Article

Bio-Char Characterization Produced from Walnut Shell Biomass through Slow Pyrolysis: Sustainable for Soil Amendment and an Alternate Bio-Fuel

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Abstract: Bio-char has the ability to isolate carbon in soils and concurrently improve plant growth and soil quality, high energy density and also it can be used as an adsorbent for water treatment. In the current work, the characteristics of four different types of bio-chars, obtained from slow pyrolysis at 375 °C, produced from hard-, medium-, thin- and paper-shelled walnut residues have been studied. Bio-char properties such as proximate, ultimate analysis, heating values, surface area, pH values, thermal degradation behavior, morphological and crystalline nature and functional characterization using FTIR were determined. The pyrolytic behavior of bio-char is studied using thermogravimetric analysis (TGA) in an oxidizing atmosphere. SEM analysis confirmed morphological change and showed heterogeneous and rough texture structure. Crystalline nature of the bio-chars is established by X-ray powder diffraction (XRD) analysis. The maximum higher heating values (HHV), high fixed carbon content and surface area obtained for walnut shells (WS) samples are found as ~ 18.4 MJ kg⁻¹, >80% and 58 m²/g, respectively. Improvement in HHV and decrease of O/C and H/C ratios lead the bio-char samples to fall into the category of coal and confirmed their hydrophobic, carbonized and aromatized nature. From the Fourier transform infra-red spectroscopy (FTIR), it is observed that there is alteration in functional groups with increase in temperature, and illustrated higher aromaticity. This showed that bio-chars have high potential to be used as solid fuel either for direct combustion or for thermal conversion processes in boilers, kilns and furnace. Further, from surface area and pH analysis of bio-chars, it is found that WS bio-chars have similar characteristics of adsorbents used for water purifications, retention of essential elements in soil and carbon sequestration.

Keywords: walnut shells; pyrolysis; higher heating values; bio-char; surface area

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1. Introduction

Continuous environmental issues, ascending prices of petroleum, energy crisis, exhaustion of fossil fuels, increasing application and need for energy are the serious motivations, due to which there is much insistence on substitute sustainable energy sources. Environmental friendliness, sustainability and biodegradability are the important characters which have made the biomass a primary candidate for the generation of bio-energy. The conversion technologies are the possible options to explore the economic potential of bio-resources. Bio-fuels and bio-chemicals are formed through thermo-chemical conversion, which includes pyrolysis, gasification, liquefaction and combustion [1]. Pyrolysis is the most striking process for converting biomass into bio-fuels [2]. Volatiles and semi-volatiles are discharged from the

feedstock residues during pyrolysis of biomass and yields gases, bio-oil and chars. Further, bio-char may be formed with re-condensing vapors into the bio-char material depending on the residence time of vapor, which increases the bio-char products [3,4].

Bio-char is the solid yield of pyrolysis and has different properties in comparison to the corresponding feedstock's, and can deliver considerable and sustainable diversity in securing an upcoming resource of green energy [5]. It has got several commercial applications, such as fuel production [6,7], energy storage [8], soil improvement [9], soil conditioner [4,10] animal farming, building sector, drinking and wastewater treatments, biogas production, industrial materials (plastics, carbon fibers), exhaust filters, energy production (substitute for lignite, pellets), electronics semiconductors, batteries), paints and coloring (industrial paints, food colorants), cosmetics (therapeutic bath additives, skin-cream, soaps), medicines (detoxification, carrier for active pharmaceutical ingredients), etc. [10–14] as illustrated in Figure 1. Further it can be upgraded by using appropriate methods [15], to form activated bio-char and value-added yields. Due to these applications, bio-char may be used as soil amendment and solid fuel due its high porosity, specific surface area and heating value near to coal. In Taiwan, bio-char is largely used for soil alteration as a result of its high-water absorption and surface area and acting as an activated carbon [16].

Figure 1. Bio-char potential applications of different sectors.

The origin of biomass source is an important parameter, which influences the characteristics of bio-char yield. Diversified potential biomass residues exist for bio-char formation including municipal wastes, animal manures, forestry and agricultural residues and another growing biomass. A large number of characters should be considered, however, when determining biomass feedstock suitability, like the sustainability requirements, possible toxicity of the bio-char, desired bio-char characteristics and end use [17]. The characteristics of the bio-char are affected by number of variables, such as pyrolysis temperature (maximum or minimum), feedstock size, retention time at the maximum temperature and the pyrolysis atmosphere [4,17,18]. A number of studies reported that the surface area of bio-char is higher as compared to their respective biomass [19] which makes bio-char a

suitable candidate to be either used as an adsorbent or as bio-fuel. Additionally, bio-char obtained from biomass is rich in minerals, therefore it can also be used to improve soil conditions [4,17]. Walnut shell bio-char may be a future and eco-friendly candidate for solid biofuel. Due to its high heating value and may replace the coal fuels (30 MJ kg^{-1}) in future. Jiang et al. [20], obtained chestnut bio-char by pyrolysis and the preparation were done by catalytic pre-oxidation with urea and sulfuric acid. The high heating (35.48 MJ kg^{-1}) value was recorded by this method.

