

Mixing Hardwood Pulp Greenhouse Gas Emissions: A Review

Dr. Nirmal Sharma, Research Engineer, Avantha Centre for Industrial Research and Development, Yamuna Nagar, Hariyana
Dr. Ram Avatar, Professor, Dep. Of Biotechnology, CCS University, Meerut (U.P)

ABSTRACT

An all-encompassing technique is required for both the development of treatment procedures and the evaluation of pollutants. One of the most significant contributors to the global pollution problem is the wastewater that is produced by the pulp and paper industry. The process of wet oxidation involves transferring organic molecules, which may be either liquid or solid, to water and then exposing them to an oxidant at high pressure and temperature. This is the fundamental notion of wet oxidation. In this method, a liquid or a solid might be used as the medium of choice. In order to get the fuel value of medium-grade coal, it is possible to produce carbon from waste that has been pulped with water via the process of wet oxidation. A wide variety of effluent is produced as a result of a number of processes that finally come together. Treatment for these conditions has included the use of a wide variety of technologies, as well as combinations of these technologies. Systems that are used following primary therapy, such as biological treatment, as well as sequential anaerobic and aerobic systems, are the ones that are used the majority of the time. Additionally, there is a problem with the management and removal of solid garbage across the country.

INTRODUCTION

In line with the Integrated Pollution Prevention and Control Directive (IPPC), permits are required for all new or large rebuilding projects in the Indian Union that involve paper factories. This requirement went into effect on October 30, 1999. The fact is that this is the case regardless of the plant's capability for production. It is very necessary to make use of cutting-edge technology in order to lessen the impact that the wood processing industry has on the surrounding environment. It is possible to lessen the destructive effects that technological processes have on the environment by implementing stringent environmental protection regulations, such as those that are in place in Europe, and by designing equipment with great care.

Oxygen-containing chemicals and enzymes are used in the bleaching process of pulp. During the process of developing the bleaching method, the goal is to reduce the quantity of chlorine dioxide that is used and to totally do away with the utilisation of molecular chlorine. This is done in an attempt to reduce the amount of chloroorganic compounds that are discovered in wastes and goods that are sold to consumers.

When comparing ECF bleaching to TCF bleaching, it is necessary to take into mind the fact that low-substituted, low-toxic chlorophenols and chlorides are often produced during chlorine dioxide bleaching. This is something that proponents of ECF point out. The use of this method does not have any negative consequences on the surrounding environment. Furthermore, it is believed that the use of a local system for the treatment of filtrate enables producers of pulp and paper to function inside a closed water system environment. After making the statement, the following considerations are not taken into account:

1. The high explosiveness of chlorine dioxide, especially in the summer;
2. The formation of molecular chlorine in the process of manufacturing chloride dioxide and bleaching chlorine dioxide;
3. The likelihood that the completed items comprise components that fall under the category of chloroorganic. The experience of paper companies in Scandinavia suggests that the cost of creating TCF pulp is around ten percent more than that of ECF pulp. This is seen despite the fact that the brightness and strength of TCF pulp are lower than those of ECF pulp.

It would seem that this is the cause for the widespread usage of "soft" ECF-bleaching, particularly in the setting of national contexts in European countries. TCF pulp bleaching has been more economically possible in recent years as a result of the development of ozone bleaching. As a result of the fact that ozone is unstable and has a low solubility in hot water, the utilisation of this substance in the process of pulp cooking is not well thought out.

Wastewater

The amount of water that is required for each of the several pulping procedures is significant, despite the fact that the amount of water that is needed changes from step to step. According to Billings and Dehaas (1971), the pulping and bleaching operations both result in the production of wastewater, the quality of which might vary substantially. This occurs due to the fact that every treatment employs a unique collection of chemicals and a distinct set of procedures.

According to Cecen et al. (1992), the production of one tonne of pulp requires the use of a substantial quantity of highly polluted water, namely wastewater that is left over after the chemical pulping process. Using this water, a total of two hundred cubic metres of pulp is created. The activities that are associated with the preparation of wood, pulping, washing of pulp, screening, washing, bleaching, paper machine, and coating are the primary sources of pollution that occur throughout the process due to the several phases that are involved. Other causes of contamination include cleaning, bleaching, and screening in addition to cleaning. The pulping process results in the production of a significant amount of wastewater, the bulk of which is made up of wood debris and soluble wood components. Additionally, this effluent comprises a number of chemicals that are formed as a result of the chemical pulping process. In the course of the bleaching process, wastewater is produced, and this wastewater has a distinct personality. The strength of these wastewaters is not much higher than that of wastewater formed during the pulpification process, despite the fact that dangerous compounds are present in these wastewaters.

