Prepublished copy

Nature Environment & Pollution Technology

This is a peer-reviewed prepublished version of the paper to be published in Vol. 25, No. 4, December 2026 issue

Physicochemical Characterization of Pulp and Black Liquor Derived from Corn Husk and Coir Blends

Madhuri Pydimalla[1], Shrinidhi Tavag[1], Surya Tej Valluri[1], Nukala Mohith Satya Vardhan[1] and A. V. Raghavendra Rao[2]†

[1]Department of Chemical Engineering, Chaitanya Bharathi Institute of Technology, Hyderabad 500075, Telangana, India

[2]Department of Chemical Engineering, B. V. Raju Institute of Technology, Narsapur, Medak -502313, Telangana, India

†Corresponding author: A. V. Raghavendra Rao; raghusrf@gmail.com

Madhuri Pydimalla1[0000-0003-3243-8691], Shrinidhi Tavag1[0009-0003-1560-4827], Surya Tej Valluri1[0009-0009-1321-663X], Nukala Mohith Satya Vardhan1[0009-0008-3156-194X], A. V. Raghavendra Rao2[0000-0002-6064-505X]

Key Words	Kraft cooking, Bleaching, Black liquor, Water retention value, Agrowaste biomass, Corn husk, Coconut coir, Kraft pulping
DOI	https://doi.org/10.46488/NEPT.2026.v25i04.B4427 (DOI will be active only after the final publication of the paper)
Citation for the Paper	Madhuri Pydimalla, Shrinidhi Tavag, Surya Tej Valluri, Nukala Mohith Satya Vardhan and A. V. Raghavendra Rao, 2026. Physicochemical characterization of pulp and black liquor de-rived from corn husk and coir blends. *Nature Environment and Pollution Technology*, 25(4), B4427. https://doi.org/10.46488/NEPT.2026.v25i04.B4427

ABSTRACT

The current research work examines the suitability of agrowaste biomass blend i.e corn husk and coconut coir for production of sustainable pulp using kraft pulping and Elemental Chlorine-Free (ECF) bleaching. An equal amount of oven-dried corn husk and coir (1:1 w/w) was pre-treated by steam at 120ºC 1 hour and then kraft pulped in a batch reactor at 80 °C for 2 hours with white liquor (NaOH and Na_2S) in a 1:18 solid-to-liquid ratio. The unbleached pulp with a yield of 38.7% was bleached with hydrogen peroxide (1:10 (w/v) pulp-to-peroxide ratio) at 60 °C over 1 hour. The properties of unbleached and bleached pulps were determined using Fourier Transform Infrared Spectroscopy (FTIR) data, Water retention value (WRV), Cellulose content, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Thermogravimetric Analysis (TGA). The analysis of black liquor collected in the reactor, following pulping, was carried out with the help of UV-Visible spectrophotometer. Analysis of SEM showed a fibril-bound network in unbleached pulp to a more porous and fibrillated structure in bleached fibers. The elimination of lignin was established through FTIR spectra by reducing aromatic bands in the range of 1600 -1400 cm^{-1} range. The total cellulose percent is improved from 60.2 to 85.4 after bleaching. The Water retention value was also better, which showed increased swelling and porosity of the fiber. TGA showed thermal degradation peaks between 200–350°C in bleached pulp, indicating improved thermal stability. The UV-visible analysis of black liquor has shown considerable lignin peaks (Absorption-0.8 at wavelength 200-205 nm) which suggests considerable removal of lignin from wood cells. The findings confirm the viability of the employed pulping and bleaching regimes in the manufacture of fine quality, cellulose-based pulp to be utilized in the manufacture of environmental friendly material applications.

INTRODUCTION

Paper is a nonwoven sheet made of pulp fibers that are 0.25 to 4.5 mm in length and 10 to 50 μm in width (Pydimalla & Adusumalli 2020). They are interwoven to form a three-dimensional matrix. The use of paper products is often taken as an index of the educational advancement of a country. Paper is essential for many elements of modern life, including communication and knowledge distribution. There are now roughly 759 pulp and paper manufacturing plants worldwide, with India accounting for around 4% of global paper output, ranking 15th (Pydimalla et al. 2020). Projections suggest that India's paper consumption will reach 23.51 million tonnes per year by 2030 (Van and Stegemann 2016). India's paper mills are mostly concentrated in Andhra Pradesh, Telangana, Tamil Nadu, Maharashtra, Punjab, Madhya Pradesh, and Gujarat. The raw materials employed in the manufacture of paper differ according to the region. For instance, subabul wood is used in Andhra Pradesh mills, bagasse of seasonal crops in Karnataka mills, and wheat straw in Punjab mills. Recycled paper is also commonly used to generate various paper grades. The paper business is typically classified into four major categories: printing and writing (P&W), packaging paper and board, speciality papers and newsprint (Dutt 2013). Within these categories, the pulp and paper industry produces a wide range of paper types, including printing and writing sheets, packaging boards, corrugated materials, newspaper, and tissue paper. Writing and printing papers account for around 26% of global paper output. Packaging-related items, such as corrugated board and paperboard, make up the majority of the market, accounting for around 51% (Furszyfer Del Rio et al. 2022). Meanwhile, newsprint and tissue paper account for around 7% and 8% of worldwide output, respectively.

Fibers, which are the primary raw material for paper production, are elongated, hollow, non-living plant cells that consist mainly of lignocellulosic biomass (Smook 2002). These plant-based fibers are crucial in the making of paper, which is widely utilized in a variety of human activities. Chemically, a typical fibers is composed of around 40-50% cellulose, 25-30% hemicellulose, 25-35% lignin, and a tiny fraction (1-5% extractives) (Rowell RM 2012). Cellulose is the structural backbone of the fibers and has a significant impact on the mechanical strength and bonding capability of paper. It is a linear polymer comprised of β-D-glucose units. The intermolecular hydrogen bonding between cellulose chains across neighboring fibers is a significant element in creating fibers-to-fibers adhesion inside the paper matrix (Wohlert et al. 2022). Hemicellulose is the second most prevalent carbohydrate found in wood fibers. Unlike cellulose, it is made up of branching chains of several sugars, including glucose, xylose, and mannose. These shorter chains help greatly to paper making by improving the fibers's water retention and swelling capabilities, which aids fibers bonding during sheet creation (Pere et al. 2019). Lignin, the third main component, is a complex aromatic polymer that covalently bonds with cellulose and hemicellulose. It provides stiffness and mechanical integrity to the plant cell wall, especially in the secondary wall layers and middle lamella (Peracchi et al. 2024). Lignin works as a natural adhesive, binding cellulose microfibrils together and providing a protective barrier against environmental deterioration. However, its presence reduces paper strength as it prevents good fibers bonding. As a result, one of the fundamental goals

of pulp and paper manufacture, as well as viscose rayon production, is to minimize lignin content while maintaining the cellulose percentage.

The contemporary cellulose industry makes use of a wide range of fibrous raw materials derived from hardwoods (such as eucalyptus and subabul), softwoods, and non-wood species including bagasse, wheat straw, and rice straw. Both hardwood and softwood fibers are used as key raw materials in the manufacturing of paper and board goods (Karlsson 2006). In India, fast-growing hardwood species with short rotation cycles are often employed. Fiber length generally range from 0.2 to 4 mm, with cell wall thicknesses of 3-4 µm (Liu et al. 2024). One of the primary characteristics between hardwood and softwood is their chemical composition: hardwoods often have larger quantities of cellulose and hemicellulose, as well as lower lignin concentration than softwoods. This makes them more suited to pulping methods that prioritise higher yield and fibers bonding (Tarrés et al. 2023). With all these promises, the Indian paper sector faces numerous challenges, such as high cost of energy, limited technical development, environmental regulations and above all lack of good quality raw materials. The main obstacle is a poor accessibility to forest resources that are owned and controlled by the government. To counteract the shortage of raw materials, various paper manufacturers have promoted the practice of agro forestry, especially in those regions that are favorable to the fast growth of trees. The agricultural leftovers are a better substitute of wood-based fibers as asserted by industry observers due to their better environmental friendliness. The relatively porous cell wall structure enables them to be pulped faster under the same cooking temperatures producing pulp with the same quality (Worku et al. 2023). Consequently, the agricultural residues normally take less water, energy and chemicals to be digested (Gavrilescu 2008). The Indian pulp and paper industry is today receiving the fibrous materials in the form of wood (30-35%), agricultural wastes (20-22%) and recycled fibers (45-50%), which shows a balanced way of utilizing resources in accordance with environmental and economic demands.