Thermochemical conversion technologies such as pyrolysis are dominant to avert secondary pollution and beginning circular bioeconomy [21]. Environmentally sustainable and economically feasible technologies must be engaged to execute industrial-scale pyrolysis for manufacture of biochar, thus ease to commercialization and possible applications of biochar-based yields [4]. Pyrolysis of lignocellulosic biomass residues is an energy strategy and carbon-negative, needs profound investigation activities internationally [22] in the field of renewable energy substitutions [23], environmental pollution control [24], climate mitigation [25], sustainable towards food security and agriculture [26].

Ghodake et al. [27] reported an extensive work on pyrolysis mechanism and physicochemical properties of biochar. They discussed various aspects of in-management of biomass feedstocks supply chain, biomass feedstock composition and pyrolysis products. They discussed the possibility of a sustainable way of bio-char production and also how this could be a great material for soil amendment, agricultural and to achieve circular bioeconomy. Further, Lin et al. [28] have studied the torrefaction of fruit peel waste to yield environmentally friendly biofuel. In their work, it was reported that they used *Ananas comosus* peel and *Annona squamosa* peel samples to produce bio-char as a renewable energy source. Interestingly, it was found that the higher heating value of both bio-char was increased to $19.1\text{--}27.7 \text{ MJ/kg}$ after torrefaction. Additionally, they reported a high energy return on investment for renewable energy. Moreover, it was emphasized that the application of bio-char for partial coal substitution can reduce CO_2 emissions by $83.7\text{--}94.3\%$. Further, Romanowska-Duda et al. [29] discussed the promotive effect of Cyanobacteria and Chlorella sp. foliar biofertilization to produce feedstock production, solid biofuel and biochar. It was reported that triple foliar plant spraying with non-sonicated monocultures of Cyanobacteria and Chlorella sp. exhibited a considerably progressive impact on metabolic activity and development of plants. Bio-char can be produced in all scales from individual, domestic as well as the industrial levels and is most prominent and leading industry at various socioeconomic settings. The opportunity of multi-functionality structures and sustainable bio-char production practices creates an increasing demand in the fields of cutting-edge materials, soil amendment, environmental protection, agricultural sustainability and to achieve mitigation of climate variation and circular bio-economy. There is a necessity to understand the prediction of organic molecules, bioavailability, toxicity, concentration, surface functions, surface radicals, mobility and environmental fates about bio-char structures. The correlation between the structure, applications and mechanisms of bio-char is progressively developing to enhance their agronomic uses, to achieve precisely designed bio-char with a zero-waste dream [27–29].

In addition, circular bioeconomy focuses on the sustainable and resource-saving value of biomass in a broad and multi-generational production chain. Additionally utilizing residues and waste to optimize the value cascade of biomass in production. Recently, D’Adamo, Morone and Huisinigh [30] discussed a sustainable shift towards bioenergy. In this work they reiterated that bioenergy should be included in the bioeconomy sector. In that case, it would also include the agriculture and forestry and new manufacturing sectors. Currently, several types of agrochemical and biochemical processes are adapted to convert lignocellulosic residues into value-added yields. The microbial delignification joined with hydrolysis to increase biofuel yields such as methane [31], butanol [32], ethanol [33], hydrogen production [34] and fuel briquettes [35]. None of the literature reported the comparative study of four different types of walnut shells. In addition to this, we have carried out research work on the biomass agriculture residues available in

the State of Jammu and Kashmir, India, which has been again not studied earlier for this particular geographical area.

In the present study, walnut shells are considered as biomass residue for the production of bio-char. Walnut is cultivated mainly in Asian, European and American regions and is one of the important agricultural products for dry fruit industry. In the last decade, the production of walnut has increased by ~25% [36]. Walnut consists of oily material kernel (60%) and a hard covering shell (40%) [37]. The walnut shells, lignocellulosic biomass, have no utilization except being directly used for combustion in furnace, otherwise it is dumped in open areas. This study investigates the physio- and thermochemical characterization of bio-chars obtained from hard-shelled walnut (HSW), medium-shelled walnut (MSW), thin-shelled walnut (TSW) and paper-shelled walnut (PSW). HHV and molar ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) are determined. The pH values and surface area of different bio-chars are determined to propose their specific applications. Three different heating rates are used for TG analysis. Furthermore, bio-chars are also investigated by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectrometry to understand the product profile of bio-char samples obtained from different walnut shell samples.

2. Materials and Methods

2.1. Sample Collection and Preparation

Walnut samples of HSW, MSW, TSW and PSW were collected from the walnut business unit Jammu and Kashmir, India, and sundried for three days at a temperature of 25 °C with less than 47% humidity. Thereon, it was crushed by high speed ball mill and passed through screens in order to obtain particle sizes of 2.5–3, 1.5–2.5 and 0.5–1.5 mm. The sample biomass residues (Figure 2) was packed in an airtight PVC jar and stored in desiccators for further experiments.

Figure 2. (a) The original shape of walnut (b) shell residues and (c) their respective bio-chars.

