

**RESEARCH ARTICLE** 



# Characterization of biochar produced from paperboard sludge: A sustainable approach for waste management and resource recovery

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# Abstract

The pulp and paperboard industry are a significant industrial sector that consumes large quantities of fresh water and generates substantial volumes of wastewater. Treating this wastewater produces a considerable amount of sludge, which poses serious environmental challenges. This study proposes a sustainable solution by converting paperboard sludge (PBS) into biochar through slow pyrolysis at temperatures  $\leq$ 500°C, offering an alternative approach to waste management and resource conservation. The physicochemical analysis of paperboard sludge biochar (PBSB) revealed a neutral pH of 7.49, electrical conductivity of 0.09 dS m<sup>-1</sup>, an organic carbon content of 38.12% and a calcium carbonate (CaCO<sub>3</sub>) content of 24.5%. Proximate analysis of PBSB revealed an increased fixed carbon content of 10.27 %, total organic carbon (TOC) of 7.13%, and reduced volatile matter and moisture levels. Micronutrients *viz.*, iron (Fe) (5.06 mg L<sup>-1</sup>), Manganese (Mn) (419.3 mg L<sup>-1</sup>), Copper (Cu) (26.3 mg L<sup>-1</sup>) and Zinc (Zn) (66.1 mg L<sup>-1</sup>), were also observed in PBSB.

FTIR analysis identified various carbon-containing functional groups, including C-Cl, C-N, C-C, H-C=O, C-H and -C $\equiv$ C-H, indicating substantial chemical transformations during pyrolysis. Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) analysis revealed that PBSB consists of fine particles with a coarse, fluffy, spongy, porous structure, making it ideal for water adsorption. Elemental analysis through x-ray diffraction (XRD) showed high carbon and oxygen content and significant amounts of aluminosilicates, carbonates and nutrients like phosphorus and potassium, suggesting PBSB as a potential slow-release fertilizer.

This research highlights the potential of biochar derived from paperboard waste as a sustainable solution for effective waste management and resource recovery.

#### **Keywords**

AAS; biochar production; FTIR; physicochemical analysis; proximate analysis; SEM-EDX; TOC; XRD

# Introduction

In India, the pulp and paperboard industry are a significant consumer of water, with each tonne of paper production generating 72 to 225 cubic meters of wastewater, depending on the production method employed (1). Sustainable solutions for waste management, such as biochar production through methods like pyrolysis, gasification, hydrothermal carbonization (HTC), slow pyrolysis and fast pyrolysis, are being explored (2, 3). These methods reduce waste and produce biochar, which has environmental and agricultural applications, offering a dual benefit to waste management in the paper industry.

The large volumes of wastewater this industry generates must be treated to meet environmental quality standards before reusing. Effluent treatment in the pulp and paperboard industry generates a substantial amount of sludge, creating a significant environmental burden (4). One tonne of paper typically generates 40-50 kg of dry sludge (5). Landfill disposal is the predominant practice for managing this sludge (6). However, landfilling poses significant environmental risks, including leaching contaminants into groundwater and releasing greenhouse gases, exacerbating pollution and climate change concerns.

Given these challenges, implementing effective sludge management strategies is essential to mitigate the environmental burden (7). With increasingly stringent environmental regulations, waste management remains one of the primary challenges for the pulp and paperboard industry (1). Sustainable and efficient solutions must address both environmental and economic considerations. Historically, landfilling has been the primary method for sludge disposal, but the need for alternative approaches is now more pressing than ever (6).

Waste from the paperboard industry can be repurposed as raw material for various applications, underscoring the need to establish sustainable processes. Over the past two decades, researchers have explored innovative methods to transform this waste into valuable resources. Among the most notable approaches are carbon sequestration and soil amendment. In acidic soils, it serves as a liming material, neutralizing pH levels and creating a favorable environment for plant growth. Additionally, in loamy soils, it enhances water-holding capacity. Biochar, in particular, has been shown to increase soil organic carbon content and stimulate carbon sequestration by suppressing organic matter turnover (8).

As reported by previous studies, paperboard sludge (PBS) can also be utilized in dried formulations as agricultural fertilizers, building materials and insulation materials (6). Its high carbon content makes PBS a potential feedstock for producing activated carbon, which can be applied to soils to enhance carbon levels (9). This method enriches soil carbon and addresses environmental concerns related to waste disposal while conserving natural resources.

