

## Material Using for Making Paper: Review in order to Bleaching Method

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### ABSTRACT

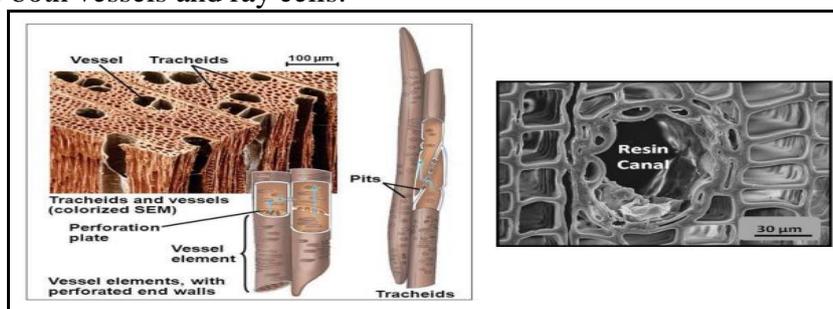
In today's world, the most common types of pollutants that are discharged into water streams are organic waste and solid trash. In a general sense, the effluents that are produced by pulp and paper mills are composed of a complex mixture of various organic compounds. Lignin, extractives, and byproducts of the breakdown of carbohydrates are all examples of components that fall under this category. A number of processes, including pretreatment of the wood, pulping, washing, screening, paper machine, coating, and bleaching, are responsible for the production of hazardous effluents. Bleaching is the most significant of these processes however. The fact that the quality of wastewater from various stages of the process is influenced by factors such as the kind of raw material and process, the amount of water that is used, and the recirculation of the effluent should not come as a surprise to anybody. By recycling, reusing, and reducing the amount of waste that is produced, one of the primary goals is to lessen the impact that human activity has on the environment.

### INTRODUCTION

There is a challenging environmental scenario that the pulp and paper (P&P) industry is now coping with. Positive aspects of the industry include the fact that it relies on the use of renewable photosynthetic resources. On the other hand, the industry is responsible for the enormous quantities of aqueous effluents that are discharged into the environment. There is a production of one metric tonne of paper; however, the amount of wastewater that is generated throughout the manufacturing process may range anywhere from seventy cubic metres to seventy cubic metres, depending on the characteristics of the raw material, the kind of final product, and the degree of water reuse (Rintala and Puhakka, 1994; Latorre et al., 2001). The process water sector accounts for about seventy percent of the massive amount of water that is consumed by the P&P industry.

### RAW MATERIALS FOR PAPER MAKING

many kinds of wood that are harvested from plantations Hardwoods, which are deciduous trees like eucalyptus and subabul, and softwoods, which are coniferous trees like pine, spruce, and other similar species, are the two categories that are used to classify these types of trees. Hardwoods are classified as these two groups. According to Karlsson (2005), the manufacturing of paper and board involves the utilisation of a wide range of fibre sources, which typically include both hardwood and softwood lumber. The majority of the fibre that is used in the production of paper and board in India comes from hardwoods. These hardwoods have cell wall thicknesses that range from three to four millimetres, mean fibre lengths that range from two to four millimetres, and rotation cycles that are relatively short. There are a number of components that go into the construction of hardwoods. Some of these components include bibriform fibres, fibre tracheids, which are tubular structures, and conducting vessels, which include both vessels and ray cells.



**Figure: Cross-section of hardwood block revealing different cells**

It is possible for the containers to have walls that are thin, ends that are open or perforated, and be anywhere between 200 and 400  $\mu\text{m}$  in length and 500  $\mu\text{m}$  in width. As a consequence of this, fluids could be able to flow through. Hardwood also contains parenchyma cells, which are

cells that are dense, thin, and have short ends when seen from above. The cells that make up hardwood are referred to as parenchyma.

