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Optimal Hypochlorite Bleaching Duration for *Sesbania grandiflora* Pulp

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Sesbania grandiflora is a fast growing species with 3 to 4 years of harvest rotation. Meanwhile, high cellulose content of the plant has made it a potential commercial pulpwood in Malaysia however the information is limited. Bleaching is an important process in pulp and paper manufacturing. Sodium hypochlorite was commonly used as the bleaching agent due to its strong oxidising bleaching in brightening the pulp. To reveal potential of *Sesbania grandiflora* as pulpwood, this research was carried out to determine the optimal duration by bleaching the *Sesbania grandiflora* with sodium hypochlorite. *Sesbania* pulp was treated with 5.00wt% of sodium hypochlorite solution in the water bath under the temperatures of 50°C. Three bleaching durations were taken: 20mins, 40mins and 60mins. The procedures of laboratory handsheets making and testing were conducted according to modified TAPPI standard. The results proved that 60mins was the optimal bleaching duration which showed the highest brightness percentage and the least lignin content. The reduction of lignin content also the kappa number had contributed to the brightness of the pulp. However, the overall strength properties of the *Sesbania* handsheets such as bursting test, tearing test and folding endurance test were decreased due to the fibre degradation when bleaching. The optical properties and strength properties of bleached handsheets showed significantly difference as compared to the unbleached handsheets and the differences become obvious as the bleaching duration increase.

1. Introduction

Nowadays, the invention of paper has contributed a lot to the progress and development of society. The excessive consumption of paper has made pulp and paper industry become one of the world's biggest industries. In 2013, the manufacturing of global paper and board production have achieved 0.8% and reached a new record of 403 million tonnes even though there was persistence dropped in Europe and North America. Based on the Annual Review of Pulp and Paper Statistic report published by RISI in 2014, China remained the top position in the paper production sector over the past 5 years while United States maintained in second place. In 2013, United States remained as the top producing country as it

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produced 49.4 million tonnes of pulp, followed by Canada with 17.3 million tonnes and China with 17.1 million tonnes [1]. Malaysia is capable in producing pulp and paper at over 1 million tonne per year. During the "Asian Crisis" in 1997, pulp and paper industry was one of the industries that able to survive the economic downturn in Malaysia [2].

Therefore, it is important to explore a new potential industrial pulpwood in order to support the growth of paper products in Malaysia. There are many research has been done in previous seeking for new pulp resources including oil plam which is one of the largest crop in Malaysia. However the heterogeneous structure of oil palm trunk has obstructed its potential. Some critical challenges also influence the productivity of pulp and paper industry such as the slow growth and seed supply problems for the plantation of Sabah softwood, *Pinus caribaea*; diseases and potential threats such as heart rot, root rot and phyllode rust to most promising plant species in Malaysia, *Acacia mangium* which definitely damage the pulp properties [3]. Therefore, *Sesbania grandiflora* is a newly introduced softwood as a pulp source for papermaking in the pulp and paper industry due to its outstanding strengths such as development of straight and cylindrical bole, rapid establishment from seed, tolerant to the wide range of soil types and rainfall environments, high ability to adapt the environment, and high availability within a year. Most importantly, this tree species is a native plant in Malaysia. Orwa et al. [4] found that the *Sesbania grandiflora* fibres of the plant are short and they can be blended together with long fibre with suitable proportion to give good strength of pulp. According to Boon et al. [5], beating is essential to improve the quality of *Sesbania grandiflora* pulp in paper formation.

In the bleaching process, bleaching agent plays an important role in decolourizing and whitening the pulp. Basically, it destroys the chromophores via oxidation or reduction of these absorbing groups. The use of hypochlorites for bleaching wood pulp began in the early 1880s. Sodium hypochlorite is recommended because it is cheap, easy to make and use, and capable in bleaching the pulp to high brightness. Besides, the shelf life of sodium hypochlorite is not a factor if kept sealed for 1 to 2 months [6].

Overall, this paper aims to determine the optimal duration for bleaching the *Sesbania grandiflora* pulp with sodium hypochlorite and to evaluate the effect of bleaching duration on the pulp and paper properties that derived from *Sesbania grandiflora*.

2. Materials and Methods

2.1. Preparation of wood pulp and sodium hypochlorite bleaching (H stage)

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

2.2. Lignin measurement or kappa number measurement

The lignin content of pulp was tested according to standard TAPPI 236.

