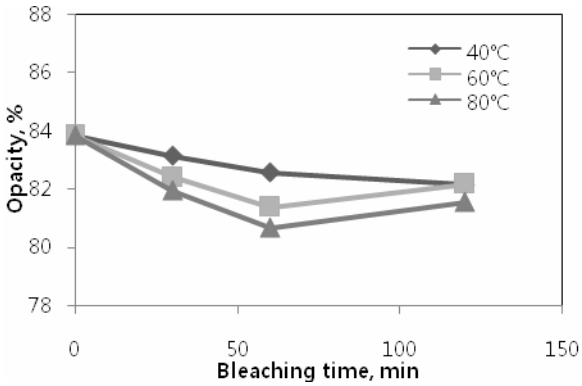

Fig. 2. The effect of bleaching time and temperature on opacity.

Fig. 2 shows that when bleaching temperature was 40℃, the opacity kept decreasing with increase of bleaching time. The reason is that some components, especially lignin, were dissolved out and resulting in the collapse of cell walls. At the same time, alkaline swelling made the fibers more flexible and softer. As a

result, the contact area between fibers was increased and the light scattering coefficient of paper sheet was reduced, which caused the decrease of opacity. In terms of 60℃ and 80℃, the opacity decreased firstly and then increased again. That is because in the later stage of bleaching, xylan which had been dissolved out and removed of acetyl groups began to redeposit on fiber surface. Some research proved that the removal of acetyl groups happened in the earlier stage of bleaching could facilitate the re-adsorption of xylan and other hemicelluloses on fibers, as the solubility of the hemicelluloses without acetyl groups was much lower than the one with acetyl groups[10].

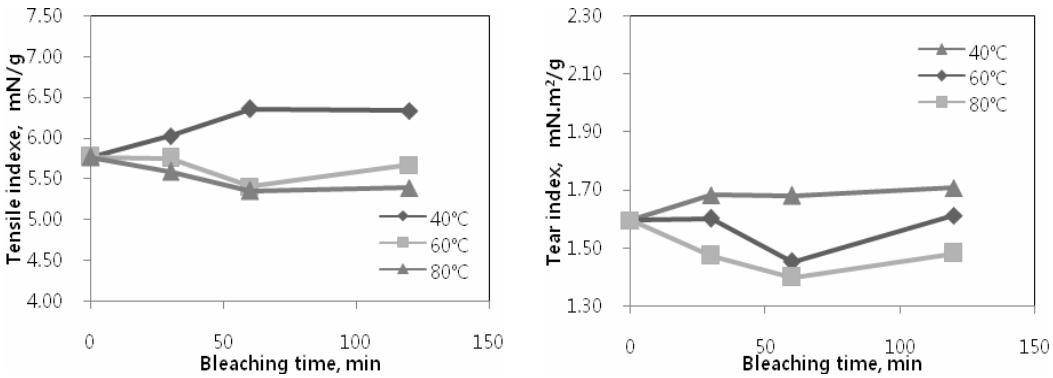

Fig. 3. The effect of bleaching time and temperature on tensile index and tear index.

In Fig. 3, it can be observed that the mechanical properties (i.e. tensile index and tearing index) were promoted steadily when the bleaching temperature was 40 ℃. However, in case of 60℃ and 80℃, the tensile index and tearing index dropped firstly and went up again after bleaching for 60 minutes. To understand this phenomenon, analyzing the chemical and physical change of pulp in bleaching stage is necessary.

Basically, there were mainly five factors affecting the properties of pulp. a). The dissolving of both adsorbed xylan on fiber surface and native one located in the cell wall of fiber had negative effect on the physical properties of pulp. b). The bleached reaction species of alkaline hydrogen peroxide were the hydroperoxy anion HOO^- and its decomposition intermediates as hydroxyl $HO^{\cdot}$ and superoxide anion $O_2^{-\bullet}$ radicals, which had generally undesirable influence in bleaching process and also attacked the carbohydrate resulting in strength loss of the fibers[11]. c). The collapse of cell walls caused by delignification and dissolving of other wood components increased the contacting area between fibers, and therefore the fiber-

to-fiber bonding was strengthened, which facilitated the development of mechanical properties of paper sheet[12]. d).The alkaline environment of bleaching increased the swelling of the cellulose fiber, thereby increased the surface area, which was believed to result in improved paper strength. e). The removal of acetyl groups from hemicelluloses species promoted the re-disposition of xylan and other hemicelluloses, which gave rise to the strength properties of sheet[13].