In paper making, pulp fibers are derived either through mechanical or chemical pulping processes by using wood or non-wood. Pulping has a primary aim of releasing the individual fibers by dissolving the lignocellulosic matrix, particularly by removing lignin which is a naturally occurring glue that is present in the intermediate lamella (Manfredi 2024). The kraft process is the most widely applied chemical pulping method worldwide due to its ability to utilize a wide variety of raw materials and produce high-quality pulp. It also offers an efficient and time-tested way of reclaiming and reusing of pulping chemicals. The main active ingredients in the kraft process are a combination of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). By cleaving β-aryl ether bonds, which are among the most prevalent connections in lignin structure, this combination, sometimes referred to as white liquor, makes it easier to remove lignin selectively (Madhuri et al. 2016). Consequently, the lignin becomes soluble, releasing the cellulose fibers. In order to help with the delignification process, NaOH is also essential for neutralizing organic acids and interacting with resinous materials in the raw material.

The primary objective of bleaching is to remove residual lignin without degrading carbohydrate components, particularly cellulose. This preserves the pulp's strong qualities while also improving its brightness. Removal of residual lignin during bleaching is regarded as a continuation of pulping process but it is done in a gentler way (Bajpai 2012). In chemically pulped fibers, the residual lignin is usually more condensed, with a larger percentage of carbon-carbon and lignin-carbohydrate connections and less β-O-4 ether bonds (Britt 1970). Bleaching, which targets the lignin fractions left over after initial delignification, is frequently seen as an extension of the pulping process. Although reductive techniques are occasionally used, oxidative processes remain the mainstay of chemical bleaching (Gellerstedt 2003). In contemporary bleaching procedures, oxidizing chemicals including hydrogen peroxide (P), chlorine dioxide (C), oxygen (O), and ozone (Z) are frequently utilized. By providing hydrophilic functional groups and encouraging lignin breakdown through depolymerisation, these chemicals improve pulp's overall processing properties and increase pulp whiteness.

In the recent years, researchers have been paying increased attention to non-wood fibers as a sustainable paper making substitute (Pydimalla et al. 2019, El-Sayed et al. 2023, Nagaraka Ganesh et al. 2022, Das 2023). Agricultural residues such as maize stalks, bagasse, rice straw and wheat straw have been explored in terms of their pulping potential than traditional wood sources because they have reduced environmental impact and less energy requirement. Studies have indicated that non-wood fibers can be used to manufacture high-quality bleached pulp suitable for specialty papers. The efficiency and environmental friendliness of processing the non-wood material has been enhanced due to the improvement of the pulping process, including organic acid pulping and enzymatic treatment (Singh et al. 2025, Wang et al. 2022). Indicatively, research on maize stalks revealed that lignin could be effectively extracted by the caustic soda anthraquinone process with the generation of pulp with desirable tensile properties (Mishra et al. 2020). Moreover, the application of bast fibers like hemp and kenaf has been investigated, and it could potentially provide long-term and eco-friendly paper products (Austin et al. 2024). These trends underscore the possibility of the non-wood fibers in meeting the increasing demand of a green paper making.

There is still a large research gap in the assessment of the synergistic potential of mixed agricultural residues. Although there has been progress in the use of non-wood biomass for pulp production, most of the research is conducted on individual materials. Also, there is a limited focus on combined processing of fibrous materials with high percentage of cellulose like corn husk and coconut coir. The aim of the current research work is to determine whether a blend of coconut coir and corn husk which are two commonly available agricultural wastes can be utilized as alternative source of fibers to produce potential pulp for paper making. The research also aims at a systematic study of pulp and black liquor characteristics after cooking and bleaching. The pulp production and fibers quality and paper making suitability were assessed by use of Kraft pulping and Elemental Chlorine-Free (ECF) bleaching. This is a unique nature of the work as it promotes the efficient use of the mixed lignocellulosic wastes, which contributes to the development of the sustainable raw material alternatives. This plan enhances the principles of the circular economy, as well as solves the issue of fibers shortage in the paper industry. In this study, the pulping

conditions were selected as baseline laboratory parameters based on preliminary screening trials to enable effective fibers separation and detailed physicochemical characterization of the produced pulp and black liquor.

2. MATERIALS AND METHODS

Corn husk and coconut coir were obtained in Hyderabad, India in local markets. The raw materials were manually washed to take off the dust and other impurities. Corn husk was cut into small uniform pieces and coconut coir was sieved through a 100 mm mesh to get well-sized particles that can be used in pulping. The two materials were then dried in the oven at 103.5ºC until a constant weight is attained which confirms removal of moisture (Fig. 1). Sodium hydroxide (NaOH), sodium sulfide (Na_2S), acetic acid, nitric acid, ethanol, and hydrogen peroxide or (H_2O_2) are all chemicals of analytical grade and were purchased at Merck Specialties Pvt. Ltd. For pulping, dried corn husk and coconut coir (50 grams each) were mixed, in an equal proportion. The chosen cooking parameters (temperature, alkali charge, and cooking time) are mild laboratory-scale optimizations meant to minimize excessive carbohydrate degradation and achieve controlled delignification. Preliminary experimental trials were conducted to determine conditions that ensured adequate fiber separation and acceptable pulp yield. An equal ratio (1:1 w/w) of corn husk and coconut coir was chosen as the baseline formulation to investigate the synergistic pulping properties of a mixture of agricultural residues. Corn husk is comparatively richer in cellulose content and has lower lignin, which makes delignification easier, whereas coconut coir has higher lignin and is more fibrous. The equal mixture was chosen to provide a balanced ratio of both materials, allowing the assessment of their compatibility, uniformity of chemical saturation, and delignification properties. The equal ratio was chosen as a screening criterion for process feasibility prior to any future optimization work involving different ratios.

Fig. 1: (a) Corn husk; (b) Coconut coir

In order to improve chemical impregnation by removing any remaining moisture trapped in the chips, the dry raw materials were processed in an autoclave set at 120°C for one hour. Additionally, by partially eliminating low-molecular-weight organic extractives, this step improved the effectiveness of the pulping procedure that followed. The pulping experiments in this study were conducted at a laboratory scale to evaluate the feasibility of utilizing mixed agro-residues for pulp production and to investigate the physicochemical characteristics of the resulting pulp and black liquor. The processed biomass samples were fed into a batch reactor together with white liquor, which is made up of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), at a wood-to-

liquid ratio of 1:18. Active pulping was maintained for two hours and was conducted at a regulated temperature of 80 °C (Fig. 2). The kraft pulping temperature of 80 °C used in this study is a mild, laboratory-scale cooking condition. The objective was to facilitate controlled and progressive delignification of agro-residues with minimal cellulose degradation and fibers integrity. The pre-steaming process at 120 °C prior to pulping, improves fiber swelling, extractive removal, and chemical penetration, thus making delignification easier at lower cooking temperatures. Such low-temperature alkaline pulping conditions (around 70-100 °C) have been used in laboratory-scale experiments on non-wood lignocellulosic materials for selective delignification and fibers retention prior to bleaching or further processing (Rousu et al. 2002, Ververis et al. 2004).

After the cooking process, the delignified pulp samples were separated from the black liquor and thoroughly washed 4-5 times with deionized water to remove extractives and any residual black liquor adhering to the pulp fibers surfaces. The washed pulp was then dried in a hot air oven at 103.5°C for 12 hours until a constant weight was achieved. Thus, the pulp and black liquor obtained were characterized to analyze the amount of lignin present in black liquor and the amount of lignin remaining (residual lignin) in the pulp.