Increasing soil carbon content provides numerous environmental benefits aligned with sustainability goals. A key advantage is carbon sequestration, which suppresses the longterm turnover of soil organic matter. Enhanced soil carbon improves soil health by boosting nutrient retention, waterholding capacity, microbial activity and overall soil structure, increasing agricultural productivity. Furthermore, higher soil carbon aids water conservation by enabling soils to retain more moisture, reducing irrigation needs and improving aeration (10). This study aims to address these challenges by exploring the uniformity of carbon-rich biochar derived from the pyrolysis of PBS. It evaluates the biochar's physical and chemical properties and examines how varying input components influence these properties to determine potential applications. Techniques such as Fourier Transform Infrared Spectroscopy (FTIR), SEM-EDX, XRD, proximate analysis, and comprehensive physicochemical analysis were employed to characterize both raw paperboard sludge and the resulting biochar.

# **Materials and Methods**

#### Study area

The study area is in Mondipatti Village, Manaparai Taluk, Tiruchirappalli district, Tamil Nadu, at Tamil Nadu Newsprint and Paper Limited (TNPL) - Unit II. This facility utilizes waste paper and imported pulp as raw materials to manufacture Multi-Layer Coated Paper Boards. Positioned at approximately 10° 41' N latitude and 78° 26' E longitude, the plant has an annual production capacity of around 200,000 tons. Additionally, it processes approximately 5,000 cubic meters of effluent daily through a state-of-the-art Effluent Treatment Plant (ETP).

## **Sample collection**

Paperboard sludge (PBS) was sourced from the Effluent Treatment Plant (ETP) of TNPL Unit II in Mondipatti, Tiruchirappalli, Tamil Nadu. These solid wastes were generated as a by-product of the effluent treatment process. The raw PBS was collected in clean polyethylene bags and shade-dried for 3 to 5 days to reduce its moisture content effectively, preparing it for further analysis. The bags were properly sealed and stored in moisture-free areas to prevent contamination during sample collection to ensure sample integrity.

### **Biochar production**

Pyrolysis is a widely used method for the thermal conversion of biomass. In this study, slow pyrolysis was employed to convert PBS into biochar. This process involves thermally treating biomass in an environment with limited or no oxygen (11). A pyrolyzer with a capacity of 10 kg was used for biochar production. Slow pyrolysis, characterized by a low heating rate of approximately 0.1-1°C per second, is known for yielding a higher proportion of char. During the slow pyrolysis of PBS, the biomass was heated to approximately 500°C for 1 to 4 hours.

This process effectively transformed the PBS into carbonrich biochar, as Figs. 1 and 2 illustrated. After pyrolysis, the biochar was allowed to cool, ground into a fine powder and made suitable for various applications, including soil enhancement, water filtration and carbon sequestration (1).

#### Physicochemical analysis of PBS and PBSB

All physicochemical parameters were measured following standard procedures. The samples' pH and electrical conductivity (EC) were determined using a digital pH meter and conductivity meter with a solid-to-water suspension ratio of 1:2.5 (12). Organic carbon (OC) content was assessed using the Walkley-Black method (13). The total nitrogen (N), phosphorus (P), potassium (K), calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) content in the samples were extracted using a mixture of HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. The CaCO<sub>3</sub> content was determined by treating the sample with HCl and measuring the volume of CO<sub>2</sub> evolved.



Fig. 1. Biochar production through a slow pyrolysis process.



Fig. 2. Visual observation of (A) PBS and (B) PBSB.

Micronutrients such as Cu, Fe, Mn and Zn were extracted using an acid digestion method and analyzed with an Atomic Absorption Spectrophotometer (Thermo Electron; Model IRIS Intrepid IIXDL, iCe 3000 series, USA) (14).

#### **Proximate analysis for PBS and PBSB**

Proximate analysis offers insights into the moisture content, volatile matter, ash content and fixed carbon content of PBS and PBSB, providing a comprehensive understanding of their composition.

#### Moisture content

The moisture content of PBS and PBSB samples was determined by heating the sample to a temperature slightly above the boiling point of water (105°C) for 8 hours. This process allows the water within the PBS and PBSB to evaporate, leading to a change in weight. Once the weight stabilizes, the difference between the initial and final weights is used to calculate the moisture content, expressed as a percentage of the sample. The formula for moisture content as shown in equation number (1) (15):

Moisture content (%) = 
$$\frac{M_i - M_f}{M_i}$$
 X 100 ...(Eqn.1)

Where  $M_i$  is the initial weight of moisture content,  $M_f$  is the final weight of moisture content.