### **BLEACHING METHODS**

Through the process of boiling the pulp, it is possible to safely dissolve up to ninety percent of the lignin without causing any damage to the cellulose fibre. Bleaching is one method that may be used to proceed with the delignification process. It is possible to bleach high-yield chemical pulps by decolorizing them with either an oxidising agent (which combines oxygen) or a reducing agent (which combines hydrogen). Some examples of oxidants are chlorine dioxide, sodium hypochlorite, oxygen gas, and hydrogen peroxide. Other examples include oxygen gas. Chlorine dioxide is just another illustration of this. Sodium hydrosulfite and other reducing agents are used in this process. In order to remove the lignin that has become soluble in the cellulose, alkali is often used. Everyone has their own set of advantages, disadvantages, and constraints.

#### **Acid-catalyzed activation of pulp of different nature**

Due to the significant structural variations that exist between hardwood and softwood pulp, it is hypothesised that an acidic pre-treatment would have a distinct impact on the residual lignin that is present in each kind of pulp. Given the fact that the residual lignin in softwood pulp has a larger proportion of inactive lignin than that of hardwood pulp, it is reasonable to anticipate that hardwood pulp would react more favourably to an acidic treatment. As a result of this, it is clear that a higher concentration of acid solution is required in order to remove the inactive lignin from the pulp of softwood during the acidic treatment. On the other hand, in order to remove the inactive lignin from hardwood pulp, a lower concentration of acid solution is required. Furthermore, the initial Kappa value of the pulp may have an effect on how the pulp reacts to an acidic pre-treatment.

### **REVIEW LITERATURE**

**Parveen Kumar (2005)** The use of pulp bleaching that adheres to the DEPD and ODED sequences has been the subject of investigation, and it has been hypothesised that this might assist minimise the amount of pollutants that are present in the effluents. In accordance with the International Organisation for Standardisation (ISO), the mixed hardwood kraft pulp is bleached in a laboratory environment in order to achieve a certain brightness level of 87%. Describing the effluents that are produced at each step of the pulp bleaching process allows for a comparison to be made about the increase in pollutant loads. It was determined that a NaOH dosage of 20 kg/t of O.D. pulp was the most effective method for achieving a kappa number decrease of 45% after oxygen delignification. On top of that, this dosage resulted in the least amount of viscosity loss, which was around 12 percent. After looking at both sequences, it was found that the KF value of 0.3 was the most effective one to use in order to get the desired level of brightness. It was found that the ODED sequence required a lower amount of total active chlorine ( $aCl_2$ ) when compared to the DEPD method. When compared to the DEPD technique, the use of O<sub>2</sub> delignification results in a reduction of the bleach chemical ( $aCl_{100}$ ) by a factor of 45%. It was discovered that the effluents from the ODED series had a reduced pollution load compared to the effluents from the DEPD sequence. Due to the fact that the pulp's initial kappa number was reduced by forty-five percent after the O<sub>2</sub> delignification stage, this outcome was achieved.

**Ravi Dutt (2003)** An investigation into the ways in which the lignin-degrading fungus influenced the bleaching qualities of mixed hardwood chips was the objective of the fungal pretreatment conducted. The levels of active alkali that were applied to wood chips that had been pretreated as opposed to chips that had not been treated were lower. When compared to the data obtained from untreated chips with a higher alkali dosage, the findings obtained from pretreated chips with a lower alkali dosage were similar. Because of the fungal treatment, the amount of chlorine that was used was reduced by 4.8% in comparison to the control technique, which resulted in an improvement in the energy efficiency of the operation. The pretreatment of *Ceriporiopsis subvermispora* resulted in a reduction of 4.7% in the amount of lignin that was present, a reduction of 14.3% in the number of permanganates, and a reduction of 15.5 kg/T in the total amount of  $Cl_2$  that was used. As soon as the CD stage was reached, the pollutant load

saw a reduction of 32.6% in terms of COD and 41.5% in terms of BOD. In addition, the effluent from the pretreated pulp shown a reduction of 12% in the amount of AOX compounds.

## RESEARCH METHODOLOGY

### AREA OF THE STUDY

The results of the experiments are shown in a schematic format using Figure. Eucalyptus hardwood, which was the basic material, originated from Yamuna Nagar, which is located in the state of Haryana in India. Dry cleaning, dicing the raw material into very small pieces that measured between 10 and 15 millimeters, and then washing it with hot water at a temperature of 70 degrees Celsius were the steps that were taken in order to remove the dust, dirt, and silica that had collected on the surface of the raw material. Straw that had been cleaned and squeezed was then centrifuged and dried at room temperature until it reached 85% dryness. The next step was to store it in poly bags so that there would be no accumulation of moisture.