Greenhouse gas emissions

On the other side, the pulp and paper industry is also a contributor to the pollution of the air and the accumulation of petrol emissions. Vapours of water are the most major kind of pollutants that are produced by gasoline exhaust. In addition to particulates, nitrogen oxides, sulphur oxides, sulphur reduced sulphur compounds (TRS), and volatile organic compounds (VOCs), this category also contains several other types of substances.

Despite the fact that the removal of pollutants from wastewater is the major purpose of wastewater treatment, one of the secondary goals of wastewater treatment is to reduce the formation of new pollutants, especially gaseous emissions. In their study, Ashrafi et al. (2000) brought attention to the impact that various wastewater treatment technologies have on the emissions of greenhouse gases (GHG). The greenhouse gases that are produced during the process of treating wastewater, which are caused by the utilisation of energy, are something that must be taken into account (Baig and Liechti 2001; Ashrafi et al. 2000). In addition to the greenhouse gases that are released by the waste products, such as carbon dioxide and methane, these gases are also released with the waste products. According to Castillo and Vivas (1996), Buzzini and Pires (2002), and El-Ashtoukhy et al. (2005), there are instances in which these techniques may use a greater amount of power than conventional treatment alternatives. By way of illustration, modern reactors that are designed for the treatment of biological wastewater are often capable of achieving higher treatment rates and operating more efficiently. There are instances in which these techniques may also use a greater amount of energy than conventional treatment approaches.

REVIEW LITERATURE

Sandeep Tripathi's (2004) A series of experiments were carried out using both types of bleaching chemicals in order to investigate the influence that green bleaching chemicals (oxygen, enzyme, and ozone) and conventional bleaching chemicals (chlorine and chlorine dioxide) have on the production of pollutants during the bleaching process. According to the findings, the levels of adsorbable organic halogens (AOX), colour, biochemical oxygen demand (BOD), and chemical oxygen demand (COD) in the bleaching filtrate were shown to decrease by 49–56, 49–56, 70–72, and 48–66, respectively, when oxygen was used prior to the traditional bleaching process. When conventional bleaching chemicals were used, this aspect of the situation was not present. The amount of AOX and colour in the bleaching filtrate was decreased by 5.6 and 9.12%, respectively, when xylanase enzyme was introduced prior to the bleaching process. This is in contrast to the results that were attained when conventional

bleaching chemicals were used. A decrease of 64–68, 73–77, 70–77, and 70–79, respectively, in the levels of BOD, COD, colour, and AOX in the bleaching filtrate was made possible by ozone treatment and oxygen administration prior to the application of conventional bleaching. In contrast, this was not the case with the results that were produced using traditional bleaching chemicals. According to the environmental impact assessment carried out by the Index of Global Pollution Methodology, the utilisation of green bleaching chemicals as opposed to conventional ones has the potential to enhance the quality of the ecosystem, thereby elevating it from class "C" (which causes discomfort to life forms) to class "B" (which is acceptable to life forms). The use of a variety of green chemistry strategies throughout the bleaching process of mixed hardwood pulp resulted in a considerable reduction in the quantity of bleaching chemicals that were utilised as well as the formation of pollutants, all while resulting in an improvement in the quality of the pulp.

Daljeet Kaur (2000) states that rapid industrial and urban growth is causing environmental problems that the world is struggling to control. These problems include greenhouse gas emissions, pollution, deforestation, waste management, and the depletion of nonrenewable resources. Governments in both industrialised and developing nations are passing extremely strict laws to safeguard natural resources. As a result of these problems, the pulp and paper industry is mockingly experiencing a shortage of raw materials obtained from forests for the production of paper. This is particularly valid for the production of paper. Currently, most mills start their production processes with recycled papers or non-wood raw materials instead of the traditional forest-based resources that were previously employed. One type of lignocellulosic waste that is readily available in countries with limited forests, such as China and India, is eucalyptus hardwood. This waste material has the potential to be utilised in the pulp and paper industry. The composition of eucalyptus hardwood was determined to be $33.3 \pm 0.47\%$ cellulose, $27.3 \pm 0.36\%$ pentosan, $13.0 \pm 0.07\%$ lignin, $12.6 \pm 0.11\%$ ash, and 11.7% silica, based on the results of this investigation. Because it contains more carbohydrates and less lignin than hardwoods and softwoods, eucalyptus hardwood has the potential to replace raw materials used in pulp and paper mills. A comparison of the soda and soda anthraquinone methods was conducted regarding the conversion of eucalyptus hardwood into pulp. Based on the results, it was concluded that the latter method produced more pulp (62.4%) and better pulp strength characteristics. Soda-anthraquinone eucalyptus hardwood pulp bleaching was found to be more effective when chlorine dioxide was used as opposed to elemental chlorine. This resulted from the bleaching sequence based on chlorine dioxide, which increased the pulp's strength characteristics while also producing less bleaching effluent. Chlorine dioxide bleaching was used to reduce the adsorbable organic halides, which are a marker of biorefractory, accumulative, and dangerous compounds, by 66%. The practice of using agricultural waste as a raw material for papermaking is beneficial for waste management, pollution prevention, and the advancement of sustainable industrial growth.