2.2. Pyrolysis Setup: Pyrolysis of Biomass in a Fixed-Bed Reactor

Pyrolysis was carried out in a fixed-bed reactor. The internal diameter and length of the reactor were 122.26 and 1200 mm, respectively. The design pressure and temperature were 12 bars and 950 °C, respectively. It was surrounded by an electric furnace with P&ID controller to supply power for heating. Ni-Cr thermocouple was used to sense the temperature inside the reactor. A batch of 300 g of the individual feedstock was charged for pyrolysis by increasing the temperature from ambient to 375, 450, 550, 650 and 750 °C, respectively, at a heating rate of 10, 20 and 50 °C/min^{−1}. Nitrogen at a flow rate of 50, 100 and 150 cm³/min was used to keep the environment inert and oxygen-free, and also to carry over the condensable vapors produced during pyrolysis. These vapors were collected in a condensers I and II to collect oil and scrubbing tank to collect gas. The reaction was

performed for 35 min, or till no further release of gas was observed. Further, the bio-char was collected after cooling down the pyrolyzer to room temperature. The bio-char samples were stored in airtight PVC containers for further analysis.

2.3. Material Analysis

The proximate analysis of the bio-char samples was carried out as per ASTM standard procedures: E871–82 (2013), D1102–84 (2013) and E872–82(2013) for ash and volatile matter contents, respectively. Ash and volatile matters were determined at a temperature of 580 °C for 30 min and at a temperature of 950 °C for 7 min, respectively. Fixed carbon was calculated by subtracting the summation of the percentages of moisture, ash and volatile matters from 100. All percentages were on the same moisture reference basis (ASTM E871–82, 2013; (ASTM D1102–84, 2013; ASTM E872–82, 2013) [38–40].

Energy yield and densification of the bio-char yield produced at 375 °C were also calculated, according to the method proposed by Chowdhury et al. (2017) [41]. The energy densification was obtained by high heating value (HHV) of bio-chars divided by the HHV of biomass residues and the energy yield was calculated as the energy densification multiplied by the bio-char yield [42]. Ultimate analysis was achieved by using a CHNS elemental analyzer (Euro EA3000, Euro vector, Pavia, Italy) as per ASTM procedure D5373–08 (ASTM D5373–08, 2008) [43]. Higher heating values of the bio-char were determined by bomb calorimeter (CC01/M3; Toshniwal, New Delhi, India) using ASTM procedure D2015–85. 1.0 g bio-char samples was implanted in a calorimeter, and inflamed in the presence of oxygen. The heat of combustion was recorded for the calculation of HHV of bio-char samples (ASTM D–85, 2015) [44].

Surface area, pore volume and average pore size measurements of bio-char samples, obtained from different walnut shell residues, were investigated by nitrogen (N₂) adsorption/desorption isotherms at 77 K using Micromeritics ASAP 2060 V3.05 H Surface Area Analyzer (Brunauer–Emmett–Teller). About 3 mg of bio-char samples was degassed for 6 h at 200 °C under vacuum. Pore volume and average pore size were observed by using Barrett–Joyner–Halenda (BJH) and surface area with BET method.

The pH bio-char samples was measured using the following procedure: A total of 20 mL of deionized water was mixed with 0.5 g of bio-char with the help of magnetic stirrer, for 24 h at 100 °C at 150 rpm, in order to get homogeneous solution [43]. The suspension is filtered and equilibrium was reached after one hour. pH of the filtered sample was measured by using Orion pH meter (Thermo Scientific, Cambridge, MA, USA) for bio-char samples.

TGA was carried out by the thermogravimetric analyzer (SII 6300 Exstar; Hitachi, Tokyo, Japan). Runs were accomplished non-isothermally at three different heating rates (10, 20 and 50 °C/min). Nitrogen was used as a carrier gas, at a flow rate of 100 mL min^{−1}. Bio-char samples were placed on an open platinum sample pans during the TG analysis. A bio-mass sample of 10 ± 0.26 mg was used in the experiments. The changes in mass of samples with temperature were recorded for further analysis.

The morphology of the bio-char samples of different walnut shell residues was determined using a SEM (S 3600; Hitachi, Japan) analysis. Images were taken at 15 kV with 10,000× magnification. The X-ray source was tungsten filament dazed with lanthanum hexaboride (LaB₆), which was equipped with a secondary electron detector (i.e., Evedhart-Thornley detector (ETD)). The biomass samples were circulated on a carbon coated adhesive pursued by vapor-deposition with gold before investigation. XRD was performed on the bio-char samples using the diffractometer (D8-Advance; Bruker, MA, USA) (fitted with a Lynx eye high-speed strip detector) with Cu Ka radiation ($\lambda = 0.15432$ nm). One gram of each bio-char samples was granulated for powder diffraction using X-Ray source with 2.2 kW Cu anode (40 kV, 40 mA) under angular range 2θ (5–1200). For collection of data from 0.5° to 5° of 2θ a regular mode was employed at a scanning speed of 2°/min.