#### Volatile matter

The volatile matter content of PBS and PBSB was determined using standard methods as described by (14). A pre-weighed crucible containing a dried sample of PBS or PBSB was heated in a muffle furnace at 900°C for 1 hour in a non-oxidizing atmosphere. After heating, the crucible was cooled in a desiccator and weighed. This process was repeated in 30-minute intervals until a constant weight was achieved. The percentage of volatile matter was calculated using the following formula and was shown in equation number (2):

Volatile matter (%) = 
$$\frac{M_f - V_f}{M_f} \times 100$$
 .....(Eqn.2)

 $\label{eq:Where M_fis} \ensuremath{\text{Where M_fis}}\xspace \ensuremath{\mathsf{Where M_fis}$ 

# Ash content

To determine the ash content of PBS and PBSB, the dried samples were weighed with the crucible and then heated in a muffle furnace at 750°C for 1 hour. After heating, the crucible containing the ash was cooled in a desiccator and reweighed (15). The ash content percentage was calculated using the following formula and also shown in equation (3):

Ash content (%) = 
$$\frac{W_{AF}}{M_f}$$
 .....(Eqn.3)

Where  $W_{\text{Af}}$  is the final weight of ash content and  $M_{\text{f}}$  is the final weight of moisture content

#### Fixed carbon

The fixed carbon content of PBS and PBSB is calculated by subtracting the percentages of moisture content, ash content and volatile matter from the total composition. This relationship is represented by the following equation (15):

Fixed carbon (%) = 100 - (%MC+%Ash+%VM)

## Total organic carbon (TOC)

Dry the sample at 105°C until it reaches a constant weight. Weigh the dried sample and transfer it to a pre-weighed porcelain crucible. Heat the crucible containing the sample in a muffle furnace at 550-600°C for approximately 4 hours. After 4 hours, allow the crucible to cool and then weigh it. Calculate the weight loss by determining the difference between the initial and final weights of the crucible with the sample. This weight loss corresponds to the total organic carbon content in the sample (1).

TOC (%) = (Weight loss upon ignition / initial weight of the sample) x 100

(Weight loss upon ignition = Initial weight of sample - Weight of crucible with residue after ignition)

#### Fourier transform infra-red spectrometer (FT-IR)

FT-IR spectra were recorded using a PerkinElmer Spectrum II Fourier Transform Infrared Spectrometer with KBr pellets. The sample was dried, powdered and sieved through a 2 mm sieve. A homogeneous mixture of PBS was prepared using a mortar and pestle before FT-IR analysis. The samples were placed directly into the holder and data were collected from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> using 21 CFR Part 11 software. Reference spectra were obtained before each sample analysis. Peak values were recorded and each analysis was repeated twice for confirmation (16).

# Scanning electron microscope – energy dispersive x-ray spectroscopy (SEM – EDX)

For scanning electron microscopy (SEM), 10 mg of PBS and PBSB were placed on high-purity aluminum stubs and allowed to air dry at 37°C. Using a sputter coater, the samples were coated under a vacuum with approximately 25 nm of high-purity platinum. A specific area was selected for elemental analysis of PBS and PBSB and the sediment elements were analyzed using a high-resolution scanning electron microscope equipped with an EDAX system (14).

# X-ray diffraction analyzer (XRD)

X-Ray Diffraction experiments were performed with a PANalytical empyrean diffractometer (PANalytical Expert TERP) equipped with a Cu-X ray source (k = 1.5404 Å), operated at 45Kv and 30mA. The prepared samples were placed on a quartz holder for analysis. Each diffractogram was measured at 2 $\theta$  intervals of 0.05°, within the range of 5°-90° (4).

# **Results and Discussion**

# Physico-chemical properties of PBS and PBSB

Table 1 presents a comparative analysis of the physicochemical properties of PBS and PBSB. PBS's pH was slightly acidic at

Table 1. Physicochemical parameters of PBS and PBSB

6.84, whereas PBSB's pH was neutral at 7.49. PBS's electrical conductivity was measured at 2.43 dS m<sup>-1</sup>, compared to 0.90 dS m<sup>-1</sup> for PBSB. These results are consistent with previous studies (9, 16-18).

The slightly acidic pH of PBS (6.84) can be attributed to its low CaCO<sub>3</sub> content, which is insufficient to neutralize the acidity present in the material. This relationship between reduced CaCO<sub>3</sub> levels and lower pH has been documented in prior research (14). On the other hand, PBSB's neutral pH of 7.49 results from its production at lower pyrolysis temperatures ( $\leq$ 500°C), resulting in neutral conditions. The shift towards neutral to alkaline pH in biochar is primarily due to the increased CaCO<sub>3</sub> content (17-20).

