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Valorization of peanut shells through biochar production using slow and fast pyrolysis and its detailed physicochemical characterization

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Valorization of peanut shells has recently gained prominence in the context of thermally converting agricultural waste into biochar, a carbon-rich byproduct with significant potential as a soil amendment. The present study delves into understanding the influence of slow (450°C and 500°C) and fast (550°C and 600°C) pyrolysis temperatures with a resident time of 60 and 30 minutes, respectively, on the physico-chemical properties of peanut shell biochar produced in a low-cost kiln. Results of the Scanning Electron Microscopy analysis revealed that increased pyrolysis temperature increased porosity and surface roughness with crystalline deposits. Thermogravimetric analysis showed that increased temperatures contributed to enhanced thermal stability but reduced biochar yield. Pyrolysis temperatures of 450, 500, 550, and 600°C exhibited 32.19, 29.13, 21.8, and 19.43 percent conversion efficiency with organic carbon content of 11.57, 6.48, 8.64, and 7.76 percent, respectively. The intensities of functional groups (C-H and C-O) declined, whereas the intensity of C=C and stable carbon content increased with the rise in temperatures. The concentrations of heavy metals in all biochar samples were below permissible limits outlined by international biochar initiatives. The study concluded that slow pyrolysis at 450°C for 60 minutes resident time is an ideal pyrolytic condition for producing peanut shell biochar in terms of qualitative and quantitative characteristics.

KEYWORDS

peanut shells, biochar, slow and fast pyrolysis, SEM-EDX, FTIR, TGA

1 Introduction

Soil is a dynamic realm that is pivotal in the natural geochemical cycle. It encompasses decaying organic matter, plant nutrient cycles, and carbon sequestration (Holatko et al., 2022). Soil organic matter (SOM) comprises soil organic carbon (SOC), which constitutes approximately 45–60% of the total mass of SOM (Lal, 2016). The maintenance of the SOC pool

is paramount for optimal soil structure, aeration, water retention, nutrient retention, and rhizosphere processes (Chander et al., 2023). Soil management has a significant impact on whether carbon is released into the atmosphere or remains in the soil (Ray et al., 2022; Singh et al., 2022). Agricultural waste can be used to create customized carbon-based materials due to its high oxygenated functional groups and low condensation levels (Bai et al., 2020; Zhang et al., 2023).

Thus, regenerative agriculture practices such as the incorporation of crop residues into soil, mulching, composting, biochar production, and their subsequent application in the soil will increase the SOC and build resilience in the agriculture sector (Jat et al., 2022; Venkatesh et al., 2023). In this context, biochar, a carbon-rich product obtained through the pyrolysis of organic materials, has garnered attention for its myriad applications in soil amendment, carbon sequestration, and waste management (Murtaza et al., 2021; Hu et al., 2022; Kumar et al., 2024; Yadav et al., 2021). It is anticipated that chemical fertilizer usage will decrease when biochar is applied as a soil amendment because it can enhance soil quality (Doran and Zeiss., 2000; Das et al., 2021; Osman et al., 2022).

Globally, peanut cultivation covers 327 lakh hectares with a production of 539 lakh tonnes annually. India ranks first in the cultivation of peanuts (45.53 lakh hectares). It is the world's secondlargest producer (101 lakh tonnes) with a productivity of 1863 kg ha⁻¹ (Crop Outlook Reports of Andhra Pradesh: Maize, 2022). Peanut shells, which account for 30% of the weight of peanuts, are expelled as waste during deshelling processing (Singh, 2004). Although the peanut industry produces approximately 11 million tonnes of waste (shells) annually, its potential uses remain largely untapped (Verheijen et al., 2010). It is currently used on a limited scale for producing valueadded products viz., biodiesel, bioethanol, carbon nanosheets, and building material through industrialized processes (Duc et al., 2019; Zheng et al., 2023). The peanut shells have a unique composition of cellulose (45%), hemicellulose (6%), and lignin (36%), making them suitable for recycling and can be used as a soil amendment. However, due to high lignin content, peanut shells have a slow decomposition rate in the natural environment. Thus, producing biochar through pyrolysis using a low-cost kiln offers an effective solution for recycling peanut shells (Gupta et al., 2022; Kumar et al., 2023), which has demonstrated positive impacts on soil health, as evidenced by various studies (Omidi et al., 2017; Fall et al., 2018).