FTIR spectroscopy of different bio-char samples was carried out using a Nicolet 6700, Thermo scientific USA instrument. FTIR analysis the sample powder diluted in 1% potassium bromide (KBr). The FTIR spectrum in the range of 500–4000 cm^{−1} was measured with a resolution of 4 cm^{−1}.

The bio-char showed maximum yields at 375 °C and the characteristics of biochar, like proximate analysis, ultimate analysis, HHV and molar ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C), were determined at 375 °C. The pH values, surface area, TG analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectrometry were analyzed in the same temperature.

3. Results and Discussion

3.1. Proximate and Ultimate Analysis

The results obtained from proximate (on dry ash free (daf) basis) and ultimate analysis, and the corresponding H/C, O/C and HHV data, are shown in Tables 1 and 2. For the purpose of comparison, the earlier work reported on bio-chars obtained from different biomass residues, such as almond shell [45], palm shell [17], wheat straw [46] and also for coal [47], were included in Tables 1 and 2. For a bio-char sample to be considered as bio-fuel, moisture content is an important component. The higher moisture content lowers the heating value and hence affects physical properties and the quality of the yields, which in turns affects the behavior of fuel properties. The results show that moisture contents in the bio-chars are in the range of 0.2–0.8%, which are comparable with wheat straw [46] but much lower than the moisture contents reported for coconut shell bio-chars (7.1 wt%) [17], lignite (34 wt%) and bituminous coals (11 wt%) [47].

Fixed carbon (FC) and volatile matters (VM) contents of the bio-char are significant depending on the type of its utilization as an energy source. For bio-chars used in the present work, the VM contents fall in the range from 8.7–14.4%, which are comparable with palm shell [17] but higher than coconut shell [17] and wheat straw bio-chars [46]. However, the values are much lower than lignite (29%) and bituminous coals (35%) [47]. the highest and lowest VMs were observed in PSW and HSW bio-chars, respectively. The reduction of volatile matters was due to conversion of volatile matter into pyrolysis products.

FC contents varied from 78.4–85.6%, which are comparable with the values reported for almond shell [45] and palm shell chars [17]. However, they were found much higher than bituminous and lignite coals. The highest carbon content present in HSW bio-char (85.6%) implies that hard-shelled bio-char yield would be the largest among all types of bio-char samples.

Table 1. Proximate analysis, high heating values, energy density and energy yield of bio-char obtained at particle size of +1.5–2.5 mm, heating rate 20 °C/min at 375 °C and comparison with other bio-chars.

Types of Bio-Char	Proximate Analysis (wt% daf)							References
	M	VM	A	FC	HHV (Mj/Kg)	ED	EY	
PSW	0.8	14.4	5.5	78.5	14.8	1.08	72.6	Present work
TSW	0.6	12.1	4.4	78.4	15.2	1.11	72.6	
MSW	0.3	11.7	3.2	84.2	16.6	1.15	69.7	
HSW	0.2	8.7	2.02	85.6	18.4	1.26	71.9	
Almond shells char	-	21.2	1.9	76.9	28.2	-	-	[45]
Palm shell char	2.2	11.5	6.7	88.5	33.6	-	-	[17]
Coconut shell	7.1	8.1	4.1	91.9	33.7	-	-	
Wheat straw bio-char (WSB)	0.6 ± 0.01	7.3	8.2 ± 0.2	83.9	22.0±0.7	-	-	[46]
Coal (lignite)	34	43.93	9	46.96	9.3–19.3 *	-	-	[47]
Coal (bituminous)	11	39.93	10.11	50.56	27.9–34.89 **	-	-	

M = moisture; VM = volatile matter; A = ash content; FC = fixed carbon; HHV = high heating value; ED = energy densification; EY = energy yield.

Table 2. Elemental analysis and H/C and O/C values of bio-chars obtained at particle size of +1.5–2.5mm, heating rate 20 °C/min at 375 °C and comparison with other bio-chars and coals.

Type of Bio-Chars	Ultimate Analysis (wt %)						References
	C	H	N	O	H/C	O/C	
PSW	73.4	3.0	0.8	22.7	0.49	0.3	Present work
TSW	76.6	2.4	0.8	15.2	0.31	0.19	
MSW	81.8	3.0	0.6	19.6	0.36	0.23	
HSW	82.7	2.38	0.8	14.0	0.28	0.17	
Walnut shell	55.3	0.89	0.47	1.6			[35]
Apricot Kernel shell char	72.72	3.17	1.27	19.84	0.50	-	[19]
Barley straw	74.83	3.51	0.10	8.46			[48]
Wheat straw bio-char (WSB)	64.8	3.1	0.8	23.0	0.6	0.3	[46]
Coal (lignite)	56.4	4.2	1.6	18.4	-	-	[47]
Coal (bituminous)	73.1	5.5	1.4	8.7	-	-	

The chemical composition of the ash can create significant operational problems in a thermo-chemical conversion process, such as combustion processes due to formation of slag from ash at elevated temperatures. For the various bio-chars under study, the ash contents varied from 2.0–5.5%. Where, HSW contains the lowest value, 2.0%, and PSW bio-char exhibits the highest value, 5.5%. The ash contents of the walnut shell bio-chars are well within the range as reported for palm shell, wheat straw, coconut shell, almond shell bio-chars and coals (Table 1).