PBS displayed an organic carbon content of 24.30%, lower than the 38.12% found in PBSB. The reduced organic carbon in PBS can be attributed to its high cellulose fiber content (13, 21). The feedstock composition and pyrolysis conditions influence the organic carbon content in biochar. During pyrolysis, organic carbon primarily forms polyaromatic structures. It is noted that pyrolysis facilitates the development of aromatic rings that are resistant to microbial degradation, contributing to the enhanced stability of carbon in biochar (17).

stable aromatic carbon is a significant factor in biochar's increased organic carbon content (22, 23). Additionally, pyrolysis leads to the volatilization of organic compounds, with noncarbon elements such as oxygen and hydrogen being released. This process results in a higher concentration of carbon in the biochar. The reduction in mass of non-carbon components further stabilizes the carbon and elevates the organic carbon content in biochar (24).

The C:N ratio of PBS was 13.9, while PBSB exhibited a higher ratio of 29.78, consistent with previous findings (9). The total N, P, K, Ca and Mg content in PBS were 1.74%, 0.58%, 0.84%, 4.39% and 2.36%, respectively, compared to PBSB, which contained 1.28%, 0.24%, 0.38%, 2.37% and 0.57%, respectively. These results align with the studies of (9, 25). The higher Ca<sup>2+</sup>, Mg<sup>2+</sup> and K levels in PBS compared to PBSB can be attributed to using virgin wood materials during paper production (14).

Virgin wood, a primary raw material for paperboard production, naturally contains significant amounts of calcium, magnesium and potassium minerals. These minerals are not fully removed during the pulping process and accumulate in the sludge. Additionally,  $CaCO_3$  and other mineral fillers, commonly used to enhance paper quality, contribute to the

S. No	Parameters	Unit	PBS	PBSB
1	рН	-	6.84	7.49
2	EC	dS m <sup>-1</sup>	2.43	0.09
3	Organic carbon	%	24.30	38.12
4	C: N ratio	-	13.96	29.78
5	CEC	C mol (p⁺) kg⁻¹	2.50	5.00
6	CaCO <sub>3</sub>	%	7.00	24.5
7	Total N	%	1.74	1.28
8	Total P	%	0.58	0.24
9	Total K	%	0.84	0.38
10	Total Ca	%	4.39	2.37
11	Total Mg	%	2.36	0.57
12	Zn	mg L⁻¹	95.82	66.08
13	Cu	mg L⁻¹	32.16	26.34
14	Fe	mg L⁻¹	1607.92	5.06
15	Mn	mg l <sup>-1</sup>	532.78	419.34

elevated mineral content in PBS. During the pyrolysis of PBS into PBSB, many of these elements volatilize or transform into gaseous forms, resulting in a notable decrease in their concentration in PBSB.

The CaCO<sub>3</sub> content in PBS was 7.00%, whereas PBSB exhibited a significantly higher level of 24.5%. The increase in CaCO<sub>3</sub> in PBSB can be attributed to the removal of inorganic fillers from recycled paper during pyrolysis (13). The cation exchange capacity (CEC) of PBS was lower, at 2.5 C mol ( $p^+$ ) kg<sup>1</sup>, compared to 5.00 C mol ( $p^+$ ) kg<sup>1</sup> in PBSB. The CEC depends on the organic matter and clay content (25). The higher CEC of biochar reflects its greater ability to retain exchangeable cations through sorption pathways (26).

The micronutrient composition also showed significant differences between PBS and PBSB. PBS contained 95.82 mg L<sup>-1</sup> of Zn, 32.16 mg L<sup>-1</sup> of Cu, 1607.92 mg L<sup>-1</sup> of Fe and 532.78 mg L<sup>-1</sup> of Mn. In contrast, PBSB contained 66.08 mg L<sup>-1</sup> of Zn, 26.34 mg L<sup>-1</sup> of copper, 5.06 mg L<sup>-1</sup> of Fe and 419.34 mg L<sup>-1</sup> of Mn.

#### Proximate analysis for PBS and PBSB

The proximate analysis of PBS and PBSB, as shown in Table 2, reveals significant differences in their composition. The moisture content of PBS was recorded at 50.6%, while PBSB exhibited a much lower moisture content of 0.55%. The ash content in PBSB was significantly higher at 78.29%, compared to 18.01% in PBS. The findings align with previously performed investigations (18, 20).

The volatile matter in PBS was 28.9%, whereas PBSB had a lower volatile matter content of 10.89%. This difference can be attributed to variations in the organic matter content between PBS and PBSB (14). Additionally, for PBSB, the volatile matter content is influenced by the pyrolysis temperature (27).

The fixed carbon content was 2.49% in PBS and increased to 10.27% in PBSB, highlighting the effect of pyrolysis

in converting PBS into a carbon-rich material. This transformation makes PBSB suitable for applications such as soil enhancement, water filtration and carbon sequestration. The total organic carbon of PBS was 1.03%, while PBSB demonstrated a significantly higher TOC of 7.13%, which aligns with a previous study (1).