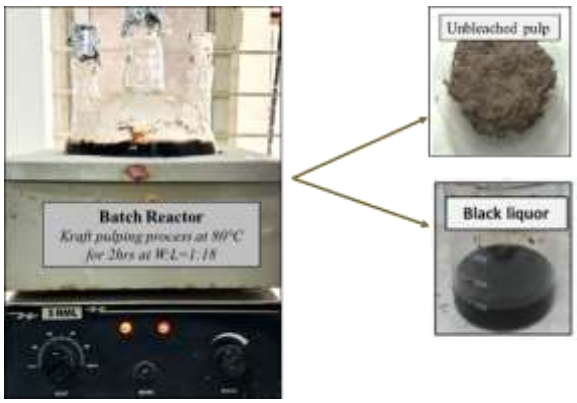

Fig. 2: Kraft pulping process in batch reactor produces unbleached pulp and black liquor

Following the preparation and analysis of the unbleached pulp, the bleaching process was conducted using hydrogen peroxide as an ECF bleaching agent. A known quantity of pulp was placed in a beaker and subjected to bleaching on a hot plate at 60 °C. Hydrogen peroxide was added in a 1:10 (w/v) pulp-to-peroxide ratio, and the mixture was maintained under constant temperature and occasional stirring for a duration of one hour (Fig. 3). Hydrogen peroxide oxidizes the remaining lignin, thereby increasing pulp brightness and reducing coloration. This method is more environmentally friendly than conventional chlorine-based bleaching, as hydrogen peroxide decomposes into non-toxic by-products, mainly water and oxygen. At the end of bleaching process, the pulp was filtered, dried in the oven to remove moisture content and a weight of the pulp was noted. The bleached pulp was further characterized and analyzed to assess the enhancement in fibers quality and optical aspects.

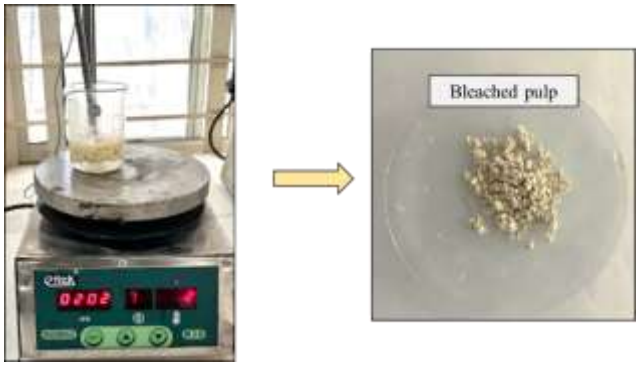

Fig. 3: Pulp bleaching process

The unbleached and bleached pulps were systematically characterized using Fourier Transform Infrared (FTIR) spectroscopy, Water Retention Value (WRV), Cellulose content analysis, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and Thermogravimetric Analysis (TGA) to evaluate their structural, chemical, and thermal properties. The black liquor recovered post-pulping was analyzed using UV-Visible spectrophotometry to determine the concentration of dissolved lignin and assess pulping efficiency.

3. RESULTS AND DISCUSSION

3.1. Pulp Yield

Fig. 4, displays digital photographs of unbleached and bleached pulps. The ECF bleaching process has a pronounced effect on fibers brightness, as shown in the figure. The images indicate the effectiveness of kraft cooking and ECF bleaching used to obtain the white colour pulp. Fig. 4(a), presents the image of oven-dried Kraft pulp obtained after the cooking process. In the mixed pulp cooked at 80 °C, clear separation of individual fibers is observed, indicating effective fibrillation. This suggests significant degradation of lignin in the middle lamella and cell wall, likely due to enhanced diffusion of white liquor through the pulp structure under temperature-driven diffusional conditions. The breakdown of lignin, especially in the compound middle lamella (CML), increases cell wall porosity, allowing deeper penetration of cooking chemicals into the fibers matrix (Kron et al. 2024). Fig. 4(b), shows the impact of ECF bleaching on pulp brightness. The bleaching chemicals target light-absorbing chromophoric groups in lignin, such as quinones. The white appearance of the bleached pulp indicates substantial removal of lignin fragments and non-cellulosic components like extractives. The images demonstrate the effectiveness of optimized Kraft pulping process followed by peroxide bleaching in producing high brightness white pulp.

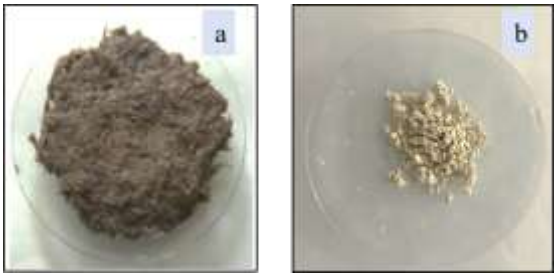

Fig. 4: (a) Unbleached pulp; (b) Bleached pulp

The pulp yield, which is the ratio between the quantity of unscreened pulp collected to the quantity of the steam pretreated wood spent in cooking process was observed to be 38.7% in case of unbleached pulp and 34.8% in case of bleached pulp. The dissolution of low molecular weight carbohydrates in the alkaline medium and peeling reactions are the main factors that cause yield loss during the kraft cooking (Knott B 2021). In the bleaching process, the treatment was successful in extracting chromophoric compounds and leftover lignin content on the cell walls, which resulted in higher levels of pulp brightness, higher cellulose content, and a slightly low pulp yield (Bajpai 2013).

3.2. Cellulose Content in Pulp

This test is used to determine the cellulose content remaining in the pulp after the cooking process. The process involves adding 15 mL of acetic acid and 1.5 mL of concentrated nitric acid to the samples, followed by refluxing for 20 minutes, as shown in Fig. 5a. The treated samples are then washed with ethanol, filtered using a cotton cloth, and dried in a hot air oven for 12 hours to obtain material A (Fig. 5b). Subsequently, the dried samples are incinerated in a muffle furnace at 525 °C until a constant weight is achieved, yielding material B (Madhuri et al. 2016) (Fig. 5c).

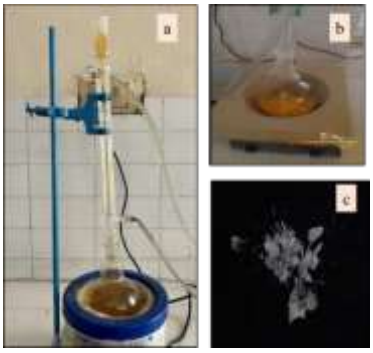

Fig. 5: (a) Cellulose isolation test; (b) Pulp sample during reflux; (c) Pulp after ash test

The cellulose content is calculated using following equation, and the results are presented in Table 1.

$$\%\ Cellulose = \frac{weight\ of\ material\ A - weight\ of\ material\ B}{Total\ weight\ of\ the\ sample}$$

Table 1. Cellulose content of pulp after pulping and bleaching.

Sample	Cellulose %
Raw material (corn husk+coir)	32.5
Unbleached pulp	60.2
Bleached pulp	85.4

The cellulose content (%) in both bleached and unbleached pulps is significantly higher than that of the raw material as shown in Table 1. This increase in total cellulose content from raw material to pulp is primarily attributed to the reduction in lignin content during the pulping process. During the pulping process, both lower and higher molecular weight lignin fractions particularly those associated with phenolic units in the middle lamella and secondary cell wall are dissolved, resulting in reduced residual lignin content and a higher cellulose percentage in the pulp fibers (Brännvall 2017). The bleached pulp, with minimal lignin content, exhibited an even higher cellulose percentage. This indicates the successful removal of extractives, acetyl groups, and uronic acids from hemicelluloses, as well as the degradation and dissolution of α- and β-aryl ether linkages in phenolic units located in the middle lamella and the primary and secondary cell wall regions (Santos 2013). Consequently, the relative cellulose level of the pulp fibers has further improved. The obtained pulp yield was 38.7%, while the cellulose content increased to 85.4% after bleaching. These values fall within the reported range for non-wood agro-residue pulps processed under mild kraft cooking conditions (Ververis et al. 2004, Rousu et al. 2002), thereby confirming the effectiveness of the applied delignification strategy.