The ultimate analysis revealed that the carbon, hydrogen, nitrogen and oxygen contents are almost comparable with each other. The ranges may also be tallied with the values reported in the literature for apricot kernel shell [19] and wheat straw and other agricultural bio-chars [48–50]. However, some large variations have been observed in hydrogen and oxygen for walnut shell [50], and nitrogen and oxygen contents in barley straw [48]. They were highly carbonaceous, with carbon contents ranging from 73.4% to 82.7%, and much less nitrogen content ($n < 1\%$), which produces a lesser amount of NO_x during pyrolysis.

The energy densification and yield vary from 1.08 to 1.26 and from 69.7% to 72.6%, respectively. These values are almost comparable with each other for the bio-chars under investigation. However, the energy densification values are lower and yields are higher than the values reported by Rather et al. (2017) [51] for weeds bio-char.

H/C and O/C data plotted on the van Krevelen diagram (Figure 3) show that the energy quality of the bio-char is improved in comparison to the feedstock, and the bio-char may be compared with lignite coal and other walnut shell and apricot Kernel shell [19,47,50] bio-chars. The reduction in O/C and H/C ratios is due to the loss of oxygen and hydrogen during pyrolysis and may be attributed to decarboxylation and demethylation, respectively [50].

From Tables 1 and 2 it can be concluded that the fuel qualities of the different bio-char samples are improved tremendously, as compared to their respective biomass residues. On comparison of bio-char samples with other biomass residues, it was observed that volatile matters, oxygen and ash contents decreased and fixed carbon and carbon content increased. This shows that bio-char samples have high potential to be used as a solid fuel either for direct combustion or for thermal conversion processes.

HHVs vary from 14.8 to 18.4 MJ/kg. The values are comparable with the results for lignite coal as reported by McKendry (2002) [47]. The results obtained in the present investigation show that the fuel qualities in terms of energy value and fixed carbon contents of the bio-chars are improved in comparison to the respective biomass residues. Thus, the bio-chars have the potential to be used as solid fuels.

Figure 3. Van Krevelen diagram of different types of walnut shells and their respective bio-char yields.

3.2. TGA Analysis of Bio-Char

The results of TGA carried out in an oxidizing atmosphere at 10, 20, and 50 °C/min heating rates are revealed in Figure 4. The weight loss range can be classified into the three divisions. Every new slope indicates the beginning of a new stage. In the first division, about ≈ 2.5 –7% mass loss was observed between the temperatures from 29 to 160 °C for all heating rates and for all types of bio-chars. In the first stage, the maximum mass loss seems to occur in TSW (7%) at 20 °C/min and the lowest in HSW bio-char (2.5%) at a heating rate of 50 °C/min (Figure 4b,d). The mass loss is due to the removal of moisture and sorbent water bounded by surface tension. The second zone starts at 330 °C and continued up to 475 °C where the mass loss from 75–81% at 10 °C/min, 78–89% at 20 °C/min, and 81–90% at 50 °C/min are recorded for all bio-chars. A huge weight loss of 90% for HSW at a heating rate of 50 °C/min and average weight loss of 82.5% were observed for rest of the bio-chars, see Figure 4d. In this zone the mass loss is due to the existence of cellulose and lignin contents which undergo a oxidation/devolatilization reaction. The third zone starts at 475 °C and continues with almost negligible loss of mass. The decomposition of lignin takes place very slowly in the third zone as a result almost straight line is observed. The behavior of TGA analysis was found in agreement with the outcomes described in the literature [52–57].

The above statement is also endorsed by the research carried out many other researchers [58–60] with respect to the decomposition of cellulose, hemi-cellulose, and lignin within the given temperature ranges. The thermogravimetric analysis of various bio-char samples in an oxidizing atmosphere suggested that produced bio-char can be used as alternative solid fuel for various processes.

From the TG curves, a decomposition performance may be illuminated by the specific constituents of bio-chars, whereby the cellulose, hemi-cellulose and lignin are the main components and extractives are the minor components. It was also noticed that the decomposition of cellulose, hemi-cellulose and lignin was accomplished at temperature intervals of 310–400, 210–325, and 160–900 °C, respectively, which is comparable to other bio-chars [56–60]. Therefore, it can be concluded that the major and minor reactions, as detected, in the active pyrolysis zone may be credited to cellulose and hemi-cellulose decomposition. The final zone revealed much less mass loss due to slow degradation of lignin at 510 to 800 °C to produce bio-char as residue [61,62]. Similar observations have also been made by other researchers [61–63]. It was also observed that, at low heating rate, the pyrolysis above 550 °C was almost negligible.

(a)

(b)

(c)

Figure 4. (a–b) TGA profiles of (a) PSW, (b) TSW, (c) MSW and (d) HSW bio-char in an oxidizing atmosphere at 10, 2, and 50 °C/min heating ranges.