## Functional groups identified for PBS and PBSB

The functional groups in PBS and PBSB, as shown in Table 3, reveal diverse chemical compositions. In PBS, the identified functional groups include =C-H (Methine group), C-C (Alkene group), N-H (Primary amine group), C=O (Carbonyl group), H-C=O (Carboxyl group) and C-H (Fig. 3). A broad band at 870 cm<sup>-1</sup> in PBS may indicate the presence of CaCO<sub>3</sub> and corresponds to significant C-H stretching in aromatic groups. The absorption of C-H bond in PBS may be due to the mulling oil used in paper production. The peak at 995.53 cm<sup>-1</sup> may be attributed to the bending vibrations of methylene or alkene groups =C-H with strong intensity. These =C-H methine or alkene groups, representing alkenes or unsaturated hydrocarbons, could arise from the breakdown of resin acids, unsaturated fatty acids, or other organic compounds in the wood or recycled fibers used in paperboard production (26). The peak at 1406.27 cm<sup>-1</sup> may correspond to C-C stretching in medium-intensity aromatic groups. A broadband at 1628.41 cm<sup>-1</sup> may be associated with the N-H bending vibrations of primary amines (asymmetric stretching), suggesting a partial breakdown of nitrogenous compounds. This breakdown may lead to amide or amine functional groups forming in PBS, which enhance its nutrient content, making it more suitable for applications such as soil amendment or fertilizer (28).

The peak at 1779.94 cm<sup>-1</sup> corresponds to C=O (carbonyl group) stretching in anhydrides, potentially formed through the oxidation of organic materials during the papermaking process (4). A medium-intensity peak at 2794.01 cm<sup>-1</sup> can be

S. NO	Parameter	Unit	PBS	PBSB
1	Moisture	%	50.60	0.55
2	Ash	%	18.01	78.29
3	Volatile matter	%	28.90	10.89
4	Fixed carbon	%	2.49	10.27
5	Total Organic Carbon (TOC)	%	1.03	7.13

Table 2. Proximate analyses and TOC for PBS and PBSB

Table 3. Summary of identified FTIR band observed in PBS and PBSB

		PBS	PBSB				
Peak value (cm <sup>-1</sup> )	Nature of Band stretching (cm <sup>-1</sup> )	<b>Functional group</b>	Intensity	Peak value (cm <sup>-1</sup> )	Nature of Band stretching (cm <sup>-1</sup> )	Functional group	Intensity
870	C-H bend	Aromatics	strong	850	C-Cl Stretching	Alkyl halides	medium
995.53	(= C – H) bend	Methylene group or Alkenes group	Strong	873.28	C-H Stretching	Aromatics group	strong
1406.27	(C-C) Stretching (ring)	Aromatics group	Medium	1031.37	C – N stretching	Aliphatic amines	medium
1628.41	N – H bend	1° amines (asymmetric)	Medium	1416.58	C – C Stretching	Aromatics group	medium
1779.94	C = O Stretching	Anhydrides group **	Strong	2813.81	H – C = O: C- H Stretching (or) -COOH	Aldehydes group (or) Carbonyl group	medium
2794.01	H-C=O:C-H	Aldehydes group	Medium	2882.99	C – H Stretching	Alkanes group	medium
2882.67	Stretching	Alkanes	Medium	3276.95	$-C \equiv C - H: C - H$ Stretching (or) O-H stretching	Alkynes (terminal) group or Alcohols groups**	(n- narrow, s - sharp) or (br-broad, s-sharp)
3364.48	N-H Stretching	1°, 2° amines and amides	Medium	-	-	-	-

Anhydrides group \*\* - due to the C - O stretch it absorbs in the fingerprint region



Fig. 3. FT-IR analysis reveals the presence of various functional groups in PBS, including (=C-H, C-C, N-H, C=O, H-C=O and C-H).

attributed to C-H stretching in aldehyde groups, related explicitly to carbonyl stretching of H-C=O. Meanwhile, the peak at 2882.67 cm<sup>-1</sup> is linked to C-H stretching, suggesting the presence of saturated hydrocarbons (alkanes). The C-H absorptions in PBS are likely due to mulling oil, commonly employed in the paperboard industry to enhance coating quality, pigment mixing and ink absorption for better print results.

Lastly, the broad band at 3364.48 cm<sup>-1</sup> corresponds to N -H stretching in primary and secondary amines and amides, indicating N-containing functional groups in the PBS.