2.3. Formation of laboratory handsheet

Formation of laboratory handsheet was made according to standard TAPPI 205.

2.4. Physical, optical and strength properties testing of laboratory handsheet

2.4.1. Physical testing The weight and grammage of handsheet was tested based on standard TAPPI 410 procedure by using electronic balance. Thickness of handsheet was tested based on standard TAPPI 411 procedure by using Precision Micrometer Model No 49-61.The handsheets were cut in required sizes by following the cutting process before optical and strength testing.

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2.4.2. Optical testing Brightness and opacity of handsheet were tested based on standard TAPPI 519 procedure by using Brightimetre Micro S5 and Opacimeter.

2.4.3. Strength properties The bursting tester was used to measure the maximum bursting strength of paper having a bursting strength of 50 kPa up to 1200 kPa (7 psi up to 157 psi) and in the form of flat sheets of up to 0.6mm (0.025 inch) thick by using bursting tester according to the standard TAPPI 403. The Elmendorf-type testing tester was used to measure the force perpendicular to the plane of the handsheet which required to tear multiple plies through a specified distance after tearing has been started by following the standard TAPPI 414. Folding endurance test of handsheet was determined by using MIT-type tester according to standard TAPPI 511. MIT-type tester tests the capability of paper to withstand the repeated bending, folding and creasing.

3. Results

3.1. Physcal properties of Sesbania grandiflora handsheet

Table 3.1 showed that the weight and grammage of the unbleached and bleached handsheets were varied from 1.21g to 1.26g and from 62.17gsm to 62.87gsm respectively. The thickness of bleached handsheets were decreased from 0.19mm to 0.17mm as the bleaching durations became longer. From the results, it can be revealed that the basic weight or grammage affected indirectly the thickness of handsheets, except for the bleaching duration. The grammage of the handsheet is calculated according to the formula, weight divided by the area of the handsheet with the SI unit, gsm (grams per square metre). With regard to grammage, the values of physical properties like thickness, bursting strength and bulk are interpreted and specified. The grammage is mainly used to calculate the index of strength properties, the paper measurement of basic weight is critical for the accurate calculation of theses indexes [7].

The basic weight of one handsheet required for the testing is fell within the weight range of 1.20g±0.10g which will produce the handsheet with the grammage of 60.00±5.00gsm.

Table 3.1. Influence of hypochlorite bleaching durations on physical properties of *Sesbania* handsheets.

Bleaching duration, min	Weight, g	Grammage, gsm	Thickness, mm
Control	1.21 ± 0.00	62.17 ± 1.04	0.15 ± 0.00
20	1.30 ± 0.04	65.11 ± 1.90	0.19 ± 0.00
40	1.30 ± 0.06	65.15 ± 2.97	0.18 ± 0.01
60	1.26 ± 0.00	62.87 ± 0.25	0.17 ± 0.00

3.2. Kappa number of Sesbania handsheet

Table 3.2 showed that the kappa number of the *Sesbania* pulp was gradually decreased as the bleaching durations became longer. The significant effects proved that hypochlorite bleaching agent started to react chemically on the residual lignin of the pulp at 20mins.

Table 3.2. Influence of hypochlorite bleaching durations on kappa number of *Sesbania grandiflora* pulp.

Bleaching duration, min	Kappa Number
Control	14.21
20	6.33
40	6.17
60	5.43

During kraft pulping process, over 90% of lignin can be removed from wood chips but small portion will still exists in unbleached pulp, known as kraft pulp residual lignin with modified structure under alkali condition. Kappa number measures the total amount of lignin content in the pulp that is oxidised with $KMnO_4$during titration process [8]. The dominant lignin content in pulps has significantly contributed to the kappa number, known as hexenuronic acid groups (Hex A). The content of Hex A

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contributes 33% to 47% to the kappa number of commercial hardwood kraft pulps whereas 5% to 15% only to the kappa number of softwood kraft pulp. Hexenuronic acid, also known as 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid is the main uronic acid group in chemical pulp and formed during chemical (alkaline) pulping through β-elimination of methoxyl groups from 4-methylglucuronic acid (MeGlcA) unit of xylan and does not exist in native wood [9]. Hex A are destroyed by some electrophilic bleaching reagents such as hypochlorite acid, chlorine, peroxy acids and ozone [8]. Overall, active alkali charge, ClO^{-} of sodium hypochlorite oxidised and destroy the Hex A in the lignin during the delignification stage, hence, the kappa number of the pulp can be decreased.

