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Effect of Hydrogen Peroxide Bleaching Duration on *Sesbania grandiflora* Pulp

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Abstract. Chlorine-based bleaching agent can brighten the pulp effectively, but it harms the environment, especially water pollution. Thus, hydrogen peroxide, a total chlorine-free (TCF) bleaching agent is applied in this research to bleach pulp derived from *Sesbania grandiflora*. *Sesbania grandiflora* is being chosen as raw material due to its ideal characteristics as pulp source and native in Malaysia. This research aims to determine the effects of hydrogen peroxide on *Sesbania grandiflora* pulp and evaluate the paper properties made from *Sesbania grandiflora* pulp. The research was carried under different bleaching durations, 20 minutes, 40 minutes and 60 minutes under a constant temperature of 50°C and 3% concentration of hydrogen peroxide. The physical, optical and mechanical properties of *Sesbania* handsheet were measured according to the standard TAPPI. The overall result presented a significant effect on kappa number and handsheet brightness but little on mechanical properties. The longer bleaching duration gave the least kappa number of the *Sesbania* pulp, thus, improving the brightness of the *Sesbania* handsheet. However, it did not affect the strength properties of the handsheet. In this research, 60 minutes of bleaching duration on *Sesbania grandiflora* pulp exhibits the optimal bleaching performance without compromising paper mechanical properties significantly.

INTRODUCTION

The pulp and paper industry is the most significant industrial sector, and it contributes economy to the world. The most commercial products produced from this industry included paperboard, graphic paper, market pulp, writing paper, cards and packaging. The global market and technology in this industry have been undergoing substantial structural changes. This change can be explained when the consumption of communication paper such as writing and printing paper was decreased due to the domination of digital media in our daily affairs [1]. However, this situation is balanced out by the growth in paper packaging, pulp for hygiene products, the new biochemical industry and tissue paper [2]. According to the report, North America is the most significant global production of

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pulp industry while Asia was the largest paper production. China, United States and Japan were the most prominent paper producing countries. Paper and cardboard production stood at approximately 400 million tonnes globally and expected to grow to 482 million tonnes in 2030 [1].

In the manufacturing of papermaking, wood chips will undergo the chemical pulping process purposely to remove the lignin content to form wood pulp fibres. The wood pulp fibres obtained during pulping will then undergo a bleaching process. Bleaching is a further delignification process of pulp to enhance the brightness and other desirable properties such as the stability of paper colour, purity of pulp, and better capacity in receiving image from printing while preserving the strength and yield pulp. In the bleaching process, chemicals were added to the pulp at certain parameters to remove the lignin [3]. Lignin is aromatic polymer that impart the brown colour intensity to the pulp. Hence, lignin must be removed to the greatest degree so that more fibres can be bonded together, thus, increasing the paper quality [4]. Meanwhile, bleaching parameters plays a significant role in pulp and paper processing [5].

Sesbania grandiflora is a potential pulp source among the pulp and paper industry. This is mainly because of its fast growth rate and high availability in a short harvest period as compared to other pulpwood. Even 3 to 4 years old of *Sesbania grandiflora* plant can undergo chemical pulping process directly without debarking in writing paper, magazine and newsprint paper. Popularly, the wood of *Sesbania grandiflora* is the major pulp source in the paper manufacturing due to the length of the short fibre and the outstanding chemical compositions, which are both suitable for pulping [6]. Numerous studies have attempted to study the potentiality of *Sesbania grandiflora* as pulpwood. Boon suggested that the beaten *Sesbania grandiflora* with 20000 revolutions improved the mechanical strength of the produced handsheet and it is compatible with properties of handsheets made from other potential pulp sources such as bagasse and oil palm empty fruit bunch [7]. Bleaching treatment of pulp source is crucial to the produced paper since brightness is one factor that defines the paper quality. A recent study has explored the application of sodium hypochlorite as a bleaching agent. With sodium hypochlorite application, *Sesbania grandiflora* handsheet achieved the highest brightness (79.44%) at 60min since sodium hypochlorite oxidized the chromophoric group of lignin effectively [8]. Based on Tan's research, 3% sodium hydroxide concentration improved the brightness of the *Sesbania grandiflora* pulp drastically [9]. However, there is little published data on the investigation of *Sesbania grandiflora* as a pulp source. And, this research mainly focused on the hydrogen peroxide bleaching effect on *Sesbania grandiflora* pulp at different bleaching duration.

MATERIALS AND METHODS

Pulp Preparation

The debarked log of *Sesbania grandiflora* was sawn into small sizes and chipped into wood chips. The wood chips were then air dried to 10% of moisture content. The mixture of 20% of sodium hydroxide and 25% of sodium sulphite was heated to 10mins to reach 170℃. The pulping process was carried out for 90mins and followed by washing the kraft pulp. Then, the sodium hypochlorite bleaching process was carried out according to standard TAPPI with modifications in 20min, 40min and 60min. The consistency of the brown stock was set at 15%.