The main surface functional groups identified in biochar include hydroxyl, methyl, carboxylic and alkene groups (28). Biochar pyrolyzed at lower temperatures (200-400°C) contains a high concentration of oxygen-containing functional groups such as (-COOH, -OH, C=O and -CHO), which stimulate nutrient exchange and improve soil fertility, as reported by (29, 30). In PBSB, the observed functional groups include C-Cl (Halo or Chloro group), C-N, C-C (Aromatic group), H-C=O: C-H (Aldehyde group) or -COOH or C=O (carbonyl group), C-H and -C=C-H: C-H (Alkene group) or O-H (alcohol group) (Fig. 4).

The broad band at 850 cm<sup>-1</sup> in PBSB may correspond to C-Cl of alkyl halides with medium intensity, enhancing the biochar's ability to adsorb and retain organic pollutants. During the impregnation process, CaCO<sub>3</sub> might transform into calcium chloride or other C-Cl groups (31). A sharp peak at 873.28 cm<sup>-1</sup> and another at 710 cm<sup>-1</sup> are associated with C-H stretching in aromatic groups with strong intensity, indicating out-of-plane and in-plane bending vibrations of the carbonate ion. This may result from cellulose, hemicellulose and lignin decomposition during pyrolysis at relatively low temperatures ( $\leq$ 500 °C).

A peak at 1031.37 cm<sup>-1</sup> may correspond to C-N stretching in aliphatic amines formed from nitrogenous biomass components during pyrolysis. These components may shift from the amine or amide group, improving the biochar's CEC and enhancing nutrient retention (32). The peak at 1416.58 cm<sup>-1</sup> indicates C-C stretching in aromatic groups, representing a more graphitic and stable structure. This structural stability is crucial for long-term carbon sequestration.

A strong absorption band near 1440 cm<sup>-1</sup> and another at 850 cm<sup>-1</sup> suggests the presence of CaCO<sub>3</sub>, with the band at 1440 cm<sup>-1</sup> corresponding to asymmetric stretching of the carbonate ion. The broadband at 2813.81 cm<sup>-1</sup> may correspond to H-C=O: C-H stretching in the aldehydes group with medium intensity or -COOH or C=O of the carbonyl group. Meanwhile, the 2882.99 cm<sup>-1</sup> band corresponds to C-H stretching in the alkanes group. The band at 3276.95 cm<sup>-1</sup> may indicate -C=C-H: C-H stretching in the alkynes group, which may form under low-oxygen



Fig. 4. FT-IR analysis reveals the presence of various functional groups in PBSB, including (C-CI, C-N, C-C, H-C=O: C-H or -COOH or C=O, C-H, and -C=C-H: C-H or O-H).

conditions and suggest unsaturated carbon structures. All the functional groups observed in PBSB are influenced by its hydration state.

## Scanning electron microscopy with energy-dispersive Xray spectroscopy for PBS and PBSB (SEM-EDX)

The surface structures and morphology of PBS and PBSB were characterized using SEM, while their compositions were determined through EDX. SEM observations of PBS revealed a rough, wrinkled and flaky texture with a porous structure and a heterogeneous distribution of particles (Fig. 5). These features enable the sludge to effectively adsorb metals and various complex organic ions. The adsorption mechanism for metal and other complex ions on soil likely involves both physical and chemical adsorption at surface sites (33).

In contrast, the SEM micrograph of PBSB showed reduced particle size, a coarse surface, small cavities, holes and a mesoporous and microporous structure. Moreover, the surface of PBSB exhibited dispersion particles in the form of fluffy sponges and spherical-shaped fragments with deeper levels of fragmentation (16). The fluffy, spongy texture of PBSB can be attributed to its carbon matrix. Combined with the interconnected pores and voids within the biochar, this structure provides a large surface area crucial for water, nutrients, or pollutant adsorption. Due to the low pyrolysis temperature, PBSB may exhibit hydrophobic properties (Fig. 6).

The pores within biochar play a crucial role in facilitating solid-liquid interactions, enabling the passage of pollutants, nutrients, water, or electrolytes into the smaller pores within its internal structure (34, 35). Biochar's fluffy and spongy texture enhances its ability to improve soil aeration and water retention (36). Moreover, biochar produced at lower temperatures tends to be more hydrophobic, contributing to its greater structural strength than biochar produced at higher temperatures (37).

The EDX spectrum of PBS is shown in Table 4. Other elements detected in PBS include calcium (5.62% by weight), silicon (2.26% by weight) and aluminum (1.43% by weight), along with various trace elements. The presence of silicon and



**Fig. 5.** SEM images of PBS at (349 x magnification) reveal a rough, wrinkled and flaky texture and a porous structure.



Fig. 6. SEM images of PBSB at (652 x magnification) reveal coarse, small cavities, holes, fluffy, spongy texture and a mesoporous structure.