3.3. Water Retention Value

Samples of 5 grams each from the raw material, unbleached pulp, and bleached pulp were analyzed for WRV using the following equation:

$$WRV = [(weight\ after\ centrifuge)/(weight\ after\ drying)] - 1$$

The wet samples were centrifuged at 2600 rpm and 23 °C for 15 minutes, followed by overnight drying in a hot air oven at 103.5 °C (TAPPI standard-UM 256).

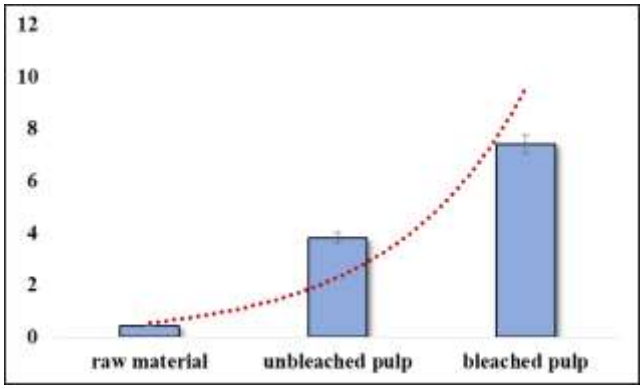

Fig. 6: Water Retention value of raw material (before cooking) and pulp (after cooking and bleaching)

An empirical measure of pulp fibers capacity to hold onto water, the WRV is often used to gauge the extent of fibers swelling. Because of its aromatic network structure, lignin is hydrophobic, which prevents it from absorbing water (Takada et al. 2020). Consequently, increased WRV is the result of more lignin elimination. Partial delignification in unbleached pulps causes more surface fibrillation and porosity at the fibers interfaces, which raises the WRV in comparison to the raw material (Fig. 6). Additional lignin removal in bleached pulps encourages internal fibrillation, which widens internal holes and results in cell wall delamination, a process known as "swelling" (Bian et al. 2016). This process is accompanied by the development of exterior fibrils, which further increases water retention. Therefore, bleached pulp has a much higher WRV than unbleached pulp due to its increased porosity, higher cellulose content, and lower levels of residual lignin and hydrophobic resins.

3.4. Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was used to measure the differences in the bleached and unbleached pulp samples and reveal different functional groups by emphasizing on the aromatic skeletal vibrations. In spectral analysis, the sample was dried and then finely ground followed by a mixture of the sample with potassium bromide (KBr) in the proportion of 1:100 (pulp: KBr) and made into thin pellets. The obtained absorbance bands were recorded for interpretation (Fig. 7). The absorption bands at the fingerprint area of 900-1800 cm^{-1} are related to different functional groups that are normally lignin-related. In particular, the bands between 1600–1400 cm^{-1} indicate aromatic or benzene rings present in the form of lignin (Pydimalla et al. 2019). The bands between 1300–1000 cm^{-1} is associated with CO vibrations of primary and secondary aliphatic alcohols in cellulose, hemicellulose and lignin, and aromatic alcohols in lignin. In both spectra, there are aromatic C-H in-plane deformations seen in the region of 1160, 1114, and 1055 cm^{-1} (Colom et al. 2003). Bands around 2130–2135 cm^{-1} correspond to C=C stretching vibrations, while peaks between 1470–1455 cm^{-1} indicate OH in-plane bending associated with cellulose. The presence of a wide absorption band within 3600–3200 cm^{-1} range is an indication of the hydroxyl (OH) groups in the unbleached and bleached pulp. Furthermore, an increase in the 2900–2800 cm^{-1} spectrum is ascribed to C-H stretching frequencies (Wong et al. 2023). The FTIR spectra show that bleached pulp has a higher percentage of transmittance than unbleached pulp, and this indicates a purer cellulose makeup. It is worth noting that the presence of a peak around 1430 cm^{-1} in the bleached pulp spectrum indicates crystalline regions of cellulose, and the band in the range of 1610–1640 cm^{-1} is the indicator of the moisture being absorbed in the cellulose matrix (Hospodarova et al. 2018).

The FTIR spectra of the Kraft unbleached pulp show clear peaks at 779 cm^{-1} and 673 cm^{-1} which represent aromatic C-H out-of-plane bending bands, indicating presence of residual lignin. These peaks are distinctly observed in the raw pulp spectrum but not in the bleached pulp which is a confirmation that the lignin has been removed during the bleaching process. Moreover, the unbleached pulp has a percentage of transmittance of 44% and the bleached pulp has 54% which indicates that functional groups that absorb light like lignin functional groups have been reduced.

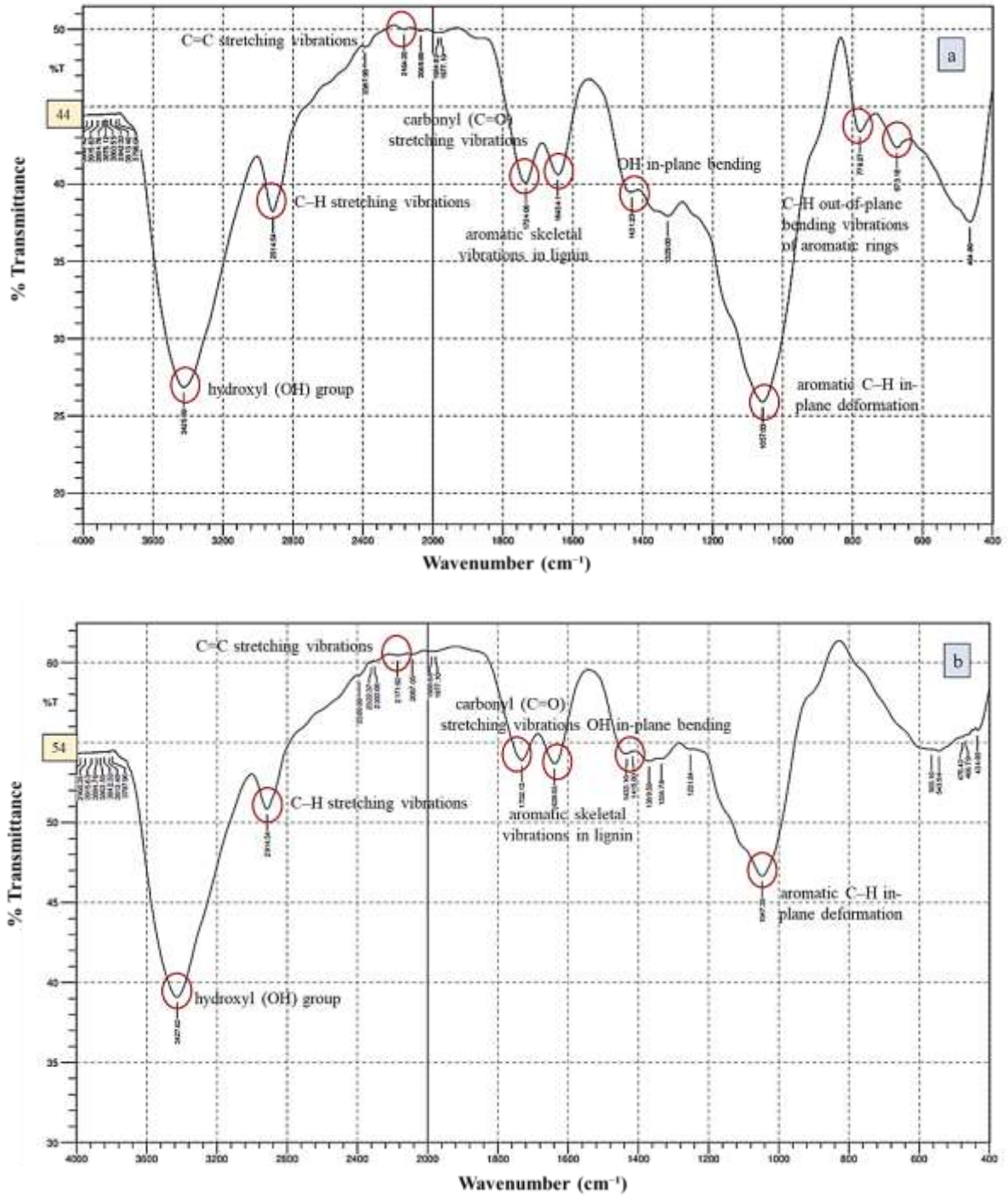

Fig. 7: FTIR analysis: (a) unbleached pulp; (b) bleached pulp

3.5. Thermogravimetric Analysis

Figure 8 illustrates the TGA curves of the pulp sample before (unbleached pulp) and after (bleached pulp) treatment. These curves were used to evaluate the thermal degradation behaviour of the pulp samples. Volatilization of low-molecular-weight organic extractives and evaporation of physically-adsorbed moisture are the cause of minor loss of weight in the unbleached pulp observed at temperatures below 100 °C (Pydimalla 2019). The peak degradation temperature (T_{max}) indicates that the main thermal degradation of bleached pulp occurred