Hydrogen Peroxide Bleaching Treatment and Determination of Lignin Content

Based on the pulp weight with 15% consistency, a 3% hydrogen peroxide bleaching solution was prepared. The pulp was bleached at 50℃ for 0, 20, 40 and 60 minutes, followed by rinsing the treated pulp with distilled water to remove the excess hydrogen peroxide. Then, the lignin content, also known as kappa number of the pulp was determined according to TAPPI 236.

Laboratory Handsheet Formation and Paper Properties Testing

Formation of laboratory handsheet was made according to TAPPI 205. The paper properties were categorized into physical properties, optical properties and mechanical properties. Physical properties of handsheet were determined by measuring the handsheet weight with electronic balance according to TAPPI 410 and handsheet thickness with Precision Micrometer Model No 49-61 according to TAPPI 411. Optical properties of handsheet included brightness and opacity were determined by using Brightimeter Micro S-5 according to TAPPI 525 and TAPPI 519 respectively. For the mechanical properties of handsheet, tearing strength was tested according to TAPPI

414 by using Elmendorf-type tester; bursting strength was tested according to TAPPI 403 by using bursting tester; folding endurance test was tested according to TAPPI 511 by using MIT-type tester.

Statistical Analysis

Tukey Test (ANOVA) with alpha level 0.05 was applied in order to analyse the optical and mechanical properties of *Sesbania* handsheet.

RESULTS AND DISCUSSION

Effects of Hydrogen Peroxide on the Physical Properties of Handsheet

The physical properties such as weight, grammage and thickness were not influenced directly by hydrogen peroxide. From the Table 1, the weight of the handsheets were fluctuated between 1.09g to 1.39g. The thickness of the handsheets were also varied irregularly as the bleaching duration increased. However, the thickness of the paper measure how dense a paper is. Therefore, thickness of paper was affected by the density of paper and the formation of handsheets but not the bleaching agent.

Grammage or basic weight of the handsheets were determined by dividing the weight by the area of the handsheets. According to the standard TAPPI, grammage is very important and most fundamental of paper property in pulp and paper industry. Most of the papers are bought and sold according to their weight per unit area of paper. Gülsoy and Simsir [10] also reported this statement. In other words, all the paper properties were influenced by the grammage of the paper and it does not affect by the bleaching agent [11]. Therefore, the grammage of the handsheets should fall within the grammage range of 60±5gsm in pulp and paper industry. In this research, the grammage of the handsheets at 40 and 60 mins of bleaching duration were out of range. This might be due to the error and mistake done during the formation of handsheet.

TABLE 1. Physical properties of *Sesbania grandiflora* handsheets treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Average Weight, g	Average Grammage, g/m^2	Average Thickness, mm
0	1.21 ± 0.00	62.17 ± 1.04	0.15 ± 0.00
20	1.28 ± 0.02	64.08 ± 1.11	0.20 ± 0.01
40	1.09 ± 0.02	54.41 ± 1.07	0.17 ± 0.00
60	1.39 ± 0.01	69.56 ± 0.91	0.19 ± 0.00

Effects of Hydrogen Peroxide on Kappa Number of Pulp

According to the Table 2, the kappa number decreased from 14.21 to 7.63 with the increased bleaching duration by using hydrogen peroxide. The kappa number was the highest at the unbleached pulp and lowest at the bleaching duration of 60 mins. This indicates that the increasing lignin loss with increase in hydrogen peroxide treatment time.

The consumption of hydrogen peroxide in pulp treatment is followed by both lignin removal that caused the formation of carboxylic acid groups by oxidative ring opening of aromatic rings and lignin bleaching chromophoric groups attacked by peroxide anions. Li [12] reported that the increase in the bleaching duration decreases the permanganate number. The effect of hydrogen peroxide bleaching duration in that research was examined between 0 to 120 mins. The research showed that the kappa number was significantly reduced between 0 to 30 mins but slightly reduced between 30 to 60 mins. The results from Li's finding were interpreted in this research, where the kappa number was significantly reduced at 20 mins, but the reduction of the kappa number slowed down after 20 mins of bleaching duration.

Moreover, the research results of Lopez [13] were also declared that the increase in bleaching durations were particularly decreased the kappa number. The bleaching durations that he used in the research were 30 mis, 120 mins and 210 mins. He found that the kappa number was highest at 30 mins but lowest at 210 mins.