Table 4. Elemental analysis of PBS and PBSB collected from Tamil Nadu Paper Limited (TNPL). The K and L following every element indicates the K and L shells of the specific atom

	PBS			PBSB	
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C – K	46.16	56.46	СK	34.46	45.43
0 – K	41.53	38.14	ОК	45.42	44.95
Na – K	0.42	0.27	Na K	0.33	0.23
Mg – K	0.43	0.26	Mg K	0.41	0.26
Al – K	1.43	0.78	Al K	3.70	2.17
Si – K	2.26	1.18	Si K	3.12	1.76
P – K	0.21	0.10	ΡK	1.31	0.67
S – K	0.88	0.40	SK	1.42	0.70
Cl – K	0.26	0.11	Cl K	0.38	0.17
K – K	0.24	0.09	КК	0.18	0.07
Ca – K	5.62	2.06	Ca K	8.45	3.34
Fe – K	0.56	0.15	Ti K	0.12	0.04
			Mn K	0.41	0.12
			Fe K	0.30	0.09
Totals	100.00		Totals	100.00	

aluminum suggests the presence of aluminosilicate minerals, such as kaolinite  $(Al_2Si_2O_5(OH)_4)$ , which are major components of clay minerals. These minerals contribute to soil's structural integrity and cation exchange capacity (CEC). The individual weight percentages of the trace elements in PBS are also detailed in Table 4.

The EDX spectrum of PBSB is presented in Table 4. The predominant elements in PBSB were carbon (34.46% by weight) and oxygen (45.42% by weight). Silicon (3.12% by weight), aluminum (3.70% by weight) and calcium (8.45% by weight) were also present. These elements are commonly associated with aluminosilicates and carbonates. Silicon and aluminum in biochar indicate the presence of aluminosilicate minerals, such as kaolinite, which are crucial for preserving structural integrity and cation exchange capacity (CEC) in both soil and biochar (38).

Additionally, the phosphorus and potassium in biochar are slowly released into the soil, improving nutrient availability (24). The calcium in the form of CaCO<sub>3</sub> plays a crucial role in regulating soil pH. Calcium carbonate in biochar can significantly enhance long-term pH regulation in soils, making it more suitable for crop applications. CaCO<sub>3</sub> acts as a liming agent, neutralizing acidic soils by reacting with hydrogen ions to form calcium ions (Ca<sup>2+</sup>) and carbonic acid (H<sub>2</sub>CO<sub>3</sub>). This carbonic acid can further dissociate into water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>), reducing the concentration of hydrogen ions in the soil and raising the soil pH. This neutralization



Fig. 7. EDX Spectrum reveals the predominately occurred elements of (A) PBS and (B) PBSB.

**Table 5.** XRD analysis of PBS and PBSB

Visible	Ref.Code	Score	Compound Name	Displ. (°20)	Scale Fac.	Chem. Formula	Ref. Code	Score	Compound Name	Displ. (°2θ)	Scale Fac.	Chem. Formula
1	96-901-6707	81	Calcite	0.000	1.011	Ca6.00 C6.00 O18.00	96-900-1298	53	Calcite	0.000	0.883	Ca5.62 Mg0.38 C6.00 O18.00
2	96-202-1018	37	Digold indium palladium	0.000	0.156	Pd1.37 Au1.77 In0.86	96-901-3220	41	Periclase	0.000	0.140	Mg4.00 O4.00
3	96-901-1683	27	Bromargyrite	0.000	0.060	Ag4.00 Br4.00	96-900-1753	36	Gypsum (deuterated)	0.000	0.152	Ca8.00 S8.00 O24.00 D16.00
4	96-900-4468	28	Richetite	0.000	0.048	U36.00 Pb8.74 Fe0.47 Mg0.83 O173.00	96-900-1273	24	Birnessite	0.000	0.079	Mn2.00 O5.40 K0.46
5	96-900-1754	21	Gypsum (deuterated)	0.000	0.096	Ca8.00 S8.00 O24.00 D16.00	96-900-8229	8	Cristobalite	0.000	0.058	Si4.00 O8.00
6	96-500-0209	16	Cerussite	0.000	0.085	Pb4.00 C4.00 O12.00	96-900-9235	22	Kaolinite	0.000	0.074	Al2.00 Si2.00 O9.00 H4.00

process improves the availability of essential nutrients that may otherwise be locked in acidic conditions, enhancing plant growth and crop productivity (8, 39). Iron (0.30%) and manganese (0.41%) are redox-sensitive elements that play a key role in redox reactions within the soil, undergoing oxidation and potentially triggering permeability transition pores (PTP). Phosphorus (1.31%) and potassium (0.18%) by weight are essential nutrients in the soil and may enhance the value of PBSB as a slow-release fertilizer. Fig 7 shows the XRD crystalline and amorphous phases of PBS and PBSB.