Martin A. Hubbe (2001), the pulp and paper (P&P) sector has made significant strides in removing pollutants from process water and effluent, which has reduced the amount of toxins released into receiving rivers. These developments have been made worldwide. Several wastewater treatment techniques are covered in this study. P&P businesses can reduce biological or chemical oxygen demand, toxicity, solids, colour, and other indicators of pollutant load economically by using these techniques. The P&P industry has made extensive use of conventional wastewater treatment systems, which typically involve primary clarity followed by activated sludge processes. Higher concentrations of contaminants may be removed by additional treatments like membrane filtering technologies, bioreactors, advanced oxidation processes, and anaerobic biological stages. These represent just a handful of the agents that can be strategically utilised to improve the efficacy of wastewater treatment processes. Among the agents that can be used are flocculants, coagulants, filter aids, and bacterial or fungal cultures that have been optimised. Furthermore, P&P mills have the option to introduce upstream process modifications, such as kidney-like operations, filtration save-alls, and dissolved-air-flotation (DAF) systems, to clean process waters and lessen the amount of pollutants and effluent that are sent to end-of-pipe wastewater treatment plants.

RESEARCH METHODOLOGY

LABORATORY SCALE PULPING

On the basis of a comprehensive review of the literature on the pulping of agricultural wastes in India (Bhardwaj et al., 2005; Abdel-Mohdy et al., 2004; Rodriguez et al., 2000), the methods of pulping with soda and soda anthraquinone were shown in batch digesters for the manufacture of pulp. The pulping variables, which include the alkali concentration on oven dry (o.d.) weight basis of raw material, temperature, cooking time, and AQ concentration (catalyst), were tuned in order to produce a pulp with a kappa number of 15. Detailed information may be found in Table. In accordance with the criteria outlined in procedure T 236 om-99, the Kappa number refers to the volume of 0.1 N potassium permanganate solution that is necessary for the production of 1 gram of moisture-free pulp. What it represents is the amount of lignin that is still present in the pulp. For the purpose of reaching the pulping temperature, a slow ramp rate was used. This was due to the fact that the pulping of raw materials involves an interaction between solid and liquid components. In order to get superior cooking results, it is necessary for the liquid components to be completely absorbed by the raw material during this period of time. After the heating process, the pulps were cleaned, and the black liquid was separated. Following the removal of any raw material with the use of a Somerville screen filters, the pulp was then shredded in order to achieve homogeneity.

Table: Conditions for pulping

Variables	Conditions
Raw material (g, o.d.)	300
Active alkali concentrations, (%)	15, 16, 17, 18, 19
Maximum temperature (°C)	162
Time to temperature (min)	90
Time at maximum temperature (min)	60
Anthraquinone concentration, catalyst (%)	0.0, 0.05
Bath ratio	1:3

ANALYSIS OF BLACK LIQUOR

For the purpose of determining the pH (IS:3025 Part11), residual alkali content (IS:3025 Part15), and total solids (IS:3025 Part15) of the black fluid that had been isolated from pulp, Indian Standard procedures were used. For the purpose of determining the optimal pulping conditions, the physical features of pulps that were produced in a variety of cookers, pulp yield (Young, 1997), kappa number, and black liquor analysis (T 650 om-99 and T 625 cm-85) were used. These were the results of the experimental settings. For the purpose of bleaching research, a pulp with a kappa number of around 15 was used.

DATA ANALYSIS

THE CHEMICAL COMPOSITION

Eucalyptus hardwood

The composition of eucalyptus hardwood was analysed, and it was found that its holocellulose content was about similar to that of other raw materials generated from wood, notably hardwoods. This was revealed when the eucalyptus hardwood was analysed. According to the findings of the study, the holocellulose content of eucalyptus hardwood was determined to be $66.4 \pm 0.18\%$. This value is pretty comparable to the findings of prior studies and is presented accordingly in Table. The amount of hemicelluloses found in the eucalyptus hardwood was significant, with pentosans accounting for 27.3% with a standard deviation of 0.36%. The presence of hemicelluloses, which increases the properties of paper, is responsible for the enhancement of the capacity to produce H-bonds (Gautam et al., 2001). The pulp and paper industry can benefit from eucalyptus hardwood as an alternative source of wood since it has a high percentage of cellulose and hemicellulose. In comparison to both hardwoods and softwoods, the lignin content of eucalyptus hardwood was found to be lower, measuring at $13.0 \pm 0.07\%$. In addition to this, Shao et al. (2002) found that the pulping process necessitates the use of chemicals and low cooking temperatures. Because of these advantages and the scarcity of resources found in forests, eucalyptus hardwood is indisputably more ecologically friendly than other materials. The eucalyptus hardwood, which is mostly composed of silica