When the bleaching temperature was 40℃, the effect of c) and d) played a main role and the effect of a) ,b) and e) were weak due to the mild reaction condition, which lead to the steady increasing of paper strength. On the other hand, when the bleaching temperature was raised to 60℃ or 80℃, the influence of a) and b) played a primary role in the earlier stage while the impact of c), d) and e) overcame the effect of a) and b) in the later stage.

3.2 The effect of Initial pH

All the hydrogen peroxide stages for researching the effect of initial pH were performed at 80℃, with 0.05% $MgSO_4$ dosage for 120 minutes.

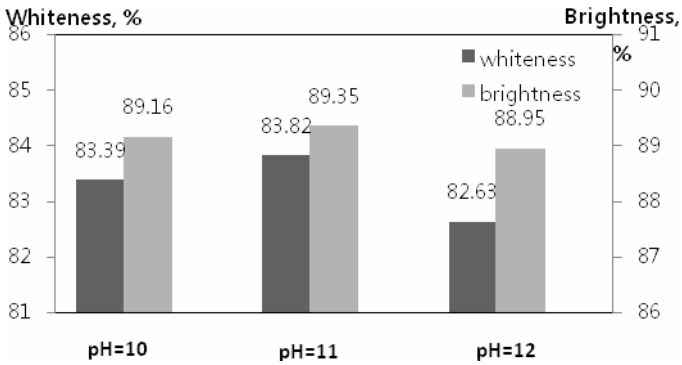

Fig. 4. The effect of initial pH on whiteness and brightness.

The data in Fig. 4 demonstrates that the peroxide bleaching from initial pH 11 provided both highest whiteness and brightness value. The explanation is that lower initial pH made weak alkaline condition which could not supply enough OOH^- for the bleaching system. As a result, insufficient bleaching caused lower whiteness and brightness. On the other hand, when the initial pH was too high, excess alkali would increase hydroxyl ion, which in turn caused producing perhydroxyl ion too rapidly to be used. That could lead to the following reaction:

$$H_2O_2 + OOH^- \leftrightarrows OH^- + O_2\,(g) + H_2O \quad (3)$$

Consequently, hydrogen peroxide would be decomposed before it was used for bleaching[9]. At the same time, pulp can also darken due to alkali darkening reactions, simply described as:

$$\text{Lignin} + OH^- \longrightarrow \text{Chromophore groups} \quad (4)$$

where phenolic lignin units could be oxidized by alkali to light absorbing structures and resulted in lower optical properties.[9]

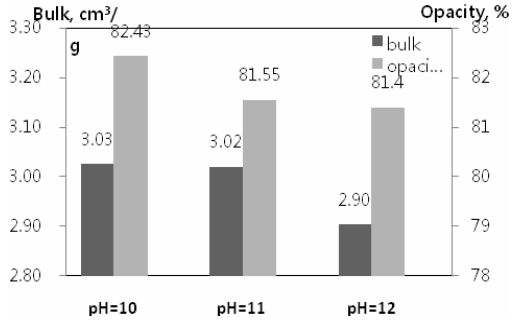

Fig. 5. The effect of initial pH on bulk and opacity.

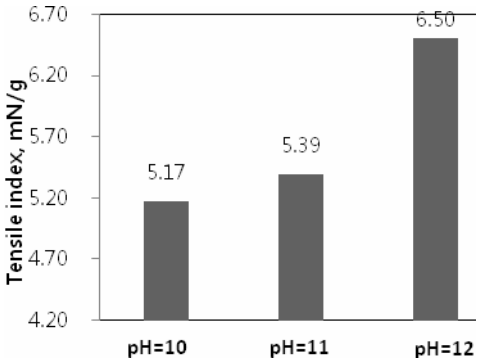

Fig. 6. The effect of initial pH on tensile index.

The experimental results for the effect of initial pH on bulk, opacity and tensile index are shown in Fig. 5 and Fig. 6 respectively. It is obvious that both bulk and opacity declined with the increasing of initial pH, whereas the tensile index boosted largely. The reason is higher initial pH created stronger alkaline environment which facilitated the collapse of fiber cell walls caused by delignification and dissolving of other wood components. As a result, the bulk was decreased. But the collapse of fiber cell walls increased the contacting area between fibers. In addition to the better swelling of fibers, the tensile index of sheet was promoted evidently. At the same time, owing to the reduction of non-contacting areas between fibers, the light scattering coefficient went down and thereby the opacity declined.