#### X-ray diffraction (XRD)

The crystalline and amorphous peak patterns of PBS and PBSB are shown in Table 5. XRD analysis was conducted to assess the properties of PBS (Fig. 8). PBS exhibited distinct peaks corresponding to its more crystalline phase. The strong crystalline peak at 29.6301°  $2\theta$  is attributed to calcite, aligning with the calcium utilized in paper manufacturing. Calcite is commonly used in the papermaking process to enhance the brightness and opacity of paper (40). The diffraction peaks at 44.66° 20 and 64.84° 20 are associated with periclase. The diffraction peaks at 11.7389° 20, 20.7562° 20 and 31.20° 20 suggest the presence of gypsum, a common by-product in paperboard production, particularly in processes that use calcium sulfate. The presence of gypsum in PBS is anticipated owing to the use of sulfur-containing chemicals in the pulping and bleaching procedures (41). Birnessite and cristobalite were also identified at 42.5348° 20 and 31.2087° 20, respectively.





Fig. 8. XRD patterns reveal the crystalline and amorphous phases of (A) PBS and (B) PBSB.

Cristobalite likely formed during high-temperature processes or was present in raw materials containing silica, which is linked to using siliceous materials in paper production. The peak at 12.5676° 20 indicates the presence of kaolinite, a common filler and coating material in the paper industry. Kaolinite contributed to the mineralogical composition of the sludge due to its abundance in raw materials and its stability during processing (42).

X-Ray Diffraction was performed to evaluate the PBSB properties (Fig. 8). PBSB exhibited distinct peaks of a more crystalline phase. The higher crystallinity may enhance the structural integrity of biochar, making it more resistant to microbial degradation and physical breakdown in the soil. This increased crystallinity helps biochar persist in the soil over the long term. The strong crystalline peaks observed at 29.4806° 20, 23.1277° 20 and 39.4954° 20 are attributed to the presence of calcite, indicating the presence of CaCO<sub>3</sub> used in paper production processes, which may serve as fillers or pigments (43, 44). During pyrolysis, calcite remains stable due to its resistance to low temperatures. Diffraction peaks observed at 38.433° 20, 44.6943° 20 and 8.2525° 20 indicate the presence of digold indium palladium. Additionally, bromargyrite and richetite were identified at the peaks of 30.9986° 20, 12.3800° 20 and 24.1132° 20, respectively. The amorphous peaks observed at 6640° 20, 20.7772° 20, 51.1810° 20 and 55.1871° 20 correspond to gypsum (deuterated), while cerussite was identified at the peaks of 19.9383° 20, 24.8730° 20, 25.4680° 20, 35.0031° 20 and 41.2524° 20.

# Conclusion

This study highlights the potential of converting PBS into biochar through slow pyrolysis, which significantly modifies its physicochemical properties. PBSB generally has high levels of organic carbon, fixed carbon, TOC, carbonates and aluminosilicates, as confirmed by FTIR spectroscopy and SEM-EDX analyses. These findings emphasize the efficacy of slow pyrolysis in enhancing carbon content and refining the chemical composition of PBS, corroborated by XRD reports.

Biochar improves soil structure by increasing porosity and enhancing water retention capacity, which promotes better root growth and moisture availability. It also boosts nutrient retention and exchange, improving nutrient accessibility for



plants. These enhancements increase agricultural productivity while promoting sustainable and eco-friendly management practices. Additionally, biochar shows considerable promise as an option for pollutant removal.

The sustainable development of biochar production is particularly evident when utilizing industrial waste. This approach transforms waste materials into valuable resources, reducing reliance on landfills and minimizing greenhouse gas emissions. By creating closed-loop systems, where by-products of one process serve as inputs for another, this strategy supports the principles of the circular economy. Such integration promotes innovation, resource efficiency and environmental sustainability while enhancing local economies, improving waste management and enabling energy recovery. The circular bioeconomy addresses waste issues through these practices and supports the transition towards more sustainable agricultural and industrial systems.

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## **Authors' contributions**

All authors have made substantial contributions to the conception, design, analysis, and interpretation of data for the work. VP and SJRT have contributed to critically drafting and revising the manuscript for important intellectual content. All other authors, BM, VC, RSA, SK and SM, gave final approval to publish the version. They agreed to be accountable for all aspects of the work, ensuring that questions related to the accuracy or integrity of any part are appropriately investigated and resolved.

# **Compliance with ethical standards**

**Conflict of interest:** The authors declare no conflict of interest.

Ethical issues: None

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