3.3. SEM and XRD Analysis of Bio-Chars

The surface morphology of bio-chars, collected from SEM analysis, is exhibited in Figure 5. It is evident that PSW (a) shows porous cracks and HSW (d) shows the agglomerated rocky-like structure. However, TSW (b) and MSW (c) show planner sheet-like structures. The structures have rough textures and are heterogeneous in nature. The results are similar to those found by Guerrero et al. (2008) [64], where they mentioned melting followed by devolatilization and finally vesicle formation responsible for the formation of such structures [64,65]. As temperature gets increased with high heating rate, there is release of various volatile components. Devolatilization results in morphological changes of bio-char, followed by the formation of high pore surface structure of bio-char samples [54].

The XRD patterns of the bio-chars at a temperature of 375 °C are shown in Figure 6. The peaks are in the range of 5–900 on the base line of the diffractograms. The peaks at 14° (d-space~5.96 Å), 15° (d-space~5.7 Å), 16° (d-space~5.3 Å), 22° (d-space~4.0 Å), 26° (d-space~3.34 Å) and 35° (d-space~2.5 Å) were assigned to cellulose and hemi-cellulose, respectively. Different types of bio-char samples in the diffraction angle (2θ) have a wide halo in the 2θ range from 6 to 20°, showed that chain contains large number of carbons containing components substances. The band at 2θ = 22° showed disordered structure, which occurred due to presence of aliphatic and distorted arrangement of carbon chain. Broad peak at 2θ ≈ 26° of bio-char indicated presence of silica in the X-ray diffractogram. The peak at 15 and 16° were derived from cellulose constituent. Bio-char samples showed narrow and sharp bands over the examined 2θ, due to the presence of inorganic constituents in the carbon chain. The XRD graphs confirmed the aromatic and crystallinity nature of the bio-chars, which is in agreement with other bio-chars [65–67].

(a)

(b)

(c)

(d)

Figure 5. (a–d) Scanning electron micrographs (magnification 10,000×) of (a) PSW, (b) TSW, (c) MSW and (d) HSW biochars.

Figure 6. XRD of the different types of bio-char.

3.4. FTIR of Bio-Char

Functional group analysis of various bio-char products, obtained using FTIR spectroscopy, is shown in Figure 7, and the band assignment is discussed in Table 3. The FTIR spectrum in the range of 500–4500 cm^{-1} was measured with a resolution of 4 cm^{-1} . Major components of biomass are hemicellulose, cellulose and lignin. Lignin, unlike cellulose, possesses olefinic carbon-carbon ($-\text{C}=\text{C}-$) double bond in cyclic as well as side chains and is aromatic in nature [68]. The band peaks at the wave numbers of 3465, 3428, 3411 and 3442 cm^{-1} are for PSW, TSW, MSW and HSW bio-chars, respectively, which indicated the stretching vibration of $-\text{OH}$ hydroxyl groups of phenol. The second prominent peaks are at 3050 and 2849 cm^{-1} , and 3075, 2925 cm^{-1} , only shown by TSW and MSW bio-chars, which represent the $-\text{CH}$ stretching vibrations due to the presence of methyl/methylene group. The peak at 1587 cm^{-1} represents the aromatic $\text{C}=\text{C}$ ring stretching vibration of lignin. The medium band intensity between 1398–1401 cm^{-1} may be assigned to aromatic skeleton vibrations combined with $\text{C}-\text{H}$ in plane deformations of bio-chars. The band peak at 1265 cm^{-1} of PSW bio-char confirmed the presence of aromatic $\text{CO}-$ and phenolic $-\text{OH}$ stretching due to the presence of cellulose, hemi-cellulose and lignin. The 750 cm^{-1} band peak showed 3–4 adjacent H deformation of all bio-char samples except TSW bio-char.

From Figure 7 it can be concluded that the different peaks for different bio-char samples are almost similar. A drift of wave number from lower to higher value was due to an increase in temperature, which indicated more carbon content of the char. The wave number from 3400 to 3460 cm^{-1} indicated low frequency values between these peaks, suggested that hydroxyl groups are involved in hydrogen bonding. The non-involving OH bonds were above 3500 cm^{-1} for other groups (i.e., alcohols, phenols and carboxylic acid). Hemicelluloses and celluloses components are broken completely; it goes into either gases or liquid products. The peaks in the range of 1585–1127 cm^{-1} indicated the presence of hemi-cellulose components. The holo-cellulose (cellulose+hemi-cellulose) structure will collapse after wave number gets reduced. The band intensities were decreased at 3411 cm^{-1} ($\text{O}-\text{H}$ stretching) and 1127 cm^{-1} ($\text{C}-\text{O}$ stretching) due to the existence of a hydrogen bond, reduction of water and cellulose contents in bio-char. The band intensity of the absorbance of the $-\text{OH}$ decreased. Due to complete loss of alcoholic or phenolic groups,

the oxygen:carbon ratio of the char decreased. Further, due to high rigid structure lignin was remain within the carbon chain at 1400 to 750 cm^{-1} in the bio-char, while unconverted lignin remains within the bio-char. Similar observations were reported for different bio-chars in the literature [64,68–70].