International Advance Journal of Engineering, Science and Management (IAJESM)
 ISSN -2393-8048, **January-June 2015**, Submitted in February 2015, iajesm2014@gmail.com
 (11.7%), has a greater quantity of ash (12.6%) than other types of straw. After careful investigation, it was found that 12.9% of the total extractive content of the eucalyptus hardwood. Material that has not been treated is protected against a variety of microbiological dangers by these extractives.

Table: Proximate chemical analysis of eucalyptus hardwood raw material

Components	Present Study	Rodriguez et al., 2003	Sridach, 2004	Singh et al.,
a- cellulose (%)	49.3 ±0.47	41.2	28-36	39.0 ±0.05
Holocellulose (%)	73.5 ±0.18	60.7		
Pentosans (%)	24.2 ±0.36	-	23-28	21.6± 0.5
Hot water extractives	1.2 ±0.30	-	7.30	-
Acetone extractives (%)	2.431±0.36	-	-	-
Lignin (%)	20.5 ±0.07	21.9	12-16	16.2 ±0.3
Ash (%)	0.95 ±.11	15.1	15-20	18.0±1.1

Characterstics of raw material

Upon doing a chemical examination, it was discovered that the holocellulose content of hardwood pulp was 73.5±0.16%. This value is about equivalent to the holocellulose percentage of other raw materials obtained from wood, such as hardwoods and softwoods, as reported by Khattak and Ghazi et al. in 2001 and Wanger et al. in 2001. A total of 24.2±0.25% of the hardwood pulp was composed of pentosans. According to the data shown in Table, the composition of hardwood pulp demonstrated a significant proportion of cellulose (49.3±0.9%) and hemicelluloses (24.2±0.7%), which makes it an appealing alternative to wood for the pulp and paper industry. Based on the findings of Jakate et al. (1981), it was discovered that the concentration of lignin in hardwood pulp was 19.2±0.09%. This concentration was found to be lower than the concentrations found in hardwoods and softwoods. As a consequence of this, the pulping process does not require the use of harsh cooking temperatures or chemicals. In light of these advantages and the decline of forest resources, hardwood pulp could wind up being more environmentally beneficial than it was previously thought. The amount of ash that was present in hardwood pulp was higher (0.95%), and the majority of it was composed of silica (0.07%). When hardwood pulp was compared to other cereal straws, notably eucalyptus hardwood, it was discovered that hardwood pulp had a lower ash content than the other straws. The combination of pulp from various wood suppliers is something that paper mills really wish to use because of this reason.

Table: Proximate chemical analysis of hardwood pulp raw material

	Present Study	Lal et al., 2001	Sridach, 2002	Kasmani and Samariha, 2003	Plazonic et al., 2004
Cellulose (%)	34.2±0.9	41.2	29-35	49.8	31.4
Holocellulose (%)	67.3±0.16 (ash free)	74	-	55.4±6.8	-
Pentosans (%)	29.2±0.5	19.8	26-32	-	-
Hot water extractives (%)	13.0±0.20	-	12.3	4.9	-
Solvent extractives (%)	3.47±0.27	2.8	4.0	-	3.0±0.57
Lignin (%)	14.9±0.09 (ash free)	19.9	16-21	19.6	24.7±1.63

Ash (%)	9.2±0.2	5.7	4-9	5.3	9.3±0.03
---------	----------------	-----	-----	-----	----------

Dosage optimisation for chlorine dioxide

As part of the process of optimising the dosage of chlorine dioxide for the sequences CD₅₀EOPD and DEOPD, a dose range of 0.3% to 1.2% of chlorine dioxide was applied to the pulp on an o.d. weight basis. As can be seen in Figure, the final D stage was determined to be the best dosage of 0.9% chlorine dioxide in each of the sequences.