3.3. Optical properties of Sesbania grandiflora handsheet

Table 3.3 showed a significant increase of the handsheets brightness percentage from 20mins to 60mins in the range of 78% to 80% as compared to the unbleached pulp (32.90%). It indicated that the hypochlorite bleaching agent and decreased kappa number of the *Sesbania* pulp along the bleaching durations contribute to the brightness percentage of the handsheet at 20min. Previous study had promoted that pulp bleaching improved the brightness of the coir fire significantly [10]. Paper brightness is measured from scale 0 to 100. The higher the scale number, the brighter the paper. During bleaching, sodium hypochlorite solution attacks some specific chromophoric groups in lignin, hence brighten the pulp easily. A number of researchers have posited that sodium hypochlorite contributes to the apparent brightness of the pulp from other plant species. For example, sodium hypochlorite contribute from 4 to 8 points of higher brightness values in sweetgum and sugar maple pulps compared to calcium hypochlorite. Furthermore, the removal of the light-absorbing substance from the pulp can increase the paper brightness. A light-absorbing substance in the pulp that derived from the lignin of the absorbing constituents allows the paper to reflect more light because these light-absorbing substance became soluble in aqueous solution through oxidizing and reducing process in order to remove them from the pulp. So, less light are absorbed [11].

Overall, the reaction between hypochlorite ions and the chromophoric groups of the lignin become active when the bleaching duration become longer, then, degrade the lignin fragment through alteration. The light-absorbing substances in the pulp also become soluble in aqueous solution and remove from the pulp, less light will be absorbed, bleached handsheet able to reflect more light, hence making the hand sheet brighter.

Table 3.3. Influence of hypochlorite bleaching durations on brightness of *Sesbania* handsheets

Bleaching duration, min	Brightness (%)
Control	32.90 ± 0.41a
20	78.76 ± 0.33b
40	79.06 ± 0.90b
60	79.33 ± 0.27b

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

Table 3.4 showed that the percentages of TAPPI opacity of bleached handsheets decreased insignificantly from 20mins to 60mins in the range of 85% to 84% but decreased significantly compared to unbleached handsheet (98%). The bleaching of pulp improved the brightness of the coir fibre obviously but had adverse effects on paper opacity. During the bleaching process, exposure of cellulose and hemicellulose which contain hydroxyl and carbonyl acid groups contributed to the interfibre bonding of the coir fibre which further increased the bonding strength of the paper. The removal of lignin content will increase the interfibre bonding. Besides, the unbleached pulp is able to absorb more light which might be influenced by the higher lignin content in the pulp [10]. The statements supported the obtained result in which the percentage of the Tappi opacity is the highest without bleaching and decreased slowly when the bleaching durations became longer. Furthermore, the decreased of the Tappi opacity percentage is due to the wood components including lignin were dissolved out during bleaching and resulted in the collapse of fiber lumens. Meanwhile, alkaline swelling made the fibers more flexible

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and softer so the contact area between fibers was increased and the light scattering coefficient of paper sheet was reduced [12].

Therefore, prolong the bleaching duration will stimulate the chemical reaction between hypochlorite ions and lignin content become more active and cause the fibers altered and become weaker. At the same time affect the handsheet opacity.

Table 3.4. Influence of hypochlorite bleaching durations on TAPPI opacity of *Sesbania* handsheets

Bleaching duration, min	TAPPI Opacity (%)
Control	98.11 ± 0.83a
20	85.10 ± 0.43b
40	84.06 ± 1.43b
60	84.03 ± 0.37b

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

3.4. *Strength properties of Sesbania grandiflora handsheet*

Table 3.5 showed that the bursting index of the bleached handsheets increased insignificantly from the unbleached handsheets along the bleaching durations. Hydrostatic pressure is the main pressure that applied at the standard rate of increase until the handsheet rupture [10]. Generally, the bonding of individual fibers is the main factor that affect the strength properties of paper sheet. The degree of fiber bonding depends largely on the fiber flexibility and compressibility of individual fibers. Thus, the collapsing of fibers will lead to the formation of paper having high tensile strength, compression strength, burst strength, tensile stiffness and elasticity. Collapsed fibers are more flexible and have a higher surface area available for bonding. Also, fiber flexibility influences the capacity of the fibers to conform around other fibers, thus influences the number of fiber-fiber contacts also the number of bonds and the bonded area in the sheet. A flexible fibre always conform to each other easily and give a large fibre-fibre contact area [13].