between 200 °C and 350 °C. Conversely, the initial stage of break in the unbleached pulp is in the range of 250 °C to 300 °C. The thermal stability of composite structural units formed by lignin residues, which create complexes with polysaccharides in the cell wall matrix, may explain the weight loss pattern observed in the unbleached pulp (Zhao et al. 2020). Conversely, the loss of lignin and the absence of composite structure (including micron-scale pores that could potentially serve as thermal insulation during heat exposure) are the cause of the weight loss in bleached pulp.

Significant weight loss is observed between 200 °C and 400 °C, which is attributed to the degradation of hemicellulose, cellulose and lignin. The unbleached pulp exhibits a broader degradation region due to the presence of lignin and hemicellulose, whereas the bleached pulp shows a sharper degradation peak, indicating a relatively cellulose-rich structure after removal of non-cellulosic components. In general, the unbleached pulp has a greater amount of residual mass because of the thermally stable aromatic structure of lignin.

To facilitate the understanding of the degradation process, the peak decomposition temperature (T_{max}) was determined from thermogravimetric trends related to the maximum rate of degradation. The unbleached pulp had a wider degradation zone, signifying the presence of lignin and hemicellulose in addition to cellulose. However, the bleached pulp had a clearer and sharper degradation peak in the range of 200-350 °C, typical of cellulose-rich material. The appearance of a sharper T_{max} in the bleached sample indicates a better homogeneity of the material as a result of lignin and non-cellulosic matter removal during the bleaching process.

The unbleached pulp exhibited a slightly greater residual mass at elevated temperatures. This may be attributed to the presence of lignin residues, which are recognized for their slower degradation and broader temperature range for breakdown. The bleached pulp, on the other hand, lost weight more quickly in the main degradation area, which suggests that the cellulose was purer and the lignin content was lower.

Thermal degradation behaviour of the bleached and unbleached pulp was monitored in the temperature range of 380–600 °C. Kraft pulping and subsequent bleaching partially remove lignin and hemicellulose from the lignocellulosic matrix, resulting in fibers with relatively higher cellulose content (Kron et al. 2025). Consequently, the bleached pulp exhibits a slightly shifted degradation profile compared to unbleached pulp. This behaviour may be attributed to compositional changes and fibers purification during pulping and bleaching. Similar modifications in thermal degradation patterns of chemically treated lignocellulosic fibers have been reported in previous studies, where removal of amorphous components alters the thermal decomposition characteristics of cellulose-rich materials.

Thermal stability of bleached and unbleached pulp was monitored between 380 °C to 600 °C. The kraft pulping and subsequent bleaching processes has led to the degradation of amorphous lignin matrix, initially from the middle lamella and later from the cell walls, resulting in collapsed cellulose fibers with moderate

crystallinity (Kron et al. 2025). The bleached fibers exhibits a slightly shifted thermal degradation profile compared to unbleached fibers, which may be attributed to removal of hemicellulose and partial lignin during pulping and bleaching, resulting in a relatively higher cellulose content and altered degradation characteristics. Similar changes in thermal degradation profiles after chemical treatment of lignocellulosic fibers have been reported in previous studies, where removal of amorphous components influences the thermal decomposition behaviour of cellulose-rich materials. Overall, the TGA analysis indicates that structural changes caused by kraft cooking and bleaching significantly modify the thermal decomposition behaviour of the pulp, primarily due to compositional changes and the relatively higher cellulose content of the bleached fibers.

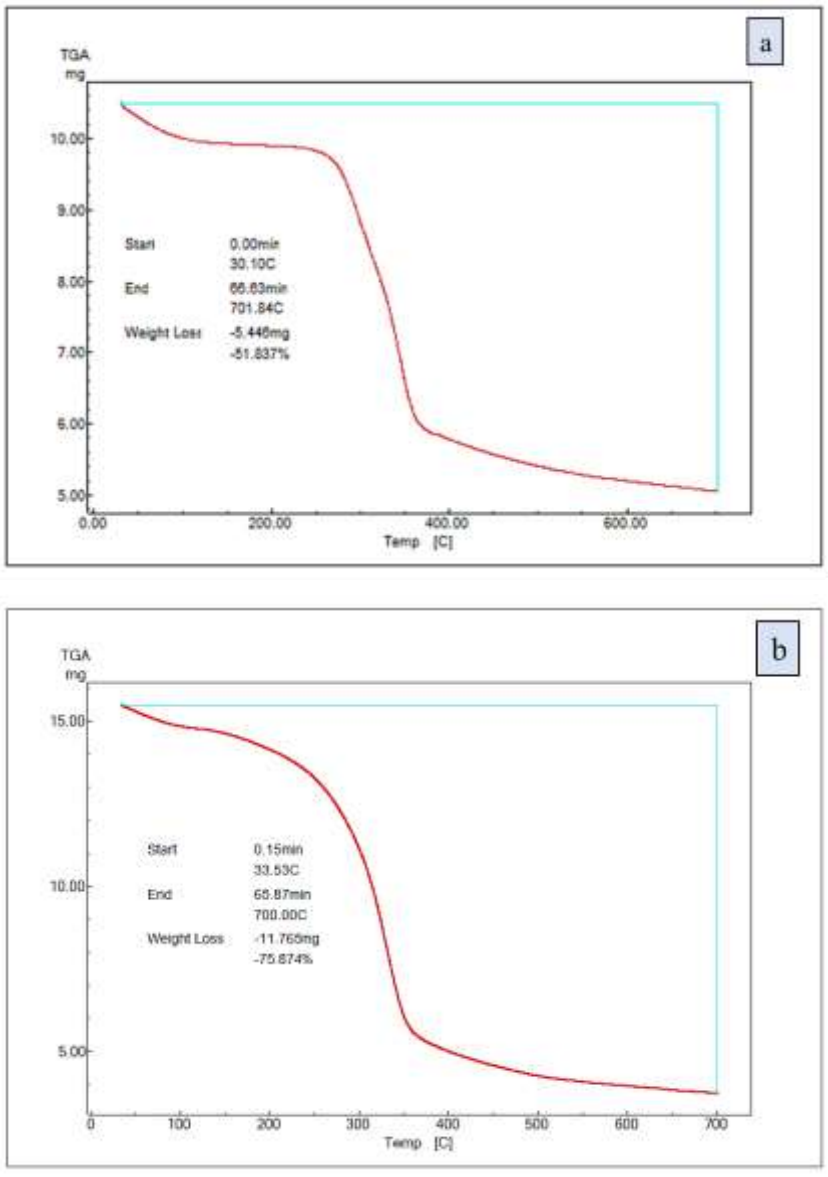

Fig. 8: TGA analysis: (a) unbleached pulp; (b) bleached pulp

3.6. Scanning Electron Microscopy

The SEM micrographs of unbleached and bleached pulp fibers are demonstrated in Fig. 9 and 10. The micrograph of the unbleached pulp (SEM) shows a thick and uneven fibers arrangement. The surface morphology is rough and has high fibrils and compact matrix. The fibers are less segregated and interwoven implying that there are remnant lignin and hemicellulose, which are binding agents. This kind of morphological compactness leads to decreased porosity and less fibers individualization.