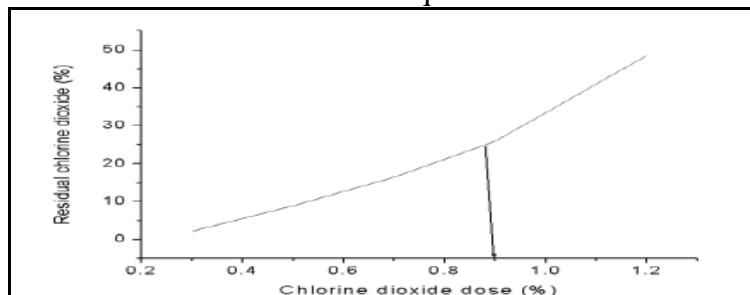


Figure: Optimization of chlorine dioxide dose at D1 stage

When the dose was raised to a level that was larger than 0.9%, a brightness ceiling was seen in the bleaching effluent. This was due to the presence of a higher residual chlorine dioxide content.

Improvements in time management during the oxygen stage

Before the eucalyptus hardwood was bleached using the ECF method, the oxygen (O) step was introduced beforehand. It is beneficial to employ O stage because it reduces the quantity of effluent and the number of toxic chemicals that are used. The original kappa number of the pulp that had not been bleached was 16.4. During the O stage, the only thing that was investigated was the impact that time had on the characteristics of the pulp and paper, and the selected length for the bulk trials was determined by the characteristics that were obtained. By boiling eucalyptus hardwood pulp for sixty minutes with about two percent of the alkali dose, a kappa reduction of twenty-two percent was achieved. Furthermore, according to Rolf et al. (2005), oxygen bleaching is gradually being implemented in non-wood fibre lines, which enables a reduction in kappa values of between 30 and 50 percent. It was determined that a reduction of 29% in the kappa number could be achieved by using the extended O stage for a period of ninety minutes in order to increase the reduction rate. The findings of the experiment conducted by Dutt and colleagues (2004) revealed that the O stage pretreatment that took place during bleaching resulted in a decline in kappa of 55%.

Thomas et al. in 2000 likewise reported the larger results for kappa decrease in the case of bamboo after they had conducted their research. It was discovered that the percentage drop for eucalyptus hardwood at both temperatures was lower when compared to the reductions that were reported by other researches for hardwoods, softwoods, and other agricultural wastes. The pulp shrunk by seven percent after the O stage, which is evidence that the O stage had an effect on the amount of cellulosic material present in the pulp. Yacoob et al. (2002) shown, through their research on hardwood pulp that the breakdown of carbohydrates results in a decrease in pulp yield that occurs after the O stage.

Impact of adding ozone stage before ECF

Incorporating Z stage prior to ECF bleaching results in an improvement in the optical properties of the pulp. The Z-based sequences ZDEOPD and ZDP were able to achieve a brightness of around 85%, which was higher than the brightness that was achieved by the conventional bleaching approaches CEOPHH and DEOPD. Liebergott (1982) conducted a study in which he found that bleaching kraft hardwood pulp with a kappa number of 14.5 using the ZDED sequence resulted in a brightness of 90%. This brightness was significantly higher than the brightness that was achieved for eucalyptus hardwood in the current inquiry. Furthermore, it was demonstrated that bleaching agents such as calcium hypochlorite and elemental chlorine were more efficient in bleaching eucalyptus hardwood pulp than chlorine dioxide bleaching. Despite this, the efficacy of this sequence was improved by the inclusion of Z at the beginning

International Advance Journal of Engineering, Science and Management (IAJESM)
 ISSN -2393-8048, **Juanuary-June 2015**, Submitted in February 2015, iajesm2014@gmail.com
 of the DEOPD process. Research on hardwood and softwood that was carried out by Marlin et al. (2000) and Vilve et al. (2004) produced results that were found to be in agreement with the findings of the study. In a similar manner, Lachenal et al. (2005) executed the ozone stage prior to the DEDD bleaching process and eventually achieved a brightness of 89.7%. Furthermore, the whiteness of the pulp was improved during the ZDP (78.2) and ZDE_{OPD} (80.4) phases of the process. There was a reduction in the yellowness of the pulp when the ZDE_{OPD} and ZDP sequence was compared to the CEOPHH and DEOPD sequence. There are several different optical properties of pulp after bleaching, which are listed in Table Below.