Pyrolysis techniques and residence time are crucial for the quantitative and qualitative aspects of biochar production (Tan et al., 2018; Moradi et al., 2019; Ong et al., 2021; Mukherjee et al., 2022; Joshi et al., 2023). Studies were conducted on producing biochar from peanut shells using different methods such as pyrolyzing units, muffle furnaces, fixed bed glass reactors, and microwave-based pyrolysis. However, more research is needed on the characterization of biochar produced from peanut shells using low-cost kilns and the economic feasibility of the process (Abbhishek et al., 2021). Slow pyrolysis performed under lower temperatures (<400–500°C) and with long contact times often results in a high yield of biochar (35%) (Meyer et al., 2011). Faster pyrolysis operates at higher temperatures (<800°C) and gives a high yield of combustible gases in relation to the solid biochar (12%) (Laird et al., 2009; Bruun, 2011; Abdullah et al., 2023).

Centralized peanut shell recycling procedures limit the scaling up of valorization and carbon sequestration potential of peanut shells, so the need for low-cost biochar production technology becomes imperative. The present prudent study uses an extensive range of analytical techniques *viz.*, scanning electron microscopy coupled with energy diffraction (SEM–EDX), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and elemental analysis characterize peanut shell biochar produced through fast and slow pyrolysis at different temperature in a low-cost pyrolytic kiln (Venkatesh et al., 2013; Pasumarthi et al., 2024) that functions based on direct up-draft principle.

2 Materials and methods

2.1 Material collection

The peanut shells used in this study were collected from the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) farm, located at the Patancheru campus (geographical coordinates: 17° 15' N latitude and 77° 35' E longitude). After collection, the shells underwent a meticulous cleaning process to remove any adhering dirt or foreign materials. They were stored in a shaded environment to preserve their integrity and moisture content until their use in biochar preparation.

2.2 Biochar production and kiln specifications

An inexpensive, indigenously fabricated portable single-barrel kiln was used for biochar preparation. The kiln is 88 cm in length, 81 cm in circumference, and 58 cm in diameter. An opening with a lid for feeding the feedstock with a dimension of 31×31 cm is provided on the upper surface of the kiln. In addition, to aid in the incinerating process, the bottom surface of the kiln has about 20 apertures with a diameter of 3.2 ± 0.1 cm (Pasumarthi et al., 2024). A wire mesh was placed in the bottom of the kiln, and the peanut shells were weighed and fed into the biochar kiln. Different pyrolytic temperatures and resident times were applied: slow pyrolysis at 450°C and 500°C for 60 min and fast pyrolysis at 550°C and 600°C for 30 min. The samples are abbreviated as follows: GB-450 (biochar produced at 450°C with 60min resident time), GB-500 (biochar produced at 500°C with 60 min resident time), GB-550 (biochar produced at 550°C with 30 min resident time), and GB-600 (biochar produced at 600°C with 30 min resident time). The below formula was used to calculate the yield of the biochar produced. The process of the thermo-chemical conversion of peanut shells to biochar using a kiln is illustrated in Figure 1.

$$Yield(\%) = (WBC / WRB) \times 100$$
(1)

WRB, weight of raw biomass; WBC, weight of biochar.

2.3 Biochar characterization

2.3.1 Chemical analysis

The analysis of biochar samples encompassed the determination of various parameters, including organic carbon -OC (Walkley-Black method), total nitrogen-N, phosphorus-P (Setter et al., 2020), potassium-K (Olsen and Sommers, 1982; Helmke and Sparks, 1996),



sulfur-S (Tabatabai, 1996), boron-B (Keren, 1996), zinc (Zn), iron (Fe), copper (Cu), magnesium (Mg), sodium (Na), calcium (Ca), and manganese (Mn) (Lindsay and Norvell, 1978; Yu et al., 2019). The investigations followed standard procedures at the Charles Renard Analytical Laboratory (CRAL) at ICRISAT.

2.3.2 Scanning electron microscopy (SEM-EDX)

The biochar samples derived from peanut shells were analyzed using SEM and EDX. The Quanta FEG 250 SEM model from Eindhoven, Netherlands, was used with a resolution range capacity of a minimum of 1 nm to examine the surface morphology of biochar samples. The instrument supported with xT microscope control V6 2.8 software was used to investigate the pore size of the biochar samples.

2.3.3 Fourier transform infrared spectroscopy

The biochar samples were analyzed using Fourier transform infrared spectroscopy (FTIR; Shimadzu, Japan) to examine their surface chemistry or functional groups. The method employed was the KBr pellet technique, recording 50 scans per sample, and each spectrum had an infrared range of $4,000-400 \text{ cm}^{-1}$ as per the protocol by Liu et al. (2015).