3.3 The effect of $MgSO_4$ dosage

All the hydrogen peroxide stages for researching the effect of $MgSO_4$ dosage were performed at 80℃, with initial pH 11 and for 120 minutes.

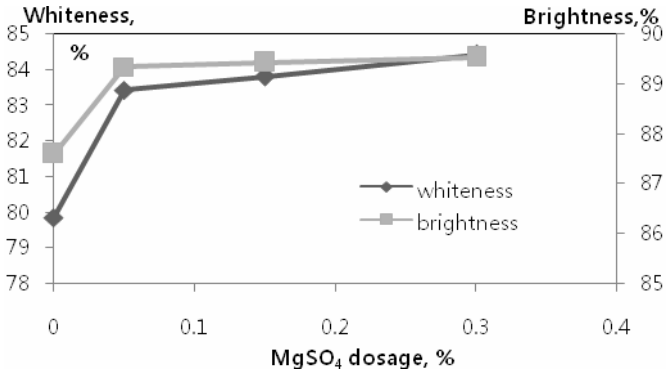

Fig. 7. The effect of $MgSO_4$ dosage on whiteness and brightness.

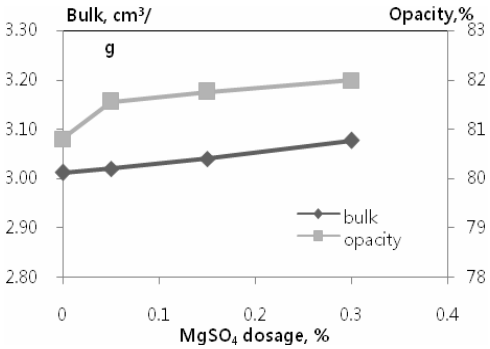

Fig. 8. The effect of $MgSO_4$ dosage on bulk and opacity.

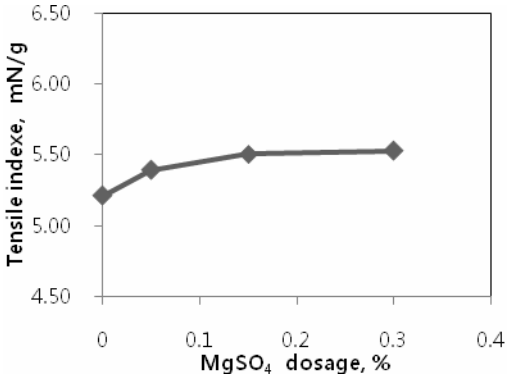

Fig. 9. The effect of $MgSO_4$ dosage on tensile index.

According to Fig. 7, 8 and 9, it appears that both optical properties and mechanical properties were improved with the addition of $MgSO_4$ increasing.

Previous studies proved that peroxide could be catalytically decomposed by some transition metal ions such as iron, manganese, and copper as following:

$$H_2O_2 + M^{2+} \longleftrightarrow M^{3+} + OH^- + OH\bullet \quad (5)$$

$$H_2O_2 + M^{3+} \leftrightarrow M^{2+} + H\bullet + OOH\bullet \quad (6)$$

$$OOH\bullet \leftrightarrow O_2\,(g) + H\bullet \quad (7)$$

$$H\bullet + \leftrightarrow H_2O \quad (8)$$

Therefore the peroxide would be consumed without having bleaching effect[14]. In addition, the new created free radicals would attack the carbohydrates and caused loss of fiber strength. However, magnesium sulfate, as compound of alkaline earth metal, could inhibit this catalytic decomposition, stabilize peroxide and protect carbohydrates. As a result, both better optical properties and physical properties could be obtained with the usage of $MgSO_4$.