Table: Optical pulp properties of Z based bleaching sequences

Parameters	ZDE _{OPD}	ZDP
Brightness (% ISO)	89.5±0.2	86.7±0.1
Opacity (%)	83.6±0.1	80.3±0.2
L*	96.7	94.6
a*	-0.12	-0.08
b*	1.9	2.2
Whiteness	80.4±0.5	78.2±0.4
Yellowness	3.7±0.04	4.4±0.05

SEM ANALYSIS OF EUCALYPTUS HARDWOOD BLEACHED PUMP HANDSHEETS

At a magnification of 2500X, scanning electron micrographs of many bleached pulp samples were taken into account. The purpose of this was to assess how the surface morphology of the handsheets was altered by the various bleaching sequences. As can be seen in Figure the fibre matrix was the root cause of the uneven surface morphology that was seen on all of the bleached handsheets. In addition to having a substantial influence on the strength of the fibres, the processes of pulping and bleaching are processes that are associated with delignification. This was illustrated in the section that was presented earlier. It is important to note that bleaching chemicals have a major impact on the final shape and structure of the fibre. The SEM photo of the DEOPD sequence, which can be found in Figure, exhibited the least degree of damage to the fibre matrix. It has been demonstrated in a number of studies that chlorine dioxide possesses a high selectivity for the removal of lignin while simultaneously preserving carbohydrates during the bleaching process (Kumar et al., 2005; Karim et al., 2001). Following the CEOPHH sequence, which displayed the greatest amount of fibre deformation and had the highest fibrillation, the ozone-based sequences ZDEOPD and ZDP presented the next highest levels of fibrillation. Additionally, these findings are in agreement with the results that were obtained for viscosity and physical strength, Considering that elemental chlorine does not have a special affinity for lignin, it caused damage to the fibre matrix. This is the reason why the sequences that are based on elemental chlorine's low strength and viscosity occurred. For the reason that the viscosity of the two ozone-based sequences was almost same, it is fair to assume that the fibre structure will also be comparable. This can be observed in the scanning electron microscopy (SEM) pictures for ZDP and ZDEOPD that are exhibited in Figure. Additionally, the incorporation of the O stage had a little bit of an effect on the structure of the fibre. Although there was some fibrillation of the fibres in the SEM picture of the ODEOPD sequence, it was not nearly as severe as the fibrillation that was seen in the sequences that were based on ozone and elemental chlorine. Considering that the process of fibre fibrillation takes place at high temperatures, it is not surprising that hot chlorine dioxide did not have any negative impacts on the fibre matrix. This sequence was shown to be the most protective for fibres in the SEM photos, followed by ODEOPD > DHTEOPD > ZDEOPD > ZDP > CEOPHH. The DEOPD sequence was found to be the most protective.

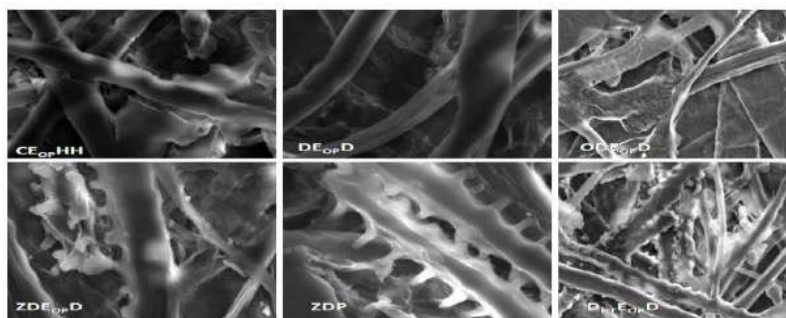


Figure: SEM images of the handsheets after bleaching of eucalyptus hardwood pulp at 1000X magnification

RESIN AND FATTY ACIDS AFFECTED BY MODIFICATIONS TO THE BLEACHING PROCESS DURING EUCALYPTUS HARDWOOD PULP BLEACHING

Both the pulping and bleaching processes, as well as the drying process, are significantly influenced by the extractives, which are a vital component of the wood. The resin and free fatty acids that are found in wood are an essential component of the total extractives that are found in wood. This is because they protect the wood from a variety of insets and microbial assault. Lipophilic tricyclic diterpenes with a low molecular weight are what we are talking about here. Abietanes and pimaranes are the two groups that make up these resin acids, which are more dangerous than free fatty acids while being classified as such. There is a significant relationship between the kind of wood species and the origin of the fatty acids and resin that are found in the effluent of the bleach plant.

According to Sharma et al. (1996), the pulping process and washing of unbleached pulp are additional factors that have an impact on the emission of these acids in the effluent of bleach facilities. According to Valto et al. (2002), the structure that consists of a hydrophobic skeleton and a hydrophilic carboxyl unit is made up of the resin acids. The presence of resin acids, which have this sort of structure, makes them good soluble agents and is the source of the toxicity that wastewater possesses.