2.3.4 Thermo gravimetric analysis

The peanut shell biochar samples were subjected to thermogravimetric analysis (TGA) using a thermogravimetric instrument (TGA-DSC, Model: Discovery SDT 650). The protocol employed for the TGA study was adopted from Kumar et al. (2019).

2.3.5 X-ray diffraction

The crystalline constituents of the biochar samples were determined by XRD analysis using an X-ray diffractometer (Make: Bruker D8 Advance) at a diffraction angle of 10–80° (Meili et al., 2019).

2.3.6 Examination of biochar stability

In accordance with Jindo and Sonoki (2019), the biochar samples were subjected to the chemical oxidation method (Edinburgh stability tool) to test for stability. Using a TCN analyzer (Skalar PRIMACS SNC 100 Carbon/Nitrogen analyzer), the carbon content of the dried residue was determined using the Dumas dry combustion method. The following formula was used to determine the stable carbon.

Stable carbon (%) =
$$\begin{cases} \left[Carbon (g) after 5\%H_2O_2 \text{ treatment} \right] / \\ \left[Carbon (g) before 5\%H_2O_2 \right] \end{cases} \times 100 \quad (2)$$

2.3.7 Examination of heavy metals

The presence of heavy metals has been tested using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

2.4 Statistical analysis

Statistical analysis such as standard deviation (SD), coefficient of variation (CV), and Standard error of the mean (SEM \pm) to estimate the significant difference between the treatments were performed using SPSS 17.0 version statistical tool.

3 Results and discussion

3.1 Biochar yield under slow and fast pyrolysis

Biochar was produced from peanut shells using a low-cost portable biochar Kiln through a slow and fast pyrolysis process. It was observed that the quantity of biochar produced was less under a fast pyrolysis process, i.e., 550°C and 600°C for 30 minutes, compared to a slow pyrolysis process, i.e., 450°C, 500°C, for 60 minutes. In a study conducted by Cheng et al. (2021), it was observed that the polygeneration process was applied to cotton stalk at six different pyrolysis temperatures, and the yield distributions of biochars, polylignous acids, and gas were investigated. As the pyrolysis temperature was increased from 300 to 500°C, the biochar yield decreased from 46.71 to 33.15%. The percentage of biochar yields obtained at 450°C, 500°C, 550°C, and 600°C pyrolytic temperatures are 32.19, 29.13, 21.8, and 19.43, respectively. In a study conducted by Sun et al. (2017), it was observed that an increase in pyrolysis temperature resulted in a decrease in biochar yield. The study aimed to determine the influence of pyrolysis temperature and residence time on the physiochemical characteristics of biochar. These findings are similar to a study conducted by Zhao et al. (2018). In a study conducted by Nazir et al. (2021) on peanut shell biochar production using a pyrolyzing unit, the yields were 41, 36, and 33% at 250°C, 400°C, and 500°C, respectively. According to Selvarajoo and Oochit (2020), biochar yield reduced from 54.83 to 26.67% as the pyrolysis temperature increased from 300 to 900°C. This phenomenon is due to the extensive decomposition of lignocellulosic components at higher temperatures, leading to a reduction in biochar yield. Therefore, it is recommended to use lower temperatures (slow pyrolysis) to achieve higher biochar yield.

3.2 Chemical analysis

The composition of biochar is greatly affected by the pyrolysis temperature; with higher temperatures, the intensity of certain elements reduces due to volatilization or transformation. The nitrogen content was found to decrease with an increase in temperature during both fast and slow pyrolysis methods; a similar trend was observed in a study on peanut shell biochar production at 250°C, 400°C, and 500°C using pyrolyzing units (Nazir et al., 2021). However, some elements, such as potassium, peaked at intermediate temperatures, suggesting complex interactions during biochar formation. This data is vital for understanding the nutrient profile of biochar and its potential application in soil amendment or other uses (Pariyar et al., 2020).