Figure 7. Infrared spectra of the different bio-chars.

Table 3. FTIR band assignments spectra of different types of bio-chars at $375\text{ }^{\circ}\text{C}$.

Band Assignment	Band Frequency (cm^{-1})			
	PSW	TSW	MSW	HSW
O–H stretching	3465	3428	3411	3442
C–H stretching	-	3050, 2849	3075, 2925	-
Aromatic vibrations of C–C/C = C stretching	1587	1585	1585	1586
C–O–H in-plane bending and aromatic vibrations	1401	1398	1400	1399
OH bending and CH deformation vibrations	1265	-	1265	1265
C–H in-plane deformation and C–OH stretch in syringyl	1121	1124	1124	1127
O–CH ₃ and C–OH stretching	-	-	1021	1015
C–H out-of-plane stretching	868	870, 806	865, 803	868
	750	750	747	750

3.5. Surface Area, Total Pore Volume, Average Pore size Volume, pH and its Potential Applications

The surface area, total pore volume, average pore size volume and pH values of different bio-chars, shown in Table 4, are significant like other physical and chemical characteristics. It may strongly influence the combustion and reactive behavior of the bio-char. The bio-chars produced at pyrolysis temperature of $375\text{ }^{\circ}\text{C}$ develop high porosity in the surface of bio-chars which emerged macro and micro porous particles. This occurs due to removal of volatile

matters from different biomass residues [71]. Due to opportunity of high pores surface area and adsorption sites which contributes to adsorptive capacity and also provides spaces for nutrients/pollutants and water retention [53] in soil treatment applications.

For different bio-chars investigated in the present work, BET surface areas are found as 40–58 m²/g, at particle size and heating rate +1.5–2.5, and 20 °C/min, respectively, for paper-, thin-, medium- and hard-shelled walnuts, at temperature of 375 °C. With an increasing temperature, reduction in the surface area values are predominantly detected, as shown in Table 4. The fusion of adjacent pores seems to predominate, leading to the decline in the surface area and thermal deactivation of the bio-chars. The bio-chars used in the present work have higher surface area and some others were comparable with the investigation reported by other examiners (Table 4) for different biomass residues [72–76]. The highest and lowest surface areas are in HSW and PSW bio-chars, respectively. Due to high BET surface area and quality of bio-chars, it could have high adsorption capacity. For the application of bio-char in wastewater treatment and soil remediation, the BET surface area and quality of bio-chars can be further enhanced by alkaline and acid treatment. Moreover, it can be transformed to activated carbon for water purification processes and in fuel utilities.

Pyrolysis of biomass involves eradication of organic/volatile matters, which enhances the alkali concentration [77]. The pH plays an important role for soil fertility, which effects the types of plants, availability of nutrients and microbes to be consumed [52]. The pH is found in between 8.1–8.3 for all types of bio-chars, respectively. All bio-char samples showed alkaline characteristics, and may be used for soil amendment to neutralize soil acidity, and also enhances the soil quality and improves the yield productivity [78]. Similar results have also been made by other investigators and are comparable with the obtained results, as reported in Table 4.

3.6. Circular Economy Models

The circular bio-economy is a concept for the transformation and management of land, food, health and industrial systems using renewable natural capital. It has the aim of achieving sustainable wellbeing in concord with nature. The prosperity of the recycling-based bioeconomy requires modern technology, innovation, traditional wisdom and biodiversity. That is ultimately the fundamental driving force for bioeconomy. Further, biodiversity affects the ability of biological systems to adapt to changing environments. Thus, it become important to ensure the resilience and sustainability of biological resources. It must be recognized its importance not only through proper nature maintenance policies, but also through locally adapted market-based means that encourage farmers, forest owners and bio-based companies to invest in biodiversity. Since the industrial revolution, human activity has been a major cause of global environmental change. Humans and the environment have a skewed connection, which has resulted in faced thresholds and turning points connected with planetary boundaries, such as biodiversity loss and the global climate catastrophe [84]. A sustainable bioeconomy also encompasses more than just the interchange of fossil and renewable resources. Low-carbon energy, sustainable supply chains, and promising disruptive conversion technologies are all required for the long-term conversion of renewable energy resources into high-quality bio-based goods, materials and fuels. The natural environment, human health and natural resources are one of the activities [85]. Circular economy means that it is fundamentally different from person to person. It has basically become an “essentially controversial concept”. This is a phrase created by Gallie [86], and although there is consensus on the means and purpose of the concept, there is disagreement on its definition. Recently used to characterize the concept of the circular economy [87], the European Commission’s bioeconomic strategy interprets the circulating bioeconomy as a framework for reducing dependence on natural resources. Manufacturing transformation: Promote sustainable production of renewable resources from land, fisheries and aquaculture. It will drive the transition to a variety of bio-based products and bioenergy while creating new jobs and industries [88]. On the one hand,

circular economy focuses on increasing efficiency and reducing speed, reducing and closing hardware loops to reduce resource consumption and system waste through reduced inputs, sustainable design, practice improvement, reuse and waste recycling [89,90]. In accordance with circular bioeconomy concepts, the bio-char was prepared from different walnut shells as a biomass residue at different temperatures, particle sizes and heating rates. The smaller particle size was considered as there may be higher temperature gradient in larger particles, which results into non-uniform heat distribution in the biomass particle. The different bio-chars showed high carbon (73.4–82.7) and lower nitrogen contents with high heating values (14.8 to 18.4 MJ/kg), which enhanced bio-char qualities and is comparable to high quality lignite coal, and, therefore, can be utilized as a renewable solid fuel.