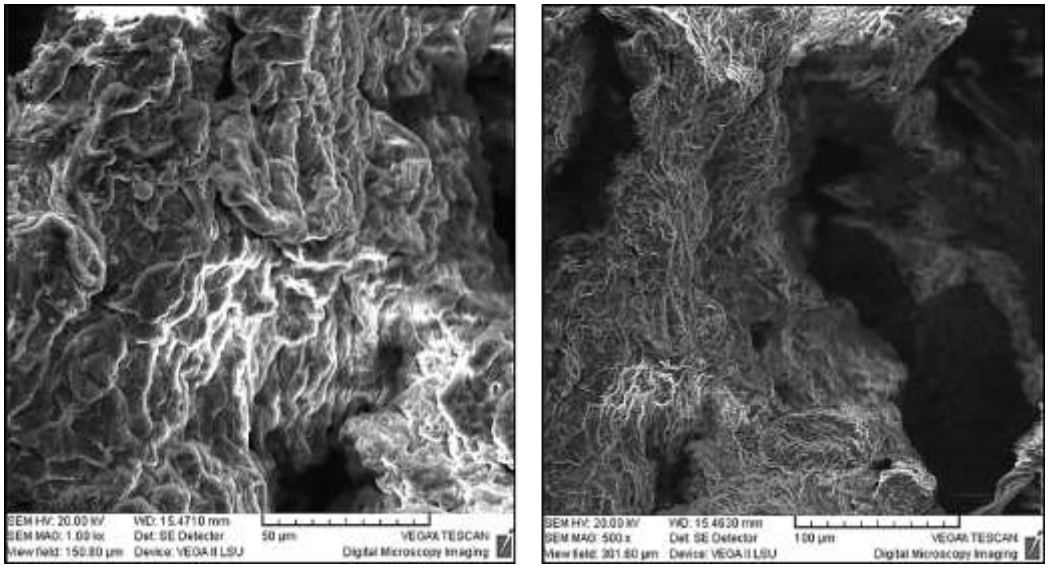

Fig. 9: SEM micrographs of unbleached pulp fibers

Conversely, the SEM image of bleached pulp has a comparatively loosened fibers structure with more visible and distinct fibrils. It is more smooth as well as the fibers are showing evidence of greater individualization because the lignin and other non-cellulosic compounds are removed in the bleaching. This morphology is desirable where good cellulose purity is needed, e.g. nanocellulose production or bioplastics. Thus, SEM characterization is a good indication of the microstructural alteration of the lignocellulosic fibers undergoing the bleaching process. The bleached pulp has a significantly refined structure that promotes the improved material development, but the unbleached pulp has natural structure and lacks liberation of fibers.

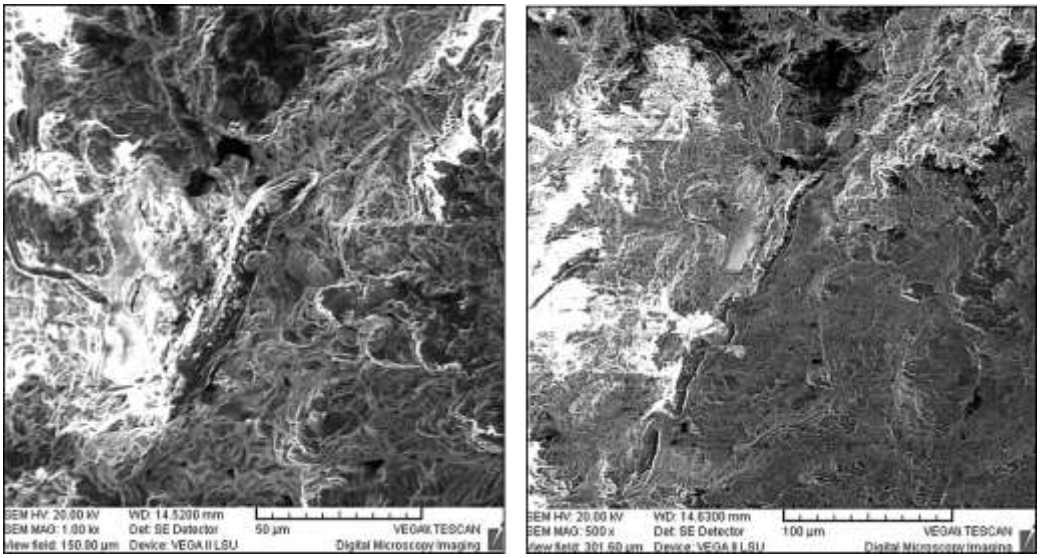

Fig. 10: SEM micrographs of bleached pulp fibers

3.7. Energy Dispersive X-ray (EDX) Analysis

Bleached and unbleached kraft pulp of a combined feedstock of coconut coir and corn husk were analyzed by EDX (Fig. 11). Carbon and oxygen-52.57 wt% C and 46.34 wt% O are predominant in both samples in unbleached and bleached pulp respectively, signifying a cellulose and hemicellulose based matrix. The carbon content of the bleached pulp is slightly higher, effective lignin removal and is in line with hydrogen peroxide bleaching process used.

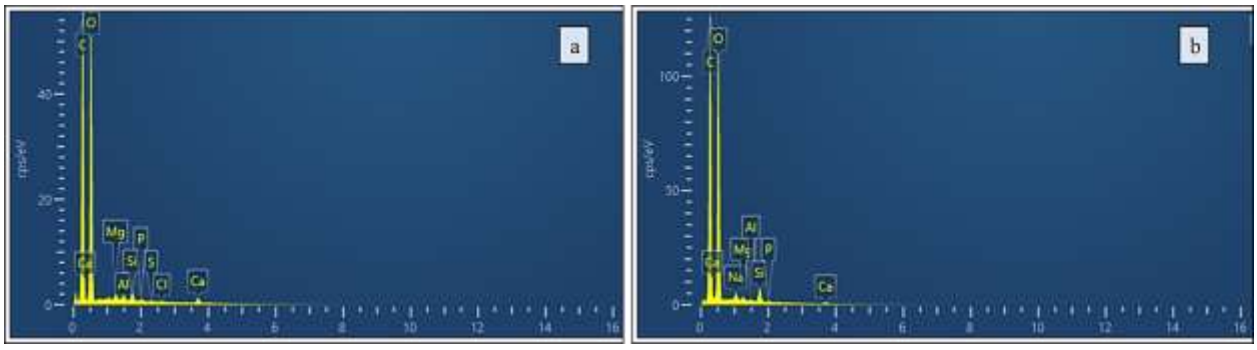

Fig. 11: EDX analysis of unbleached (a) and bleached (b) pulp

Other minor elements, including Mg (0.23%), Al (0.17%), Si (0.27%), P (0.06%), S (0.04%), Cl (0.03%), and Ca (0.28%) are also observed in the unbleached sample (Table 2). They can be of natural biomass ash or of left-over kraft pulping chemicals. Sulfur and chlorine, albeit in low amounts, prove the influence of kraft pulping process. In contrast, inorganic impurities are lower in the bleached pulp: Na (0.42%), Mg (0.13%), Al (0.04%), Si (0.43%), P (0.06%), and Ca (0.10%), with sulfur and chlorine absent (Table 3). The lack of Cl and S confirms the environmental friendliness of peroxide bleaching. Overall, bleaching has improved purity and application potential, to achieve a high-quality paper product.