There are a number of different chemical transformations that resin acids can undergo throughout the process of bleaching pulp. These transformations include isomerization, dehydrogenation, oxidation, and abiotic chlorination. The extractives in question are known to produce sublethal toxicity as well as genetic defects in aquatic organisms, as stated by Belmonte et al. (2005). According to Makris and Banerjee (2002), these resins and fatty acids are responsible for approximately 70 percent of the total toxicity that may be attributed to bleaching effluents. Dehydroabietic and abietic acids are the two types of resin acids that are frequently found in fish tissue. Fish tissue has a strong tendency to accumulate resin acids. According to Sitholé et al. (2000), extractives has the ability to influence the quality of pulp and paper, in addition to the toxicity of effluent, when they are present in pulp. Because of this, it became abundantly evident that these compounds required to be eliminated from bleaching effluents within a short amount of time and under periodic monitoring.

Impact of different bleaching sequences on fatty acids, both saturated and unsaturated

In order to construct the composite effluent, the effluent from each stage was collected and blended according to volume. This composite effluent was then put through GC-FID analysis in order to do an analysis of the resin and fatty acids that were present in the bleaching effluent. The retention duration, response factor, and fatty acid concentration of the effluent of the different bleaching sequences are presented in Tables respectively. It has been demonstrated by Lee et al. (2005) that the etherification of fatty acid esters may be accomplished rather well by the use of acid catalysis in methanol. As part of the GC analysis of fatty acids, the standard, which consisted of 37 methyl esters of fatty acids, was passed through the apparatus. Nevertheless, palmitic acid, oleic acid, stearic acid, and linoleic acid were the only four of these acids that were discovered in any of the samples. In addition, the presence of palmitic, linoleic, and oleic acid was discovered in research that was conducted on the extraction and

characterization of cereal straws (rice and wheat) as well as other non-woody species (Osman et al., 1998; Xiao et al., 2001; Sun and Sun, 2001). Silverio et al. (1997) found that the non-hydrolyzed and hydrolyzed dichloromethane extracts of eucalyptus contain sufficient amounts of palmitic, oleic, and linoleic acid. This was observed after their examination into the extractives found in eucalyptus materials. Bleaching with chlorine dioxide was discovered to quickly oxidise unsaturated acids that are present in hardwood, such as oleic, stearic, and linoleic acids, as stated by Freiere et al. (1996). Following their extraction from pulp, these fatty acids are then added to the effluent that is used for bleaching. Figures illustrate the percentage decrease in these items as compared to the previous values.

CONCLUSION

The addition of ozone stage led to a significant decrease of 58% and 63% in the total solids that were present in the wastewater used for bleaching. Compared to chlorine bleaching, Z-based bleaching was able to achieve a reduction of more than 80 percent in biological oxygen demand (BOD), chemical oxygen demand (COD), and adsorbable organic halides. In the effluents of Z-based bleaching sequences, the quantity of chlorophenols, guaiacols, catechols, vanillins, and syringols decreased to the point where they were no longer detectable (a reduction of around 90 percent). Over the course of the research, the traditional chlorine dioxide (D0) bleaching procedure was altered to include hot chlorine dioxide (DHT) in order to achieve the objective of lowering the effluent load, with a particular focus on chlorolignin compounds. Chlorophenols, chlorocatechols, chloroguaiacols, chlorovanillins, chlorosyringols, and bromophenols were all decreased by 9%, 50%, 34%, 47%, 17%, and 31%, respectively, when presented with a DHT-based sequence at the same amount of chemicals. The general environmental characteristics, such as COD, BOD, TS, colour, lignin, and AOX, were also lowered in the sequence that was based on DHT. During the bleaching process, a completely natural product based on microorganisms was introduced to the chlorination and extraction stages. For the chlorination stage, the optimal product dosage was determined to be 50 g/t, whereas for the extraction stage, it was discovered to be 150 g/t. After the extraction stage, the kappa number was determined to be 1.5 and 1.9, respectively, following the chlorine and dioxide sequence. This was a lower value than the kappa number that would have been obtained without the use of this product treated pulp. It was discovered that the brightness of the product added sequences was of 86.3% and 83.4%, which was greater than the brightness of the control bleaching. Because the tear index of the chlorine-based sequence with this product was (5.5 mNm²/g), which was greater than the tear index for the control pulp, it can be concluded that the inclusion of this product safeguarded the pulp from destruction. With the addition of this product, the effluents had a small reduction in both their colour and their lignin concentration. The use of agricultural waste as a raw material for the production of paper is a strategy that has the potential to be beneficial in terms of waste utilisation, pollution management, and the promotion of sustainable development in the industrial sector. It is possible that the technological advancements made during the early stage of bleaching, which are aimed at reducing the load of wastewater, would also put less strain on end-of-pipe technologies for waste water treatment.