In a study conducted by Omotade et al. (2020), the effect of pyrolysis temperature on the nutrient content of biochar derived from corn cobs, poultry litter, cow dung, and peanut shells was investigated. The biochar was produced at different temperatures of 300°C, 400°C, 500°C, and 600°C with a residence time of 3 h, using a heating rate of 10°C per minute. The highest nutrient contents (N, P, K, Ca, Mg, and S) were observed in corn cob biochar prepared at the lowest temperature, i.e., 300°C. Results from the present study are in agreement with those of Omotade et al. (2020). It was observed that the nutrient content of the biochar prepared by fast pyrolysis at 600°C with a resident time of 30 min was higher compared to fast pyrolysis at 550°C except for OC, B, Cu, and Mn (Table 1). The fast pyrolysis process, having a temperature of 550°C and 600°C and a residence time of 30 min, yielded less biochar with less organic carbon (8.64 and 7.76%) than biochar derived at 450°C. It was evident from these results that both fast and slow pyrolysis methods lead to a decrease in yield and organic carbon content with an increase in temperature (Table 1). Biochar produced at 450°C, 500°C, 550°C, and 600°C has OC content of 11.57, 6.48, 8.64, and 7.76%, respectively.

Studies have shown that the fixed carbon content of biochar increases with pyrolysis temperature. However, high temperatures or fast pyrolysis processes can result in a loss of carbon (Sun et al., 2017; Dahal et al., 2018; Dai et al., 2019; Yuan et al., 2019). According to a recent meta-analysis study on biochar carbon content, it was found that biochar produced at a lower temperature has a higher organic

carbon content, which is consistent with other studies that have reported similar findings (Wijitkosum and Jiwnok, 2019). This phenomenon can be attributed to the breakdown of aromatic rings at increased temperatures ranging from 500 to 600°C, leading to a reduction in organic carbon content. N, P, Ca, and Mg content decreases with increasing temperature, indicating potential volatilization or transformation of these elements at higher temperatures, whereas potassium content peaks at 500°C and decreases at 600°C. Elements such as sulfur (total-S), zinc (total-Zn), boron (total-B), iron (total-Fe), copper (total-Cu), manganese (total-Mn), and sodium (total-Na) also showed varied concentrations at different temperatures (Pariyar et al., 2020).

3.3 Surface morphology by scanning electron microscopy (SEM)

The biochar samples' surface morphology and pore size have varied with temperature. The macropore size increased with an increase in temperature. Variations were observed in surface morphology and macropore size, as the peanut shell biomass has cellulose, hemicellulose, and lignin, which respond differently to increased temperature under anoxic conditions. The observations were similar to the findings from experiments by Tanquilut et al. (2019) and Woźniak et al. (2021). The study by Yaashikaa et al. (2020) found that the surface morphology of biochar samples varied depending on the pyrolysis method and temperature. The surface morphology and macropores of the biochar prepared under slow and fast pyrolysis conditions are shown in Figure 2. Peanut shell biochar exhibits a combination of oval to slightly irregular macropore shapes. At 450°C, the structure is slightly denser with fewer visible cavities, suggesting that the lower temperature has not fully degraded the peanut shells, resulting in a less porous biochar, indicative of a preliminary stage of pyrolysis where the organic components are beginning to break down. The surface topology becomes more intricate as the temperature increases to 500°C. There is an increased prevalence of interconnected macropores, suggesting an enhancement in biochar porosity. This temperature fosters a more

TABLE 1 Elemental analysis of biochar samples produced at different temperatures.

Parameter	GB-450	GB-500	GB-550	GB-600	SD	SEM (<u>+</u>)	CV (%)
OC (%)	11.57	6.48	8.64	7.76	2.16	1.08	25.10
Total-N (ppm)	15,656	11,374	10,061	16,399	3126.99	1563.49	23.38
Total-P (ppm)	3,464	2,658	3,313	4,438	735.08	367.54	21.19
Total-K (ppm)	14,414	14,101	18,084	23,583	4412.57	2206.28	25.15
Total-Ca (ppm)	8,583	6,733	10,303	11,364	2029.61	1014.80	21.95
Total-Mg (ppm)	5,002	4,253	5,650	6,547	974.11	487.05	18.16
Total-S (ppm)	1,342	1,048	1,478	2007	401.20	200.60	27.32
Total-Zn (ppm)	743	274	1,300	553	433.48	216.74	60.42
Total-B (ppm)	104	97	190	102	44.60	22.30	36.18
Total-Fe (ppm)	10,173	10,069	14,197	9,198	2235.01	1117.50	20.49
Total-Cu (ppm)	28.72	31.75	40.46	36.62	5.19	2.60	15.10
Total –Mn (ppm)	165	265	266	202	49.70	24.85	22.14
Total-Na (ppm)	1760	1,631	2,146	2,473	382.44	191.22	19.10



FIGURE 2

Scanning electron microscopy of peanut shell-derived biochar samples at different pyrolysis temperatures: 450 (GB-450), 500 (GB-500), 550 (GB-550), and 600 (GB-600).

evolved pyrolysis process, leading to a higher degree of carbonization and pore development (Liu et al., 2015). The biochar produced at 550°C (GB-550) showed an even more fragmented morphological characteristic. The diversity in the particle shapes ranged from slender shards to more substantial fragments, hinting at a differential degradation rate and further breakdown of the organic material in the peanut shells.