Table 4. Surface area, total pore volume, average pore size volume and pH values of WS bio-chars with different temperatures, at 1.5–2.5 mm particle size and 20 °C/min heating value.

Bio-Char Types (Pyrolysis Temperature)	BET Surface Areas (m ² /g)	Total Pore Volume cm ³ /g	Average Pore Size (Å)	pH	Applications	References
PSW	42	0.012	17	8.4	Fuel, energy storage, soil conditioner, building sector, drinking and wastewater treatments, biogas production, exhaust filters, industrial materials, electronics semiconductors, cosmetics, paints and coloring	Present work
TSW	44	0.013	18	8.2		
MSW	48	0.014	19	8.1		
HSW	58	0.016	19.5	8.3		
Sugarcane bagasse (500 °C)	10.85	0.011	43.7	8.1	Solid fuel, adsorbent, soil amendment	[53]
Apricot kernel shell (550 °C)	195	0.1124	-	-	Activated carbon, fuel applications, water purification, adsorption	[19]
Rice straw (600 °C)	4.76	0.0023	18.74	-	Adsorption Water purification, activated carbon, fuel applications	[74]
Coconut fiber (600 °C)	23.2	0.04		9.6	Sequester carbon in soils, improving soil quality and plant growth	[17]
Flax straw (550 °C)	28.7	0.009	37.5	-	Soil amendment, carbon sequestration, activated chars.	[72]
Wood (450 °C)	23			6.7	Soil reduced the C-mineralization rate compared against the control soil samples	[75]
Paddy Straw (500 °C)	45.8			10.5	Fertilizer consumption reduced, and sequester carbon	[76]
Durian wood sawdust (450 °C)	45.78	5.786	80.98	6.4	Provide suitable proportions for developing clusters of microorganisms, water retention capacity in soil and enhances soil fertility.	[79]
Spent <i>P. ostreatus</i> (500 °C)	18.05	0.061	136	10.37	Potential adsorbent for removing heavy metals from wastewater	[80]
Corn stalk (450 °C)	57.80	0.081	49.1		Adsorption characteristics and mechanism of bio-char on nonpolar pollutants	[81]
Rice husk (500 °C)	92.6	0.076	22.0		Adsorptive properties	[82]
Charcoal fines (500 °C)	43 ± 3	0.035			Water retention capacities and cation exchange capacity	[83]

4. Conclusions

Persistent environmental problems, rising oil prices, energy crisis, depletion of fossil fuels, and growing application and demand for energy are important reasons why people are resolute in demanding energy sources and alternative sustainable fuels. For the environment, sustainability and biodegradability are key characteristics that make biomass a prime candidate for bioenergy production. Bio-char has the ability to sequester carbon in the soil, while improving plant growth and soil quality, with high energy density. Further, it can also be used as an adsorbent for water treatment. In the present study, the characterization

of four different bio-chars, obtained by slow pyrolysis at 375 °C, produced from hard, medium, thin seed residues and paper peels was investigated. The properties of biochar, such as proximate and ultimate analysis, heating value, surface area, pH value, thermal degradation behavior, morphological and crystalline nature and functional characterization using FTIR, were determined. The key outcome from the present work can be summarized as follows;

- The pyrolytic behavior of bio-char was studied using thermogravimetric analysis (TGA) in an oxidizing atmosphere. SEM analysis confirmed morphological change and showed heterogeneous and rough texture structure.
- Crystalline nature of the bio-chars was established by X-ray powder diffraction (XRD) analysis. The maximum higher heating values (HHV), high fixed carbon content and surface area obtained for walnut shells (WS) samples were found as $\sim 18.4 \text{ MJ kg}^{-1}$, $>80\%$ and $58 \text{ m}^2/\text{g}$, respectively.
- Improvement in HHV and decrease of O/C and H/C ratios led the bio-char samples to fall into the category of coal and confirmed their hydrophobic, carbonized and aromatized nature.
- From the Fourier transform infra-red spectroscopy (FTIR), it was observed that there was alteration in functional groups with an increase in temperature, and illustrated higher aromaticity. Therefore, it could be concluded that the bio-char obtained from walnut shell has a high potential to be used as an efficient fuel in both industrial as well as domestic furnaces for energy production.
- Further, from surface area and pH analysis of bio-chars, it was found that WS bio-chars had similar characteristics to adsorbents used for water purifications, retention of essential elements in soil and carbon sequestration.
- The improvement in characteristics of different bio-chars, as compared to their respective biomass residues, showed that it may also be used as a good adsorbent for wastewater treatment as well as for enhancing soil fertility.

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