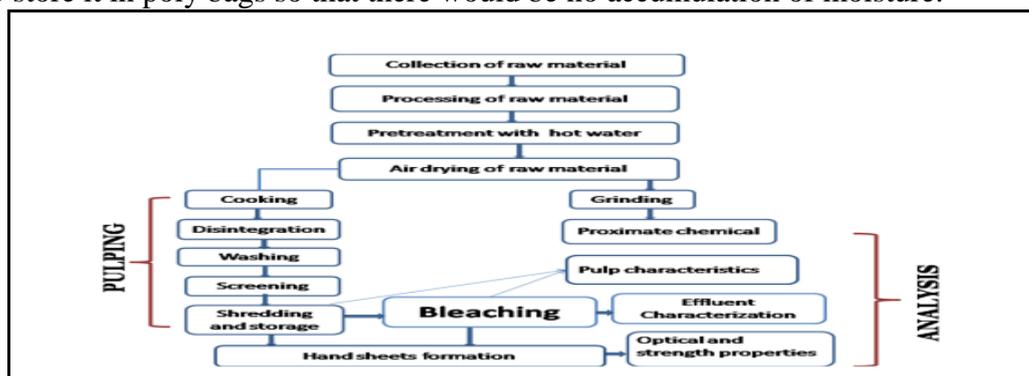


Figure: Schematic presentation of experimental work

### CHEMICALS

Both anthraquinone (AQ) and soda liquor were acquired from a paper mill in North India for the purpose of conducting the pulping investigation. Upon its arrival, the soda liquor had a concentration of one hundred grams per liter. In order to produce chlorine water, chlorine gas was dissolved in water that had a temperature of less than 10 degrees Celsius. Both the calcium hypochlorite and the chlorine dioxide were obtained from the same mill when they were extracted. Fisher Scientific's 30% hydrogen peroxide was diluted to a level of 17–20 gpl for the purpose of the bleaching experiment performed by Fisher Scientific. At each and every instance, the strengths of the bleaching agents and soda liquor were evaluated just before they were put to use. In order to keep the pH stable throughout the different analyses and other tests that were required for the bleaching investigation, glacial acetic acid, H<sub>2</sub>SO<sub>4</sub>, hydrochloric acid, sodium hydroxide, and Qualigens of the SQ grade were used. All extra chemicals of an analytical grade were supplied by Loba Chemie. These compounds included sodium thio sulfate, potassium permanganate, potassium iodide, ammonium ferrous sulfate, sodium sulphate, sodium chlorite, glucose, and glutamic acid. A certified reference material of fatty acid methyl ester was given by Sigma Aldrich (USA) in order to conduct an analysis of the saturated and unsaturated fatty acids that were present in the bleaching effluent. Additionally, a number of isomers of chlorophenols, bromophenols, chloro fatty acids, and resin acids were also introduced. In addition, the derivatization of fatty acids to methyl esters required the use of a 14% boron trifluoride in methanol solution, which was acquired from Sigma Aldrich for the United States of America.

### DATA ANALYSIS

As a result of concerns over environmental unbalancing and the demands of customers for high-quality products, the pulp and paper industry is compelled to find alternatives to woody raw materials that are composed of fibrous raw materials and processes that are ecologically acceptable for transforming these raw materials into finished goods. Paper mills are grabbing hold of these in order to support industry production. This is due to the fact that untapped lignocellulosic biomass in agricultural fields and agricultural byproducts such as cereal straws, hemp, bagasse, reed grass, jute, kenaf, and bamboo have a high potential to compete with woody materials that are derived from forests. In the countries of Asia, eucalyptus hardwood is a raw material that is abundant and simple to acquire. It is produced in almost the same