TABLE 2. Kappa Number of *Sesbania grandiflora* pulp treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Kappa Number
0	14.21
20	8.62
40	8.10
60	7.63

Effects of Hydrogen Peroxide on the Optical Properties of Handsheet

Effects on TAPPI Opacity

Opacity is the measurement of paper translucency or the light's ability to transmit through the fibre of the paper. Paper with high degree of opacity allows less light to pass through it. In contrast, paper with a low degree of opacity enables much light to transmit through the paper. The removal of lignin can increase the inter-fibre bonding as there are more cellulose and hemicellulose exposed, which contain OH-group and carbonyl acid groups that are easy to link up together. According to Li [12], the removal of lignin during bleaching caused the fibre lumens to collapse and at the same time, alkaline swelling increased the flexibility of the fibres. Thus, these increased the contact area between fibres and the light scattering coefficient of handsheet was reduce, which then decrease the opacity. However, the opacity of paper is mainly affected by the bulk and density of paper, which correlate to the thickness of the handsheets.

From the Table 3, the TAPPI opacity of the handsheets was statistically significant influenced by hydrogen peroxide. The TAPPI opacity was first decreased significantly at bleaching duration of 40 mins and it was then increased back at 60 mins bleaching duration. TAPPI opacity of the handsheets were the highest at control. This is because the handsheet was not undergoes bleaching or lignin removal. As lignins were not removed, light was not able to pass through the handsheets, hence, increase the degree of opacity.

Although lignin was significantly removed after bleaching with hydrogen peroxide, however, handsheets were formed based on pulp weight after bleaching treatment. According to Li's finding [12], the opacity of the handsheet reduced as the bleaching duration increase. In comparison, the result of this research showed that the handsheet treated at 40 mins has lower TAPPI opacity than handsheet treated at 60 mins bleaching duration. This is probably due to the lower thickness of handsheet made at 40 mins than that at 60 mins bleaching duration.

TABLE 3. TAPPI opacity of *Sesbania grandiflora* handsheets treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Average TAPPI Opacity, %
0	98.11 ± 0.83a
20	90.23 ± 1.09b
40	85.20 ± 1.19c
60	90.56 ± 0.25b

The different letter within the same column and row are statistically significant at α=0.05

Effects on Brightness

The brightness of the handsheet was increased with the increased of bleaching duration according to the Table 4. However, the result showed no significant difference between the handsheet treated at 40 and 60 mins of bleaching duration. These results were also reported by Li [12], that the longer bleaching duration enforced the delignification process. This can be verified by their research finding where the increase of bleaching duration enhanced the brightness of handsheet. From the result, the brightness was increased significantly at the first 30 mins and only increased slightly between 30 to 60 mins of bleaching duration.

Brightness is the measurement of the blue light reflectance of a specific wavelength of 457 nanometers. It is inversely proportional to the kappa number. Brightness of paper will be increase with the decrease in the kappa number. This can be showed in this research as the kappa number of the pulp treated at 60 mins was the lowest and the handsheet produced was the brightest. Moreover, these results were also reported by Shirkolaee [14] in which

the brightness of pulp was 28.1% when the kappa number was 35 while the brightness of pulp was 64% when the kappa number was 13. Thus, the lower the kappa number, the brighter the paper is.

TABLE 4. Brightness of *Sesbania grandiflora* handsheets treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Average Brightness, %
0	32.90 ± 0.41a
20	62.21 ± 0.35b
40	63.09 ± 0.31c
60	63.76 ± 0.10c

The different letter within the same column and row are statistically significant at α=0.05

Effects of Hydrogen Peroxide on the Mechanical Properties of Handsheet

Effects on Tearing Index

The tearing strength of the paper was found significantly affected by the fiber length. It was found that the tearing strength increased with increasing the fibre length. However, the paper strength properties do not only affect by the fiber length alone, it is coexisted with the individual fibers bonding ability. The individual fibers bonding ability was depended on the flexibility of the fibers. Individual fibers that are more flexible are able to form the fiber-fiber bonding more easily.

According to the Table 5, the tearing index were fluctuated between 0 to 60 mins of bleaching duration. However, there is statistically insignificant difference among the hydrogen peroxide bleaching duration tested. Thus, it can be explained that the bleaching duration used to bleached the pulp in this research has little or no effect on the tearing strength of the handsheet. Although the result in this finding showed no significant difference between 0 to 60 mins of bleaching duration. However, a different bleaching parameter or longer bleaching duration might show the changing of tearing strength of the handsheet more significantly.

According to the finding of Li [12], the bleaching duration used were 0, 30, 60, 90 and 120 mins. In that research, the tearing index was first decreased at 60 mins then increased back significantly at 120 mins of bleaching duration. Tearing strength is mainly influenced by the strength of the individual fibers. The decreased of tearing index was mainly caused by the impurities and lignin on the surface of the fibers. Zhai & Zhou [15] even stated that the impurities and lignin on the fibre surface can cause the fiber flexibility to become poor and fiber bonding strength becomes low. Hydrogen peroxide removes the impurities and lignin from the surface of fibers and promote the chemical bonding. On the other hand, the increased tearing index was due to the reduction in lignin content that reduced the modulus of elasticity of single fibers, hence, reducing the pulp stiffness [16]. The decreased in the pulp stiffness shows that the inter fibril area is less rigid and less dense, thus fibers can rearrange themselves easily. Therefore, the individual fibers become more flexible now and more effectively to form fiber-fiber bonding [17].