3.4 The comparison of pulp in different phases

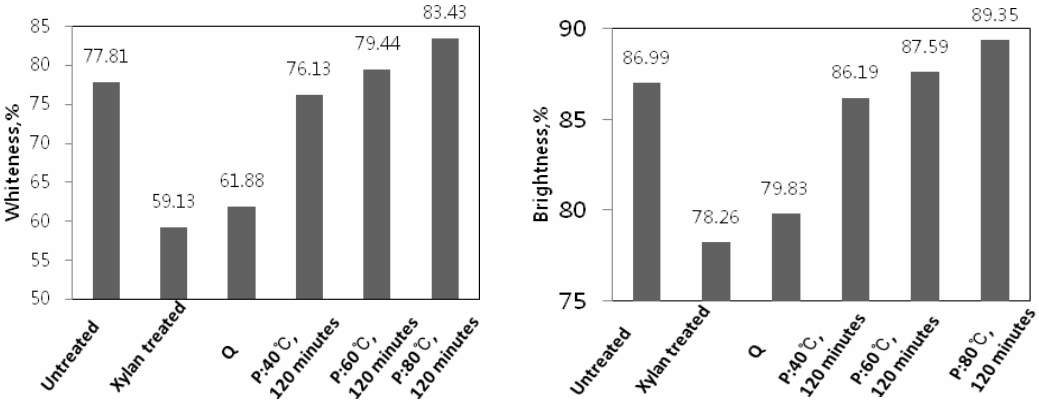

Fig. 10. The comparison of whiteness and brightness.

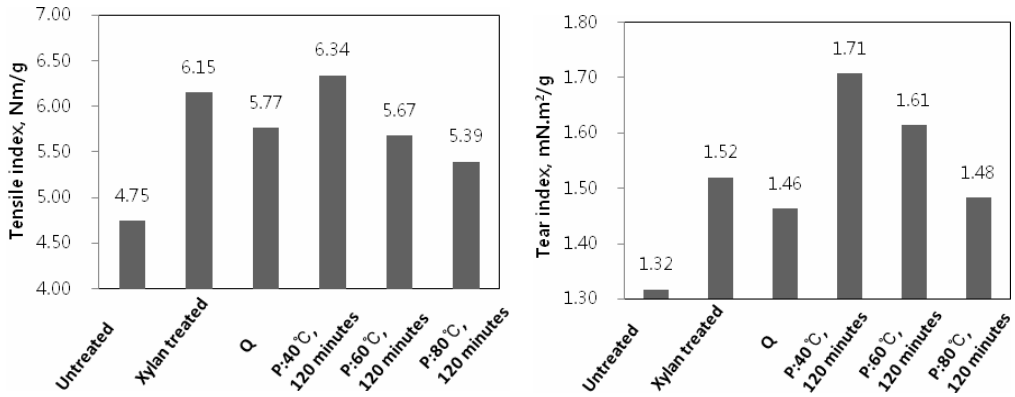

Fig. 11. The comparison of tensile index and tear index.

Fig. 10 and Fig. 11 compare the properties of untreated pulp, xylan treated pulp, chelating treated pulp and pulp bleached at different temperatures, with 0.05% $MgSO_4$ dosage, initial pH 11, for 120 minutes. The results demonstrate that the adsorption of xylan improved the strength properties of pulp by 29.5% for tensile index and 15.2% for tear index, but whiteness and brightness were decreased by 24.0% and 10.0% respectively. Chelation treatment with DTPA provided a slight increase in optical properties and a reduction in strength properties. Most importantly, when the bleaching parameters were set properly, both better optical qualities and physical properties were enhanced. For example, when bleaching temperature was 60℃ and bleaching time was 120 minutes, the whiteness and brightness of bleached pulp were as high as 79.44% and 87.59% and also the tensile index and tear index were promoted by 19.4% and 22.0% compared to the untreated pulp. Finally, it is proved that hydrogen peroxide bleaching is a suitable bleaching process for the hardwood kraft pulp adsorbed with birchwood xylan.

4. Conclusions

To summarize the results of this study, several important conclusions can be made:

1) The adsorption of xylan could improve the strength properties of paper, but the whiteness and brightness were decreased.
2) At low bleaching temperature, for example 40℃, the whiteness and brightness were enhanced, the opacity kept decreasing, the mechanical properties (i.e. tensile index and tearing index) were promoted steadily with increasing of bleaching time. When the bleaching temperature was high, for example 60℃ and 80℃, whiteness and brightness were increased, opacity and physical properties were decreased firstly and then improved again with bleaching time increasing.
3) Higher temperature of bleaching provided better whiteness and brightness, lower opacity, tensile index and tear index.
4) Bleaching from initial pH 11 showed both highest whiteness and brightness value. In addition, bulk and opacity declined with the increasing of initial pH, whereas the tensile index was boosted largely.
5) More $MgSO_4$ dosage increased whiteness, brightness, opacity, bulk and strength properties.

6) Hydrogen peroxide bleaching is an applicable method for bleaching hardwood kraft pulp with adsorption of birchwood xylan. With that, both good mechanical properties and optical properties of pulp could be achieved.

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