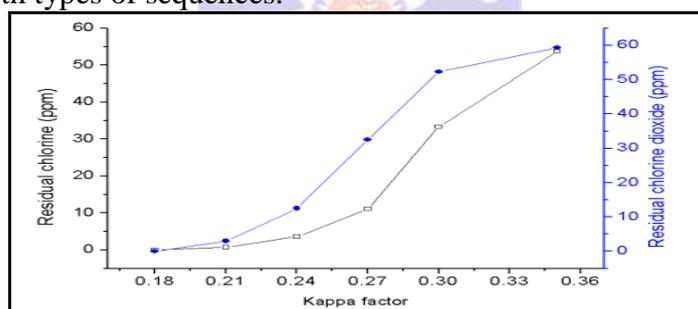
quantity as grain during the process of paddy cultivation. Ash content, cellulose, hemicelluloses, lignin, and silica are all components that are present in it.

According to Zhang et al. (2000), the farmer might be able to manage this agricultural residue without burning it on-site. This would be an effective way to address the primary source of air pollution, respiratory problems, and injuries that occur in traffic accidents. According to Hart and Rudie (2004), the pulping process that makes use of soda anthraquinone (AQ) is frequently utilised for the purpose of effectively converting non-wood materials into fibrous pulp while minimising the breakdown of cellulose residues. While the raw materials were being heated, around 90 percent of the delignification process took place. The remaining 10 percent took place during the bleaching phase, which involved the use of a variety of oxidising chemicals. With high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), colour, total solids, and toxic chlorolignin components, the pulp bleaching process is responsible for producing the most effluent of all the processes that take place in a pulp mill (Singh and Dutt, 2003).

## OPTIMISATION OF DOSAGE FOR BLEACHING CHEMICALS IN EUCALYPTUS HARDWOOD PELLETS

### DEMAND FOR CHLORINE IN THE FIRST PHASE

The amount of chlorine that was required for the initial step of the bleaching sequences for CEOPHH, CD<sub>10</sub>EOPHH, CD<sub>30</sub>EOPHH, CD<sub>50</sub>EOPHH, CD<sub>50</sub>EOPD, and DEOPD was calculated. A number of different kappa factors, including 0.18, 0.21, 0.24, 0.27, 0.30, and 0.35, were utilized in order to compute the chlorine demand. This was accomplished by utilizing equation 3.1 from the materials and procedures section. The kappa factor was determined to be best at 0.27 for chlorine-based sequences and 0.25 for chlorine dioxide sequences, as showed in Figure. This was the case for both types of sequences.



**Figure: Optimization of kappa factor to calculate chlorine demand at initial bleaching stage**

When the constraints on the application of bleaching chemicals were exceeded and there was a bigger effluent load, the quantity of bleaching chemical that was present in the bleaching effluent, which is referred to as the residual content, rose.

#### 5.1.2 Optimizing the dosage of calcium hypochlorite

In the H1 stage, calcium hypochlorite was administered in the following sequences: CEOPHH, CD<sub>10</sub>EOPHH, CD<sub>30</sub>EOPHH, and CD<sub>50</sub>EOPHH. The dosage range for calcium hypochlorite was 0.5%, 1.0%, 1.5%, 2.0%, and 2.5%. It was noticed that the brightness of the pulp grew when the dose of hypochlorite was raised from 0.5 percent to 2 percent, but that it then remained the same, as seen in Figure. It revealed that the maximum delignification had reached 2.0% of hypochlorite, and that it was now impossible to remove lignin from the mixture. Given that the 1.0% hypo dose caused a precipitous increase in the amount of calcium hypochlorite that was still present, it was concluded that this was the optimal quantity for bleaching. The remaining chemical needs were then provided during the succeeding bleaching stage.