TABLE 5. Tearing index of *Sesbania grandiflora* handsheets treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Tearing Index, ($mN/g/m^2$)
0	5.12 ± 0.61a
20	4.48 ± 0.12a
40	4.50 ± 0.08a
60	4.63 ± 0.27a

The different letter within the same column and row are statistically significant at α=0.05

Effect on Bursting Index

Bursting strength is the amount of hydrostatic pressure that the paper can tolerate before its bursts. It depends greatly on the tensile strength. Both tensile breaking strength and bursting strength exhibit good correlation. Those fibers properties and papermaking practices that enhance tensile strength tend to improve the bursting strength.

From the Table 6, the bursting index was no statistically significant different between the bleaching duration used. It means that, the bursting strength of the handsheets were not affected by the bleaching duration that used in this research. With that, it is believed that a longer bleaching duration used may only show the effect of bleaching on the bursting strength of the handsheets.

A report by Lopez [13] with the different interval of bleaching duration showed differences in the bursting strength from this research. From that research, the treatment time used were 30, 120 and 210 mins. The bursting index in that research was first increased then decreased with the increasing of bleaching duration. Delignification and disintegrating of other wood components in the bleaching process caused the fiber lumens to collapse and thus increases the contacting area between the fibers. These actions strengthened the fiber-fiber bonding, which then helps in the development of mechanical properties such as the bursting strength of the handsheet.

However, the decreased in the bursting strength was probably due to the degradation of fiber. Zeronian and Inglesby [18] reported that the decomposition intermediates, such as hydroxyl and superoxide anion radicals, have undesired influenced in the bleaching process. Furthermore, the decomposition intermediates also attack the carbohydrates, which resulting in the loss of fibers strength. Therefore, it decreased the bursting strength of the handsheets.

TABLE 6. Bursting index of *Sesbania grandiflora* handsheets treated in different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Bursting Index, (kPa/g/m^2)
0	4.92 ± 0.58a
20	5.51 ± 0.20a
40	5.59 ± 0.61a
60	5.48 ± 0.29a

The different letter within the same column and row are statistically significant at α=0.05

Effects on Folding Endurance

Folding endurance had been tested to determine the number of double folds a piece of handsheet will maintain its strength before its break. According to the Table 7, the 0 minute has the highest folding endurance. The folding endurance decreased at 40 mins bleaching duration and increased back at 60 mins of bleaching duration. The result showed that only the control folding endurance showed statistically significant while there was no significant difference among the treated samples. Therefore, it can be explained that the hydrogen peroxide bleaching duration used in this finding did not affected the folding endurance. The research of Puitel [19] reported that the bleaching agent also attacked the cellulose but not only attacked the lignin alone. Hydrogen peroxide bleaching agent causes the swelling of the cellulose and degraded the cellulose fibers too. Thus, the degradation of the cellulose fibers affects the strength of the handsheet. Although there was an increased folding endurance from 40 to 60 mins, there was no statistically significant difference happened between these handsheets.

TABLE 7. Folding endurance of *Sesbania grandiflora* handsheets treated at different bleaching duration

Hydrogen Peroxide Bleaching Duration, mins	Folding Endurance
0	9.67 ± 2.08a
20	4.67 ± 0.58b
40	3.33 ± 0.58b
60	6.33 ± 0.58b

The different letter within the same column and row are statistically significant at α=0.05

CONCLUSIONS

In conclusion, hydrogen peroxide is a potential bleaching agent in the bleaching process. It helps in brightening the pulp and show a desirable effect in removing lignin content significantly from *Sesbania grandiflora* pulp. Based on the results, the brightness of the handsheets made from *Sesbania grandiflora* pulp that treated with hydrogen peroxide was improved with the increased of bleaching duration. The optimum bleaching duration of the pulp by using hydrogen peroxide was at 60 mins as the handsheets made is the brightest (63.76%) and the kappa number in this bleaching condition is the lowest, which is 7.63. In terms of mechanical strength, both tearing and bursting strengths were not statistically significant affected by the hydrogen peroxide bleaching duration. In folding endurance, only the control showed a difference while there were statistically insignificance among the treated samples. Hence, the application of hydrogen peroxide with the required bleaching duration in this finding removes the lignin of the *Sesbania* handsheets effectively and maintains the mechanical strength of the handsheets. Therefore, the optimum bleaching duration for *Sesbania grandiflora* pulp was at 60 mins since the overall results were optimal.

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