At the highest temperature of 600°C, the biochar exhibited high porosity, with the pores appearing more irregular in dimension and varied in size. The crystalline depositions become more pronounced at this temperature, possibly because of the mineral content or residues solidifying after most volatile components have been expelled (Weidner et al., 2022). The pyrolysis temperature determines peanut shell biochar's surface morphology and porosity. As the temperature increases, the biochar undergoes more extensive carbonization, enhancing porosity and distinct structural features. These observations underscore the significance of optimizing pyrolysis temperatures to tailor the properties of biochar for specific applications (Leng et al., 2021). The porosity of biochar increases with temperature, which can enhance its water retention capacity, serving as habitat for microbial communities and improve soil health. It was observed that fast pyrolysis with less resident time generated biochar with uniform oval-shaped and bigger macropores compared with biochar produced through slow pyrolysis with more resident time.

3.4 Fourier transform infrared spectroscopy

The FTIR provides insights into the functional groups present on the biochar surfaces. The presence of hydroxyl, carbonyl, and aromatic groups can be ascertained, allowing for an understanding of biochar's chemical properties and potential interactions in environmental applications. The FTIR spectra (Figure 3) revealed that the peak near 2,920 cm⁻¹ corresponding to aliphatic C–H stretching, became less pronounced with higher pyrolysis temperatures, indicating the reduction or elimination of aliphatic compounds, which is in accordance with the findings by Antonangelo et al. (2019). These results are similar to previous research findings on the pyrolysis of bamboo conducted by Zheng et al. (2017), Qin et al. (2020), and Hadey et al. (2022).

The intensity of peaks observed around 1700 cm⁻¹ in the spectra for GB-450 and GB-500, which are attributed to the presence of carbonyl or carboxylic groups, decreased significantly as the temperature increased, which may signify a loss of more volatile components and decomposition of carboxylic materials. The high concentration of carbonyl functional groups in the peanut shell biochar implies that cellulose and hemicellulose have been broken down into volatile compounds. The results published by Sahoo et al. (2021) and Hadey et al. (2022) are in agreement with the findings of the present study. Peaks in the region of 1,600 cm⁻¹ are associated with aromatic C=C stretching vibrations. These peaks retain their intensity or become slightly more defined during fast pyrolysis at 550°C, suggesting that the stabilization of aromatic structures during pyrolysis is in agreement with the results reported by Bayartsengel et al. (2021) on biochar produced from various biowastes and the findings of Reza et al. (2020) and Zhang et al. (2020).

As the temperature increased, the peak at 1030 cm⁻¹, representing C-O stretching vibrations, appeared less intense. This suggests that the C-O groups had undergone thermal degradation. This finding is

consistent with Chellappan et al. (2018) research, which also showed similar trends in the thermal decomposition of materials derived from biomass. The reduction in peaks associated with aliphatic C– H stretching with increased pyrolysis temperature suggests that dehydration and decarboxylation reactions are prevalent, leading to a more carbon-rich and less reactive biochar (Li and Chen, 2018). The persistence and slight enhancement of aromatic C=C structures at higher temperatures indicate the formation of a more stable carbon network, characteristic of the charring process that enhances the fixed carbon content of biochar (Qin et al., 2022). The changes observed in the FTIR results indicate organic compounds' decomposition and transformation within the biochar.

Overall, the FTIR results of peanut shell biochar elucidate a decreasing trend in the functional group intensity with increasing pyrolysis temperatures except for C=C, which increased with increasing pyrolysis temperature. These changes depict the decomposition and transformation of the organic compounds within the biochar, leading to increased carbonization and aromaticity.