PRESENT STUDY FOLLOWING CONCLUSIONS CAN BE DRAWN:

- a) The material that was created of hardwood eucalyptus had properties that were suitable for papermaking, and the transformation of this material into pulp and paper might be beneficial to manufacturers, farmers, and the environment. The results of the proximate chemical analysis verified this.
- b) The soda and soda-AQ processes both produced pulps with fine pulp qualities; however, the soda-AQ process performed better than the soda pulping technique in terms of delignification, kappa number reduction, and high yield on the material. The yield, viscosity, and other strength properties of the eucalyptus hardwood pulp were negatively impacted by the rise in temperature and the length of time that was used.
- c) It was found that the optimal pulping parameters were a concentration of 12% alkali, a cooking time of twenty minutes, a temperature of 155 degrees Celsius, and a 0.05% air quality.

- d) In terms of enhancing the bleached pulps' physical features and reducing the pollutant load of the bleaching effluents, it was found that the elemental chlorine-free bleaching sequence performed better than the other bleaching sequences.
- e) It was shown that the effluents produced by the ECF bleaching sequence had the capacity to reduce the BOD and COD by up to 48 percent, in addition to reducing the colour value by up to 55 percent. This discovery provided evidence in favour of the use of this method by paper mills.
- f) When compared to CEOPHH, the DEOPD sequence achieved a significant 66% reduction in the amount of toxic and carcinogenic AOX.
- g) It was discovered that the CEOPHH bleaching sequence provided the highest levels of chlorophenolic compounds, making it the least effective bleaching method for eucalyptus hardwood pulp.

BIBLIOGRAPHY

- [1] Brink, A., Sheridan, C., & Harding, K. (2003). Combined biological and advance oxidation processes for paper and pulp effluent treatment. *South African Journal of Chemical Engineering*, 25, 116-122.
- [2] Buzzini, A. P., Gianotti, E. P., & Pires, E. C. (2005). UASB performance for bleached and unbleached kraft pulp synthetic wastewater treatment. *Chemosphere*, 59(1), 55-61.
- [3] Carre, G., & Wennerström, M. (2005). Ozone bleaching—an established technology. *IPBC, Stockholm*, 144-149.
- [4] Casado, A. G., Hernández, E. A., & Vilchez, J. L. (1998). Determination of fatty acids (C8–C22) in urban wastewater by GC-MS. *Water Research*, 32(10), 3168-3172.
- [5] Casella, V. M., & Fong, R. A. (1986). U.S. Patent No. 4,613,332. Washington, DC: U.S. Patent and Trademark Office.
- [6] Catalkaya, E. C., & Kargi, F. (2004). Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study. *Journal of Hazardous Materials*, 139(2), 244-253.
- [7] Central Pulp & Paper Research Institute. (2004). Current Awareness Services Bimonthly Publication of Central Pulp & Paper Research Institute. 10 (3).
- [8] Chakrabarti S.K., Bhardwaj N.K., Roy M., Chandra S., Kumar S., Singh S., Bajpai P.K. & Jauhan M.B (1999) Organochlorines in bamboo pulp bleaching - Indian scenario. The 6TH IAWQ symposium on forest industry wastewaters. Tampere. Finland June 6-10, 1999: 39.
- [9] Chandra, R., & Kumar, V. (2002). Detection of androgenic-mutagenic compounds and potential autochthonous bacterial communities during in situ bioremediation of post-methanated distillery sludge. *Frontiers in Microbiology*, 8, 887.
- [10] Chen, X., Yu, J., Zhang, Z., & Lu, C. (2003). Study on structure and thermal stability properties of cellulose fibers from rice straw. *Carbohydrate Polymers*, 85(1), 245-250.
- [11] Chowdhury, S. A., Majid, M. A., Huque, K. S., Islam, M., & Rahman, M. M. (1995). Effect of variety on yield and nutritive value of rice straw. *Asian-Australasian Journal of Animal Sciences*, 8(4), 329-335.
- [12] Colodette, J. L., Gomide, J. L., Júnior, D. L., & Gomes, C. M. (2003). Effect of pulp delignification degree on fiber line performance and bleaching effluent load. *BioResources*, 2(2), 223-234.
- [13] Conde, E., Fang, W., Hemming, J., Willför, S., Moure, A., Domínguez, H., & Parajó, J.C. (2001). Water-soluble components of Pinus pinaster wood. *BioResources*, 8(2), 2047-2063.
- [14] Confederation of Paper Industry. (2000). Fact Sheet: Environmental aspect of ECF and TCF chemical wood pulp bleaching, www.paper.org.uk, March 2000 as accessed on 07.06.2000.
- [15] Davies, D., Dietz, T., & Suess, H. U. (2005). A comparison of options to improve brightness stability of chemical pulp. *Pulp and Paper Canada*, 110(8), 25-31.