### EFFECTS OF REPLACING CHLORINE WITH CHLORINE DIOXIDE

The CE<sub>OP</sub>HH bleaching procedure was utilized in order to achieve an ISO brightness of 83.5% through its application. The results that are displayed in Table demonstrate that the optical characteristics of bleached pulps were improved when chlorine dioxide was used instead of chlorine during the initial bleaching process because of the substitution. As a result of replacing fifty percent of the Cl<sub>2</sub> in the preparation with ClO<sub>2</sub>, the brightness of the pulp improved to

85.8 percent ISO. Similarly, the percentage of opacity increased from 81.4% in CE<sup>OP</sup>HH sequence to 85.2% in CD<sub>50EO</sub>PHH sequence. This indicates that similar trends were seen. Due to the fact that the brightness of 83.7% ISO was attained in the CD<sub>50EO</sub>PD sequence, which is lower than CE<sub>OP</sub>HH, it was discovered that the addition of ClO<sub>2</sub> in the last step had no effect. When compared to the results achieved with the normal bleaching CE<sub>OP</sub>HH and replacement at only the first phase, it was demonstrated that the results obtained with the complete DEOPD sequence removal of elemental chlorine were not as excellent as those obtained with the replacement.

### **ADDITION OF CHLORINE DIOXIDE PROVIDES PROTECTION AGAINST DEGRADATION OF THE LONG CHAIN FIBERS**

The existence of a good balance of long and short fibers in bleached pulps made from hardwood pulp may be responsible for the high strength properties of these pulps. During the process of bleaching the hardwood pulp by utilizing the CE<sub>OP</sub>HH sequence, the tear index exhibited an increase to 5.72±0.07 when chlorine dioxide was utilized instead of chlorine and hypochlorite. In the DEOPD sequence, the tear index was found to be 5.82±0.1, which indicates that the addition of chlorine dioxide provides protection against degradation of the long chain fibers. Because of the attack of elemental chlorine, the CE<sub>OP</sub>HH sequence was found to have the highest tensile index.

This was due to the fact that the chlorine forced the fibers to fibrillate, which resulted in the production of more tiny particles, which in turn increased the tensile index. The results were further corroborated by the °SR values, which demonstrated that the CE<sub>OP</sub>HH sequence had higher SR values than the sequences that were based on chlorine dioxide. It was found that the viscosity of the elemental chlorine-based sequences was lower when compared to the DEOPD sequences. This finding suggests that elemental chlorine was responsible for the degradation and assault of cellulose fibers. In their study on the ECF bleaching of kraft pulps composed of eucalyptus and acacia, Karim et al. (2001) found that ClO<sub>2</sub> has a stronger selectivity for oxidizing lignin and retains the pulp quality. This was seen throughout their examination. The DEOPD sequence was found to be an appropriate choice when considering the connection between the strength characteristics of pulps and bleaching wheat straw. This was established via the process of analyzing the facts. Strong features were also found in a study that was conducted in 2000 by Sharma and colleagues on the bleaching of citronella grass pulp using soda-AQ DEPD.

### **STRUCTURES OF THE VARIOUS CHLOROPHENOLIC COMPOUNDS IN BLEACHING EFFLUENTS**

It was found that the wastewater that was created during the bleaching process contaminated some organohalides. These organohalides included isomers of chlorophenols, bromophenols, chlorocatechols, chloroguaiacols, chlorosyringols, and chlorovanillins. The substantial quantity of these compounds that were found in the effluents of paper mills was another finding that was made by Karn et al. (2005). In accordance with the findings of Hubbe et al. (1995), the effluent from the pulp mill included a significant quantity of about 19 different chlorophenol compounds, which included mono, di, tri, terta, and penta derivatives. In Figure the structures of the various chlorophenolic compounds that were discovered in bleaching effluents are arranged according to the chemical family that they belong to. Twenty-seven of the thirty-four isomers of different chlorophenolic compounds that were selected for research were shown to be considerably adding to the load of bleaching effluent. The greatest concentration of organohalides was found in the CE<sub>OP</sub>HH bleaching sequence, which had a concentration of 6047 mg/t. Replacement of elemental chlorine with chlorine dioxide has the potential to have an effect on the creation of these compounds. Reductions of 21%, 28%, and 40% in the generation of chlorophenolic compounds were achieved on 10%, 30%, and 50% replacement, respectively. The final stage was the removal of calcium hypochlorite using chlorine dioxide, which resulted in a reduction of chlorolignin compounds by 72%. It is possible that this occurred due to the high oxidation potential of chlorine dioxide, which was utilised less often throughout the bleaching process and thus resulted in the production of fewer chlorolignin molecules.