3.5 X-ray diffraction (XRD)

The XRD patterns of biochar produced from peanut shells at different temperatures and residence times showed crystalline phases. The presence of these crystalline phases, as well as inorganic minerals from the original organic material, can be detected using XRD (Bai et al., 2020). As shown in Figure 4, the detection of peaks ranging from $2\Theta \approx 24^{\circ}$ and 28° were predominantly linked to the crystalline configurations of calcite (CaCO₃) and sylvite (KCl) (Pariyar et al., 2020). Peaks within the 50–75° range suggested the existence of silicates and quartz associated with Mg, Ca, and Mn. XRD analysis indicated various inorganic constituents in the biochar. The results



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were similar to those of other products of biomass carbonization, such as rose petals (IIkhtiarini and Tjahjanto, 2019) and eucalyptus wood (Fernandes and Mendes, 2020). However, the biochar prepared at a higher temperature (600°C) shows a reduction of wide peaks, which are noticed in the biochar prepared at 450°C. This indicates that the amorphous structure has been reduced by increasing the temperature. Across all pyrolysis temperatures, carbon consistently emerged as the significant component of biochar, aligning with the findings of Chen et al. (2009). The material degradation at higher temperatures and exposure to minerals improves peak distinction. The peak representing calcite (CaCO₃) was intensified in slow pyrolysis at 500°C with a residence time of 60 min, and a similar pattern was observed in biochar prepared using fast pyrolysis at 600°C with a residence time of 30 min. The peak at two theta value of 42.5 represents the presence of Fe_3O_4 (Saeed et al., 2021), and the intensity decreased with an increase in temperature beyond 500°C, this might be due to destabilization and loss of oxygen at higher temperatures. This is in alignment with the elemental analysis of the present study in which Fe intensity decreased with increasing temperature. The peak at two theta value of 36.5, which was in biochar prepared at 450°C has disintegrated with an increase in temperature to 500°C and above.

3.6 Electron dispersive X-ray (EDX)

The EDX analysis results are given in Table 2 and Figure 5. The elements carbon (C), oxygen (O), potassium (K), magnesium (Mg),

and calcium (Ca) are considered important minerals present in biochar for their use as soil amendment (Zaitun et al., 2022). The EDX results indicated that carbon was the dominant element, followed by O, N, Mg, and K, which was also observed in the study undertaken by Reza et al. (2023). No significant difference was observed in carbon weight and atomic percentages with slow and fast pyrolysis at varying temperatures. However, biochar prepared using fast pyrolysis at 550°C with 30 min of resident time has slightly higher carbon weight and atomic percentages, i.e., 89.2 and 92%, respectively. Biochar prepared using fast pyrolysis at 600°C has a higher content of N, O, Mg, and K than those produced at 450, 500, and 550°C. Zhao et al. (2018) showed that the properties of rapeseed stem biochar were significantly impacted by the pyrolysis conditions, such as temperature, residence time, and heating rate. The study reported that N, Mg, and K contents decreased as the temperature increased during slow and fast pyrolysis. However, the fast pyrolysis process at 550°C resulted in lower N content than the slow pyrolysis process (Table 2).

3.7 Thermogravimetric analysis

The thermogravimetric analysis (TGA) analysis of biochar derived from peanut shells at various pyrolysis temperatures (450–600°C) is shown in Figure 6. The consistent change in the weight (or weight loss) was observed at all four temperatures, which indicates the loss of bound moisture or some light volatile components that are consistent across the samples (Tomczyk et al., 2020; Das et al., 2021). The TGA curve of the



FIGURE 4

X-ray diffractogram of biochar prepared from peanut shell biochar samples at different pyrolysis temperatures 450 (GB-450), 500 (GB-500), 550 (GB-550), and 600 (GB-600).

TABLE 2 SEM- EDX analysis results of biochar derive	ed from peanut shells.
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Sample	Carbon (C)		Nitrogen (N)		Oxygen (O)		Magnesium (Mg)		Potassium (K)	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
GB-450	82.8	87.3	0.7	0.7	14.3	11.3	1.6	0.5	0.5	0.2
GB-500	78.9	85.1	0.4	0.4	15.9	12.9	0.4	0.2	4.4	1.5
GB-550	89.2	92	1.8	1.6	7.4	5.8	0.5	0.3	1	0.3
GB-600	73.8	80.9	3.7	3.5	16.5	13.5	0.3	0.2	5.7	1.9
SD	6.50	4.62	1.49	1.40	4.19	3.51	0.61	0.14	2.55	0.85
SEM (±)	3.25	2.31	0.75	0.70	2.09	1.75	0.30	0.07	1.27	0.43
CV (%)	8.00	5.35	90.50	90.09	30.96	32.26	86.50	47.14	87.82	87.58

SD, standard deviation; SEM (±), standard error of mean; CV, coefficient of variation.