All in all, the longer bleaching duration with hypochlorite solution will collapse the pulp fibers chemically, fibers become more flexible, hence, increase the surface area for fiber-fiber bonding in the network and making the handsheet having high bursting index.

Table 3.5. Influence of hypochlorite bleaching durations on bursting index of *Sesbania* handsheets

Bleaching duration, min	Bursting Index, $\mathbf{KPa \cdot m^2/g}$
Control	4.92 ± 0.58a
20	5.17 ± 0.71a
40	5.49 ± 0.34a
60	5.55 ± 0.18a

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

Table 3.6 showed that the tearing index of the *Sesbania* handsheets were slightly decreased from 20mins to 60mins, which is from 4.20 $mN \cdot m^2/g$ to 3.95 $mN \cdot m^2/g$ but significantly decrease from the unbleached *Sesbania* handsheet. Van der Akker proposed that the consummation of energy during the tear test are the sum of fibre fracture and fibre pull-out from the network. Instead of pulling out a fibre from surrounding networks, sever a fibre is easier because less energy is consumed. So, short fibres are obviously easier to pull out than long fibres. Interfiber bonding is an essential to a sheet strength as it is a function of two factors, the strength of an individual fiber and the interfiber bonds. They contribute to the internal cohesion of paper [13]. As interfiber bonding increases, it is more likely to sever a fibre that lying in the path of an advancing tear than to pull out. Meanwhile, stress is concentrated at the apex of the tear and is hard to share with the rest of the structure. Between, fibre flexibility causes the number of bonds to provide the bonding area and resulting in more surface area for bonding [10]. During the beating of chemical pulps, the development of fiber surfaces for bonding may be considered due to the internal and external fibrillation. The surface area for bonding is directly proportional to the extent of bonding [14].

Therefore, longer bleaching duration caused the pulp fibers become less flexible because hypochlorite solution tend to alter the interfibre bonding. When the zone of interfibre bonding become weak, less surface area for bonding are made, the internal cohesion of handsheet is affected and the sheet strength become weak. Hence, handsheet is easily to be severed by the tester with low consummation of energy in low tearing index reading. In fact, the nature characteristic of *Sesbania grandiflora* having short fibre is also one of the factor that contribute to the low tearing strength.

Table 3.6. Influence of hypochlorite bleaching durations on tearing index of *Sesbania* handsheets

Bleaching duration, min	Tearing Index, $mN \cdot m^2/g$
Control	5.89 ± 0.13a
20	4.20 ± 0.09b
40	3.98 ± 0.11b
60	3.95 ± 0.11b

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

Table 3.7 showed that the bleached *Sesbania* handsheets gave a very low folding endurance compared to the unbleached *Sesbania* hand sheets. The folding endurance of bleached handsheet at 20mins was higher compared to 40 and 60mins because there was a technical error when conducting the testing. The testing results reflects the combined viscoelastic and elastic properties of paper. The folding endurance is eventually influenced by the beating process in which the weakening of interfiber bonding increase the brittleness of the paper. Hydrogen bonds of interfiber bonding are held between the surface carbohydrate macromolecules of neighbouring fibers. The exposure of polysaccharide molecules and the surface of functional groups like hydroxyl, carbonyl and carboxyl, also the extent of surface contact between fibres are greatly affect the extent and magnitude of interfiber bonding. The folding endurance is dependent on various morphological characteristics of pulp fibers like thick or thin walls of fibers and fiber coarseness. Fiber coarseness influences the collapsibility and conformability of the fiber. High coarseness of fiber usually have thicker cell walls, thus, stiffer and less conformable [13].

The bleaching with hypochlorite solution resulted in the low folding endurance in handsheets because of fiber degradation during bleaching reaction and duration, then causing the lacking of sufficient fiber length and inadequate fiber bonding. Thus, the brittleness increased. Besides, hypochlorite is a strong oxidizing agent which could attack the functional groups as well as hydroxyl group of the cellulose and carbonyl group of lignin.