## CONCLUSION

Both industrialised and developing countries confront challenges when it comes to resolving global environmental concerns. These challenges include the management of waste, pollution, emissions of greenhouse gases, deforestation, and the deterioration of nonrenewable resources brought on by the rise of urban and industrial areas. Environmental protection laws are being enacted by governments in both developed and developing countries in order to protect the resources of the environment.

As a consequence of these issues, the pulp and paper sector is humiliatingly confronted with a shortage of raw materials that are generated from forests for the manufacturing of paper. Initially, the majority of mills have begun to use recycled papers or raw materials that are not derived from wood. This is in contrast to the typical forest-based resources that were previously used. Because it is lignocellulosic, eucalyptus hardwood, which is a cereal waste, is a readily accessible raw material in countries with limited wood supply, such as China and India. Additionally, it may be used in the pulp and paper sector. Examples of such nations are China and India. The present research was conducted to assess the cellulose content of eucalyptus hardwood, which was found to be  $33.3\pm 0.47\%$ , pentosans at  $27.3\pm 0.36\%$ , lignin at  $13.0\pm 0.07\%$ , ash at  $12.6\pm 0.11\%$ , and silica at  $11.7\%$  according to the results. Because it has a lower percentage of lignin and a greater quantity of fibrous mass than other types of wood, eucalyptus hardwood is a unique raw material for pulp and paper mills. Other types of woody materials do not possess these characteristics.

## BIBLIOGRAPHY

- [1] Abdel-Mohdy, F. A., Abdel-Halim, E. S., Abu-Ayana, Y. M., & El-Sawy, S. M. (2000). Rice straw as a new resource for some beneficial uses. *Carbohydrate Polymers*, 75(1), 44-51.
- [2] Adhoc Working Group of European Commission. (2005). Revision of the ecolabelling criteria for tissue paper, Comments and background to the second draft proposal. SIS ecolabelling.
- [3] Akbari, M., & Resalati, H. (2001). Use of agricultural waste in the pulp and paper industry. In 1<sup>st</sup> International and 4<sup>th</sup> National Congress on Recycling of Organic Waste in Agriculture. Iran.
- [4] Alajoutsijärvi, T. (2001). Replacing sulfuric acid in pulp bleaching with internally formed organic acids. Espoo, 7 January, 2003.
- [5] Ali, M., & Sreekrishnan, T. R. (2000). Anaerobic treatment of agricultural residue based pulp and paper mill effluents for AOX and COD reduction. *Process Biochemistry*, 36(1-2), 25-29.
- [6] Anapanurak, W., & Pisuthpichet, S. (1997). Chemical pulp production from rice straw by alkaline soaking and cooking with added alkaline and oxygen. Final Report, The Research Project for Higher Utilization of Forestry and Agriculture Plant Materials in Thailand (HUFA).
- [7] Atchison, J. E. (1974). Present status and future potential for utilization of bagasse in the pulp, paper and paperboard industry-A world-wide review. In Proceedings of the... congress.
- [8] Atchison, J. E. (1995). Twenty-five years of global progress in nonwood plant fiber pulping-historical highlights, present status, and future prospects. In: Tappi Pulping Conference (pp. 91-102). Tappi Press.
- [9] Ateş, S., Atik, C., Ni, Y., & Gümüşkaya, E. (2004). Comparison of different chemical pulps from wheat straw and bleaching with xylanase pre-treated ECF method. *Turkish Journal of Agriculture and Forestry*, 32(6), 561-570.
- [10] Atik, C., & Ates, S. (2000). Mass balance of silica in straw from the perspective of silica reduction in straw pulp. *BioResources*, 7(3), 3274-3282.
- [11] Aujla, M. I., Rehman, I. U. R., & Javaid, A. (2005, December). Mechanism of silica precipitation by lowering pH in chemi-thermomechanical pulping black liquors. In Proceedings of the 1st WSEAS International Conference on Computational Chemistry (pp. 58-62). World Scientific and Engineering Academy and Society (WSEAS).
- [12] Bajpai, P. (2003) Microbial degradation of pollutants in pulp mill effluents. *Advances in Applied Microbiology*, 48, 79-134.