biochar derived at 450°C and 500°C (slow pyrolysis) reveals that degradation starts at approximately 274.33°C (29.02% weight loss), 286.46°C (19.74% weight loss), and culminates at approximately 361.08°C and 358.77°C, respectively. The biochar produced at higher temperatures exhibited less percentage weight loss during thermal degradation (TGA) compared to those produced at low temperatures. This means that slow pyrolysis showed increased thermal resistance with increasing temperatures. On the other hand, the TGA (thermogravimetric analysis) curve of the biochar derived at 550°C, and 600°C (fast pyrolysis) showed that degradation started at approximately 366.69°C (30.96% weight loss), and 352.07°C (19.77% weight loss), and degradation process culminated at around 486.96°C, and 493.40°C, respectively. The thermal stability of biochar increased with higher pyrolysis temperatures, which align with the findings of Cárdenas et al. (2022). The weight loss percentage decreased as the pyrolysis temperature increased. The most stable biochar was produced at 500°C and 600°C with a residence time of 60 and 30 min, respectively. The results are in

agreement with the findings by Leng et al. (2019), which indicate a significant change in the rate of weight loss around 119.13°C. The sample degradation has initiated at 362.07°C and terminated at 493.40°C in the case of the biochar produced at 600°C. Weight considerations showed a loss of approximately 1.61 mg, resulting in a pronounced percentage reduction of 30.96%. From the TGA graphs, it can be inferred that as the pyrolysis temperature increases, the stability of the biochar also increases. As the pyrolysis temperature increases during both slow and fast pyrolysis, the stability of biochar has increased, which was evident from the decrease in weight loss when heated to 1,200°C. It was observed that the thermal destabilization of slow pyrolyzed biochar initiated at low temperatures compared to biochar prepared above 500°C. This indicated the importance of temperature in achieving thermally stable biochar. Li and Chen (2018) conducted a study on the production of biochar from switchgrass, biosolids, and water oak, revealing the requirement of elevated combustion temperatures to achieve significant mass loss in biochar derived at higher pyrolysis temperatures.

3.8 Carbon stability

The results indicate a clear trend, where the percentage of stable carbon in biochar increases with the pyrolysis temperature (Figure 7). Stable carbon content is an important indicator of the biochar's quality and its potential for long-term carbon sequestration in soil. The increased stable carbon content at higher temperatures suggests a higher degree of carbonization and the formation of aromatic carbon structures resistant to decomposition (Pasumarthi et al., 2024).

3.9 Heavy metal contamination

The data presented in Table 3 indicates that the concentrations of copper (Cu), chromium (Cr), lead (Pb), and nickel (Ni) in peanut shell biochar increased with the pyrolysis temperature from 450°C to 600°C. Cadmium (Cd) was not detected in biochar prepared at any temperature. All heavy metal concentrations in the biochar are below the permissible limits set by the International Biochar Initiative (Nzediegwu et al., 2019). Therefore, the low levels of potentially toxic elements suggest that the biochar produced using peanut shells could be used as a soil amendment.



FIGURE 6

TGA of biochar samples prepared from peanut shells at different pyrolysis temperatures, 450 (GB-450), 500 (GB-500), 550 (GB-550), and 600 (GB-600).



Influence of pyrolysis temperature on the stable carbon content of peanut shell biochar, bars on the column indicates standard error mean; alphabets with different letters on the column shows significant difference as per Duncan's multiple range test.

3.10 Economics of biochar production

The production economics of biochar using a kiln is given in Table 4. The cost of six kilns is about 108.4 USD, which is inclusive of the drum, perforations, and handle fitting. The production economics was calculated considering 200 working days per annum and 100 kg biomass utilization per day. The conversion efficiency of biomass to biochar varies with temperature, highest at 450°C (32.19%) and lowest at 600°C (19.43%). The economic analysis indicates that producing

biochar from peanut shells is most economically feasible at a pyrolysis temperature of 450°C, fetching the highest Benefit–Cost Ratio (BCR) of 1.51. As the temperature increases, there is a marked decline in profitability, primarily due to a decrease in conversion efficiency. Having the existing technologies to produce biofuels, carbon nanosheets, cellulolytic enzymes, and building materials, a significant quantity of peanut shells remains unutilized in a sustainable manner due to the lack of low-cost decentralized value-addition technologies. The present study stands unique as peanut shell biochar was produced

TABLE 3 Total concentrations of heavy metals (ppm) in biochar samples	-
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Biochar	Cu	Cd	Cr	Pb	Ni
Critical limit as per international biochar initiative (2023)	6,000	39	1,200	300	420
GB-450	20.3	0	10.63	10.45	29.38
GB-500	21.2	0	11.14	12.03	36.3
GB-550	32.1	0	11.3	12.34	36.33
GB-600	33.9	0	12.95	13.9	36.93
SD	7.12	-	1.00	1.41	3.58
SEM (±)	3.56	-	0.50	0.71	1.79
CV (%)	26.49	_	8.73	11.61	10.31

ppm, parts per million; SD, standard deviation; SEM (±), standard error of mean; CV, coefficient of variation.