Table 2: EDX results of unbleached pulp

Element	Weight %	Weight % Sigma	Atomic %
C	52.57	0.21	59.87
O	46.34	0.21	39.62
Mg	0.23	0.02	0.13
Al	0.17	0.01	0.09
Si	0.27	0.01	0.13
P	0.06	0.01	0.02
S	0.04	0.01	0.02
Cl	0.03	0.01	0.01
Ca	0.28	0.01	0.09
Total	100.00		100.00

Table 3: EDX results of bleached pulp

Element	Weight %	Weight % Sigma	Atomic %
C	53.22	0.18	60.48
O	45.60	0.18	38.91
Na	0.42	0.02	0.25
Mg	0.13	0.02	0.07
Al	0.04	0.01	0.02
Si	0.43	0.01	0.21
P	0.06	0.01	0.03
Ca	0.10	0.01	0.03
Total	100.00		100.00

3.8. UV-Vis Spectroscopic Analysis

The analysis of black liquor that was obtained following kraft pulping process was done using UV-Visible spectroscopy with the intention of confirming the presence of lignin-derived compounds. The absorption spectrum was observed at the wavelength ranging 190-300 nm with a good peak at 200-210 nm with high absorbance of 0.8 (Fig. 12). In addition to the prominent absorption at 200–210 nm, Lignin-derived compounds typically absorb light within the 230–280 nm range, a phenomenon associated with substituted aromatic rings and conjugated phenolic structures. The presence of these absorptions further supports the solubilization of guaiacyl- and syringyl-type lignin units into the black liquor during alkaline pulping. This is a typical oligomeric π–π* electronic transition that is normally represented by aromatic C=C bonds and n–π* transitions associated with carbonyl-containing lignin fragments formed during oxidative and alkaline cleavage reactions (Hynynen et al. 2021). The presence of peak at 200-205 nm indicates the presence of high concentration of conjugated phenolic structures which are a product of lignin fragmentation (Pydimalla et al. 2019). Such sharp absorbance would indicate that there is an efficient cleavage of ether and carbon–carbon bonds in the lignin macromolecule during

kraft pulping, especially the β-O-4 bonds, which are most prone to cleavage when exposed to alkaline conditions. As it is observed that absorbance is proportional to the concentration, through Beer-Lambert law, the spectral data is a substantial evidence of the conclusion that the optimized pulping process conditions were effective in solubilizing lignin in the black liquor phase. Also, the absence of strong absorbance beyond 300 nm shows that highly condensed chromophoric structures didn't form very often. This suggests that the pulping conditions favoured lignin depolymerization over extensive condensation reactions.

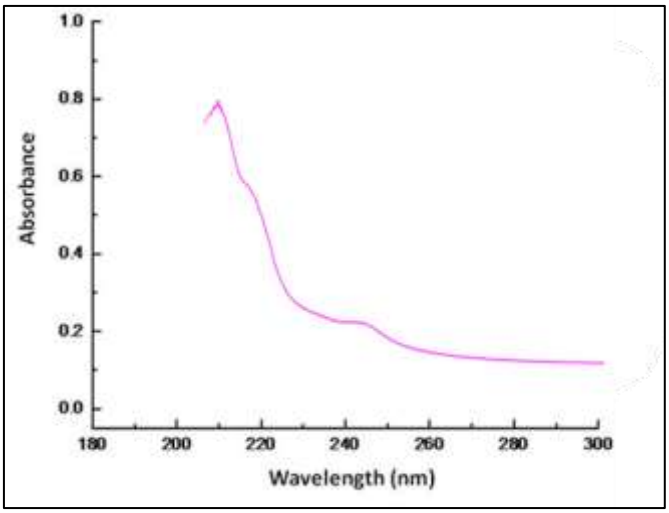

Fig. 12: UV analysis of black liquor

The present work primarily focuses on the feasibility of pulp production and physicochemical characterization of the produced fibers prior to detailed evaluation of paper making performance. While conventional pulping parameters such as kappa number and H-factor were not determined in the present study, the extent of delignification is inferred from qualitative characterization results. The FTIR spectra of the pulp show a noticeable reduction in characteristic lignin-related bands, while the UV–Vis analysis of the black liquor confirms the presence of dissolved lignin compounds released during pulping. The extent of lignin removal in this study is inferred from qualitative characterization results, including FTIR spectral changes and UV–Vis absorption of black liquor, which indicate dissolution of lignin fragments during pulping. In addition, SEM micrographs demonstrate fibers separation and surface modification, indicating that the applied treatment was sufficient to initiate lignin removal and fibers liberation. The results obtained in this study demonstrate the feasibility of producing pulp from a mixed agro-residue system consisting of corn husk and coconut coir. The physicochemical and morphological analyses confirm fibers separation and evidence of lignin removal during the pulping and bleaching processes. While the present work primarily focuses on pulp characterization at the laboratory scale, future studies will involve systematic evaluation of pulping parameters, handsheet preparation, and assessment of paper making properties to further determine the suitability of the produced pulp for paper applications.

4. CONCLUSIONS

The present study demonstrates the novel utilization of mixed agrowaste biomass-corn husk and coconut coir under optimized process conditions using kraft pulping followed by Elemental Chlorine-Free bleaching. The process was successful in attaining delignification, which was established through UV-Visible spectroscopic analysis of black liquor which exhibited a distinct absorbance peak at 200–205 nm indicating presence of phenolic lignin derivatives. The process achieved a pulp yield of 38.7% and significantly increased cellulose content from 60.2% (unbleached) to 85.4% (bleached), confirming efficient delignification and bleaching process. The removal of non-cellulosic components was further confirmed by an enhanced Water Retention Value and clear morphological changes observed in SEM images, which showed fibers loosening and increased fibrillation. FTIR spectra confirmed the degradation of aromatic lignin structures, while TGA revealed improved thermal stability in bleached fibers due to reduced lignin and a more cellulose-rich matrix. Comprehensively, the applied pulping and bleaching process not only improved the physicochemical and structural properties of the pulp but also offered a sustainable process to convert the lignocellulosic biomass into high-purity cellulose that can be used in new applications like nanocellulose manufacturing, biodegradable film, and sustainable composite material. This study contributes to circular bioeconomy strategies by advancing waste-to-value approaches in pulp and paper technologies. Future studies will focus on systematic evaluation of pulping parameters such as active alkali charge, sulfidity, and kappa number, along with process optimization to improve delignification efficiency and pulp quality.

Author Contributions: "Conceptualization, Madhuri Pydimalla.; methodology, A. V. Raghavendra.; validation, Madhuri Pydimalla., formal analysis, Shrinidhi Tavag.; investigation, Surya Tej Valluri.; resources, Nukala Mohith Satya Vardhan.; data curation, A. V. Raghavendra.; writing—original draft preparation, Madhuri Pydimalla.; writing—review and editing, Madhuri Pydimalla.; visualization, Surya Tej Valluri.; supervision, Madhuri Pydimalla.; project administration, A. V. Raghavendra.; funding acquisition, Madhuri Pydimalla.

Funding: This research was funded by CHAITANYA BHARATHI INSTITUTE OF TECHNOLOGY, sanction order no. CBIT/PROJ/-IH/I037/Chemical/D004/2024.

Institutional Review Board Statement: "Not applicable."

Informed Consent Statement: "Not applicable."

Acknowledgments: The authors would like to extend their heartfelt gratitude to Chaitanya Bharathi Institute of Technology (CBIT) for their generous funding and unwavering support under the major research project entitled "Pulp, Handsheet and Black Liquor Characterization of Hardwood Species (Beach Sheoak) after Kraft Cooking and Bleaching Process" as per the sanction order no. CBIT/PROJ/-IH/I037/Chemical/D004/2024.

Conflicts of Interest: "The authors declare no conflicts of interest."