Table 3.7. Influence of hypochlorite bleaching durations on folding endurance of *Sesbania* handsheets

Bleaching duration, min	Folding Endurance
Control	9.67 ± 2.08a
20	4.50 ± 0.71b
40	3.33 ± 0.58b
60	3.33 ± 0.58b

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

4. Conclusions

This paper prove that the bleaching of sodium hypochlorite influenced *Sesbania grandiflora* pulp significantly from all the testing. Bleached pulp displays significant results as compared to unbleached pulp because the bleaching agent start its chemical reaction at 20mins. Also, sodium hypochlorite solution play an important role in brightening the pulp slurry by oxidising the chromophoric groups of the lignin and decolourizing it efficiently through high oxidation reaction. The optimal bleaching duration of *Sesbania grandiflora* pulp is at 60mins since the brightness reading is the highest (79.44%) and the kappa number is the least, which is 5.43 due to the alteration of hexenuronic acid groups (Hex A) in the pulp during hypochlorite bleaching. Thus, reducing the formation of chromophores group that will cause yellowish of the pulp.

However, the overall strength properties of *Sesbania grandiflora* pulp were decreased due to the bleaching agent reaction and bleaching duration that cause fibre degradation. So, it is a common phenomenon in the reduction of strength properties. The bleaching process brings inverse effect to the strength properties compared to the optical properties. Through the testing, we can emphasize that individual fibre bonding that related with fibre flexibility, interfibre bonding in fibre network, fibre length and fibre coarseness are crucial to the strength properties of paper.

Last but not least, *Sesbania grandiflora* can be considered as an ideal industrial softwood pulp due to its outstanding potentials. More research can be conducted to explore the possibilities of *Sesbania grandiflora* as pulpwood source.

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References
[1] Bajpai P 2017 *Pulp and Paper Industry: Emerging Wastewater Treatment Technologies* John Fedor (India: Elsevier) p 10-11
[2] Roda J and Rathi S 2006 *Malaysia: Feeding China's Expanding Demand for Wood Pulp* (Indonesia:Center for International Forestry Research) p 1-15
[3] Murata Y, Kubo S, Togawa E, Ramle S F B M, Sulaiman O, Hashim R, Ibrahim W A, Kosugi A, Hirooka A and Abe H 2015 *Detection of Vascular Bundles Using Cell Wall Birefringence On Exposure To Polarized Light* **65** 190-197
[4] Orwa et al 2009 Sesbania grandiflora *World Agroforestry Centre* FAO (2012-2019)
[5] Boon J G, Ramle S F B M, Ibrahim N I, Che Zaudin N A, Liew J Y, Hamzah Z 2019 *Effect Of Beating On Kraft Pulp Of Sesbania grandiflora* **41** 1356-1359
[6] Gibbons John H 1989 *Technologies for Reducing Dioxin in the Manufacturer of Bleached Wood Pulp, Chapter 4: Pulp Bleaching Technology* (Washington, DC: DIANE) p 41-52
[7] Timberlake A 2013 Technical Association of the Pulp and Paper Industry *Grammage Of Paper And Paperboard (Weight Per Unit Area)* 1-7
[8] Costa M M and Colodette J L 2007 *The Impact Of Kappa Number Composition On Eucalyptus Kraft Pulp Bleachability* **24** 61–71
[9] Zhu J Y 2013 Technical Association of the Pulp and Paper Industry *Hexeneuronic Acid Content of Chemical Pulp* 1-6
[10] Mohamad Jani S and Rushdan I 2014 *Effect of Bleaching on Coir Fibre Pulp and Paper Properties* **42** 51–61
[11] Histed J A, Sandel Jr L F and Hurst M M 1996 *Hypochlorite and Hypochlorous Acid Bleaching* 395-410
[12] Li L Z, Lee S H, Lee H L, and Youn H J 2011 *Hydrogen Peroxide Bleaching of Hardwood Kraft Pulp with Adsorbed Birch Xylan and Its Effect on Paper Properties* **6** 721–736
[13] Karlsson H 2007 *Some Aspects on Strength Properties in Paper Composed of Different Pulps* **38** 1-50
[14] Wielen L C V 2006 *The Structure and Physical Properties of Pulpwood Fibers* (United State: Georgia) 1-31