TABLE 4 Cost of producing biochar from Peanut Shell using 100 kg biomass per day.

Particulars	Production economics of biochar @200 days/annum (in USD)			
(A) Capital investment	Per day	Per annum (200 working days)		
Cylindrical metal drum inclusive of perforations, top lid, and handle (@108.4 USD for 6 kilns)	108.4	108.4		
(B) Operational cost of biochar production				
Kiln operation (2 man-days)	9.6	1927.7		
Cost of Groundnut Shell @ 0.6 USD/ 100 kg	0.6	120.5		
The total operational cost of production of groundnut Shell biochar	10.2	2048.2		
(C) Production economics				
Conversion efficiency of Groundnut Shell (%)				
GB-450	32.2	32.2		
GB-500	29.1	29.1		
GB-550	21.8	21.8		
GB-600	19.43	19.43		
(D) Market Price of biochar: 0.48 USD/kg				
(E) Gross income				
GB-450	15.5	3102.7		
GB-500	14.0	2807.7		
GB-550	10.5	2101.2		
GB-600	9.4	1872.8		
(F) Benefit: Cost ratio				
GB-450	1.51	1.51		
GB-500	1.37	1.37		
GB-550	1.03	1.03		
GB-600	0.91	0.91		

using a low-cost pyrolytic kiln, which addresses multiple issues like deteriorating soil health, elevated greenhouse gas emissions, and societal perseverance towards biochar application. As per the computed economics of peanut shell biochar production in the present study, kiln-based biochar production at 450°C with 60 min of resident time is suitable for decentralized production in smallholder farmers' fields.

4 Conclusion

The study stands unique for using a portable kiln for peanut shell biochar production at 450°C, 500°C, 550°C, and 600°C with 60 and 30 min of resident time, respectively, and estimating its economics. It highlights the critical role of standardizing the pyrolytic conditions to enhance the quality and yield of peanut shell biochar. Higher pyrolysis temperature was found to result in increased porosity, crystalline deposits close to the macropores, structural changes, and increased thermal stability. However, the increase in temperature inversely affected the biochar yield. The FTIR findings reflected peak shifts and alterations across various temperatures, which can be attributed to the thermal degradation and modification of cellulose, hemicellulose, and aliphatic chains. The functional groups C-H and C-O intensities have decreased, and the C=C intensities increased with the increase in temperature but declined at 600°C. The slow pyrolytic method of producing biochar from peanut shells at 450°C was found to be better in terms of quality (11.57% OC) and yield (32.19%). In a nutshell, the present investigation advocates for the practical application of optimized biochar production method at the farm level, taking into account both economic and practical aspects and suggesting additional field research to investigate the long-term carbon sequestration potential of peanut shell biochar.

5 Way forward

Looking ahead, the research should focus on conducting long-term studies to explore the effects of biochar application on microbial diversity, plant health, and yield at the system level. Biochar, being a nature-based positive solution, needs to be assessed economically to cater to the process of curtailing carbon footprints and greenhouse gas emissions. The authors look forward to in-depth investigations on the role of catalysts in the optimization of the pyrolysis process, which will scale up biochar production for smallholder farms.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author/s.

Author contributions

GS: Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Visualization, Writing original draft, Writing - review & editing. RP: Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. SK: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. PC: Formal analysis, Project administration, Supervision, Validation, Writing - review & editing. SR: Writing - review & editing, Methodology, Conceptualization, Supervision, Visualization, Formal analysis, Validation. SM: Formal analysis, Validation, Writing - review & editing. AS: Formal analysis, Validation, Writing - review & editing. HS: Conceptualization, Methodology, Supervision, Writing - review & editing. MR: Formal analysis, Validation, Writing - review & editing. RS: Conceptualization, Formal analysis, Methodology, Supervision, Validation, Writing review & editing. MJ: Resources, Writing - review & editing. AP: Writing - review & editing, Methodology, Conceptualization, Visualization.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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