REFERENCES

1. Austin, C.C., Mondell, C.N., Clark, D.G. and Wilkie, A.C., 2024. Kenaf: opportunities for an ancient fiber crop. *Agronomy*, 14(7), pp.1542. [DOI]
2. Bajpai, P., 2012. Pulp bleaching and bleaching effluents. In: Bajpai, P. (ed.), *Biotechnology for Pulp and Paper Processing*. Springer, Berlin, pp.45–67. [DOI]
3. Bajpai, P., 2013. Pulp bleaching and bleaching effluents. In: Bajpai, P. (ed.), *Bleach Plant Effluents from the Pulp and Paper Industry*. SpringerBriefs in Applied Sciences and Technology, Springer, Heidelberg, pp.45–67. [DOI]
4. Bian, H., Chen, L., Dai, H. and Zhu, J.Y., 2016. Enzyme-assisted mechanical fibrillation of bleached spruce kraft pulp to produce well-dispersed and uniform-sized cellulose nanofibrils. *BioResources*, 11(4), pp.10483–10496. [DOI]
5. Brännvall, E., 2017. The limits of delignification in kraft cooking. *BioResources*, 12(1), pp.2081–2107. [DOI]
6. Britt, K.W., 1970. *Handbook of Pulp and Paper Technology*. Van Nostrand Reinhold Company, New York, USA. [Link]
7. Colom, X., Carrillo, F., Nogués, F. and Garriga, P., 2003. Structural analysis of photodegraded wood by means of FTIR spectroscopy. *Polymer Degradation and Stability*, 80(3), pp.543–549. [DOI]
8. Das, S., Rani, A., Gahlot, M., Kapoor, S., Sisodia, N. and Sharma, A., 2023. An overview on non-wood fiber characteristics for paper production: sustainable management approach. *Materials Today: Proceedings*. [DOI]
9. Dutt, D., 2013. Environmentally friendly and cost-effective method for manufacturing absorbent grade paper. *Cellulose Chemistry and Technology*, 47, pp.783–792. [Link]
10. El-Sayed, E.S., El-Sakhawy, M. and El-Sakhawy, M.A., 2020. Non-wood fibers as raw material for pulp and paper industry. *Nordic Pulp & Paper Research Journal*, 35(2), pp.215–230. [DOI]
11. Furszyfer Del Rio, D.D., Sovacool, B.K., Bergman, N. and Makuch, K.E., 2022. Decarbonizing the pulp and paper industry: a systematic review of measures and pathways. *Renewable and Sustainable Energy Reviews*, 167, pp.112706. [DOI]
12. Gavrilescu, D., 2008. Energy from biomass in pulp and paper mills. *Environmental Engineering and Management Journal*, 7(5), pp.537–546. [Link]
13. Gellerstedt, G., 2003. The chemistry of bleaching and post-color formation in pulp. *Proceedings of the 3rd International Colloquium on Eucalyptus Pulp*, Espoo, Finland. [Link]
14. Hospodarova, V., Singovszka, E. and Stevulova, N., 2018. Characterization of cellulosic fibers by FTIR spectroscopy. *American Journal of Analytical Chemistry*, 9(3), pp.303–310. [DOI]
15. Hynynen, J., Orelma, H., Filpponen, I. and Johansson, L.S., 2021. Lignin and extractives first conversion using UV light from LEDs. *Green Chemistry*, 23, pp.8251–8259. [DOI]
16. Karlsson, H., 2006. *Fiber Guide: Fiber Analysis and Process Applications in the Pulp and Paper Industry*. AB Lorentzen & Wettre, Kista, Sweden. [Link]
17. Knott, B., 2021. *Molecular Modeling to Increase Kraft Pulp Yield*. National Renewable Energy Laboratory, Golden, USA. [Link]
18. Kron, L., Hasani, M. and Theliander, H., 2024. Delignification behaviour of Nordic hardwoods during kraft cooking. *Holzforschung*, 78(8), pp.434–445. [DOI]

19. Kron, L., Hasani, M. and Theliander, H., 2025. Diffusion and reaction model of kraft delignification. *Industrial & Engineering Chemistry Research*, 64(3), pp.1497–1507. [DOI]
20. Liu, Y., Wang, X., Chen, Z. and Li, J., 2024. Effects of plant source selection and pretreatment on fiber properties. *Wood Science and Technology*, 58(1), pp.123–135. [DOI]
21. Madhuri, P., Reddy, K. and Dutt, D., 2016. Pulp and black liquor characterization of Subabul wood. *IPPTA Journal*, 28(2). [Link]
22. Manfredi, V., 2024. The wood pulping processes. In: Manfredi, V. (ed.), *Pulping and Paper making: A Comprehensive Guide*. Springer Nature, Cham, pp.45–67. [DOI]
23. Mishra, O.P. and Sharma, R.K., 2020. Physical strength properties of corn stalk pulp. *Cellulose Chemistry and Technology*, 54(1–2), pp.65–71. [Link]
24. Nagaraja Ganesh, B., Reddy, N., Rao, K.M. and Reddy, K.O., 2022. Producing pulp and paper from discarded fibers: a sustainable approach. *Journal of Natural Fibers*, 20(1). [DOI]
25. Pere, J., Paavilainen, L., Tolonen, L. and Paulapuro, H., 2019. Influence of hemicellulose content on handsheet properties. *BioResources*, 14(1), pp.251–263. [DOI]
26. Peracchi, M., Crestini, C. and Saladino, R., 2024. Lignin stability and properties. In: *Encyclopedia of Renewable and Sustainable Materials*. Elsevier, Amsterdam, pp.1–20. [DOI]
27. Pydimalla, M. and Adusumalli, R.B., 2020. Handsheet characteristics of Subabul wood pulp. *Nordic Pulp & Paper Research Journal*, 35(2), pp.161–171. [DOI]
28. Pydimalla, M. and Reddy, K., 2019. Influence of temperature on kraft pulping of Subabul wood. *Sugar Tech*, 21, pp.1003–1015. [DOI]
29. Pydimalla, M. and Reddy, K., 2020. Effect of pulping, bleaching and refining on fibers for paper making: a review. *International Journal of Engineering Research and Technology*, 9(12). [Link]
30. Rousu, P. and Anttila, J., 2002. Sustainable pulp production from agricultural waste. Resources, Conservation and Recycling, 35, pp.85–103. [DOI]
31. Rowell, R.M., 2012. *Handbook of Wood Chemistry and Wood Composites*. 2nd ed., CRC Press, Boca Raton, USA. [DOI]
32. Santos, R.B., Hart, P.W., Jameel, H. and Chang, H.M., 2013. Wood-based lignin reactions important to the biorefinery and pulping processes. *BioResources*, 8(1), pp.1456–1477. [DOI]
33. Singh, R. and Bajpai, P., 2025. Eco-friendly biobleaching processes. In: *Advances in Sustainable Pulping and Paper making*. Springer, Singapore, pp.345–368. [DOI]
34. Smook, G.A., 2002. *Handbook for Pulp and Paper Technologists*. 3rd ed., Angus Wilde Publications, Vancouver, Canada. [Link]
35. Takada, M., Nakagawa-Izumi, A., Ohi, H. and Aoyagi, T., 2020. Influence of lignin on pretreatment and enzymatic hydrolysis. *Bioresource Technology*, 302, pp.122895. [DOI]
36. Tarrés, Q., Delgado-Aguilar, M., Pèlach, M.À. and Mutjé, P., 2023. Lignin-containing microfibrillated cellulose: properties and applications. *Cellulose*, 30(4), pp.2325–2340. [DOI]
37. Van Ewijk, S. and Stegemann, J.A. (2016). Limitations of the waste hierarchy for achieving absolute reductions in material throughput. Resources, Conservation and Recycling, 132, pp. 122–128. [DOI]

38. Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P. and Santas, R., 2004. Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Industrial Crops and Products, 19(3), pp.245–254. [DOI]
39. Wang, Y. and Liu, H., 2022. Pulping process for nonwoody plants. In: *Nonwood Plant Fibers for Sustainable Pulping*. Elsevier, Amsterdam, pp.123–150. [DOI]
40. Wohlert, M., Bergenstråhle-Wohlert, M. and Berglund, L.A., 2022. Cellulose and hydrogen bonds: structural and mechanical aspects. *Cellulose*, 29(1), pp.1–23. [DOI]
41. Wong, L.C., Tan, Y.P., Ng, S.F. and Yusof, N., 2023. Cellulose hydrogel for dermal drug delivery. *International Journal of Biological Macromolecules*, 224, pp.483–495. [DOI]
42. Worku, L.A., Bultum, L.B., Tolesa, G.N. and Urgessa, G.S., 2023. Agricultural residues as alternative raw materials for pulp and paper production. *Membranes*, 13(2), pp.228. [DOI]
43. Zhao, Y., Wang, S., Lyu, S. and Fang, G., 2020. Lignin–carbohydrate complexes and their impact on biomass utilization. *Journal of Cleaner Production*, 253, pp.120076. [DOI]