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S. I. BIOCHAR

Feedstock-induced changes in composition and stability of biochar derived from different agricultural wastes

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Abstract

Biochar is a carbon-rich organic amendment often used to sequester carbon and sustain soil productivity. The characteristics and the potential benefits of biochars depend upon their feedstock type. Therefore, changes in stability and composition of biochars derived from different agricultural wastes viz. sugarcane filter cake (SF), farmyard manure (FM), and rice husk (RH) were investigated in this study. The feedstocks were pyrolyzed at 350 °C, and the resultant biochars (SF-BC, FM-BC, and RH-BC) were characterized for yield, proximate (moisture, volatile matter, fixed carbon, ash content) and ultimate (CEC & elemental composition) analyses, surface area (BET), surface morphology (SEM), structural and functional groups (FTIR), and thermal stability (TG-DTA). Results revealed that SF-BC exhibited the highest yield (42.18%), lower bulk density and particle density (0.131 g cm^{-3} and 0.583 g cm^{-3}, respectively), and higher porosity (76.56%) while the FM-BC had highest contents of fixed carbon (46.83%). The pH was slightly neutral for SF-BC and RH-BC but alkaline for FM-BC. The electrical conductivity and TDS were considerably higher in FM-BC while the CEC was higher in RH-BC (28.24 cmol kg^{-1}). The recalcitrance index (R_{50}) showed that all the biochars were minimally degradable ($0.7 > R_{50} \geq 0.5$). The SF-BC exhibited highest stability with R_{50} value of 0.64 and also showed highest C sequestration potential (43.68%). Hence, it is concluded that thermal conversion of sugarcane filter cake waste into biochar might serve as a potential candidate to increase soil organic C pool if applied as soil amendment.

Keywords Biochar properties · Carbon sequestration · Feedstock types · Persistence · Soil productivity

Introduction

Soils play a vital role in global carbon cycle by acting as a sink and source of CO_2 and a large reservoir of organic carbon (Schlesinger 1984; Lal 2006). Intensive agricultural practices coupled with changing climatic conditions have resulted in soil carbon depletion (Gisladottir and Stocking 2005; Saby et al. 2008; Heikkinen et al. 2013), consequently causing increased emissions of greenhouse gases and the CO_2 (Smith et al. 2007). Hence, there is need to enhance carbon (C) sequestration in soils in order to mitigate climate change and improve soil fertility and health (Cernansky 2015). Low-value organic waste materials generated in large amounts from agriculture, forestry, and livestock sources create environmental issues such as surface pollution and habitat for pests and pathogens. Techniques available for proper disposal of these waste materials are laborious, costly, and unfriendly for environment (Satpathy et al. 2014). Majority of the agricultural wastes are however enriched in organic C and thus conversion of the biomass wastes using different techniques into useful soil amendments may reduce surface pollution (Kwapinski et al. 2010; Satpathy et al. 2014). Pyrolysis, i.e., heating the organic wastes in the absence of oxygen, has been established as an effective technique for the production of biochar (black and stable C-rich material), bio-fuel, and syngas (Lehmann and Joseph 2009; Coomes and Miltner 2016). This thermochemical technology is relatively simple, inexpensive, and leads to the development of valuable soil amendment (Lehmann 2007; Keiluweit et al. 2010).

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Potential benefits of biochar have been extensively studied in the last two decades due to their significance in global climate dynamics, pollution remediation, and agronomic benefits (Lehmann 2007; Zhang and Ok 2014; Santin et al. 2017). Biochar has been established as a useful product for C sequestration, reduction in greenhouse gas emissions, and nutrient losses in soils (Sohi 2012; Novak et al. 2015; Van Zwieten et al. 2015; Abrishamkesh et al. 2015; Arif et al. 2017). As the biochars can be produced from a wide range of organic wastes such as forest residues, sewage sludge, poultry, livestock and agricultural waste materials, the biochar production is considered as an eco-friendly and cost-effective remediation technology (Shareef and Zhao 2017). However, it has been observed that the biochars produced from different feedstocks under similar pyrolysis conditions vary greatly in their physicochemical properties and performance (Mandal et al. 2017; Li et al. 2017a, b; Ok et al. 2015). Hence, it is difficult to predict stability, recalcitrance potential, and the agronomic performance of a particular biochar that greatly depend upon the composition of its feedstock and pyrolysis conditions (Keiluweit et al. 2010; Zimmermann et al. 2012). Research efforts are in progress in this regard to get a biochar with desired characteristics (Ok et al. 2015).

Feedstock biomass is the single most important factor affecting characteristics and composition of the produced biochar (Bruges 2010; Tag et al. 2016). Feedstock affects pH (Li et al. 2017a, b), EC, ash content (Zhang et al. 2017), and ion retention capacity of the biochar (Silber et al. 2010) along with its surface area and porosity. Feedstock is a more important parameter than pyrolysis temperature for predicting ash content and C/N ratio of the biochar (Fungai et al. 2013). Biochars derived from plant materials contain low contents of N and P but a high concentration of C as compared to manure-derived biochars (Waters et al. 2011). Biochars prepared from softwood material have high surface area than hardwood (maple) biochars (Fungai et al. 2013). Biochars produced from forest wastes and rice husk can stimulate indigenous soil microbial activity (Nishio 1996). Biochars of poultry and sheep manure have the similar effects and are more effective in carbon sequestration (Bhattarai et al. 2015). Biochar produced from wood-based raw material and sugarcane bagasse enhances water retention in soil (Kameyama et al. 2017). The presence of carboxyl, lactones, and phenols in the biochar induces surface acidity while the carbonates induce surface alkalinity (Yadav et al. 2016), and the acidic functional groups influence adsorption and cation retention capacities (Kloss et al. 2012; Mukherjee et al. 2011). Thus, it is important to investigate chemical, physical, and structural characteristics of a biochar to identify its potential use and practical applications as soil amendment (Nartey and Zhao 2014).

Waste generation from industrial, livestock, or agricultural sources is a major environmental issue in present time (Cely et al. 2015). For example, sugarcane industry produces several waste materials including bagasse (crushed cane stalks), cane trash (leaves and stalk tips removed during harvest), and filter cake (a sludge removed via filtration after the juice clarification). Previously, sugarcane bagasse has been used to produce biochar (Chen et al. 2010; Kameyama et al. 2012; Bashir et al. 2017). The bagasse is a valuable by-product for the generation of heat and electricity in distilleries as well as for the production of biofuels (George et al. 2010); thus, the use of bagasse for biochar production can affect its other benefits. Sugarcane filter cake contains high quantity of nutrients and water content (Prado et al. 2013) which makes it costly to transport and difficult to apply (George et al. 2010). Conversion of this nuisance waste into a valuable soil amendment by producing biochar may serve as a beneficial approach (Eykelbosh et al. 2014). On the other hand, manure production has increased worldwide in the last few years due to expansion of livestock industry and is intensively being used as an organic soil amendment causing environmental problems such as eutrophication and methane emissions. Therefore, it is necessary to apply other suitable waste management techniques for the safe and environment-friendly use of the manure. Conversion of manure into the biochar and its use as a soil amendment is thus a viable option that may result in drastic reduction in CO_2 emissions compared to the direct application of manures to the soils (Cely et al. 2015). Likewise, burning of the rice and wheat stubbles in fields after harvesting is a common practice in most part of the world which results in nitrogen and moisture losses as well as the emission of greenhouse gases from the fields (Bhattarai et al. 2015). Rice husk, a by-product of rice processing mills, is produced in large quantity in rice-producing countries and remains unutilized causing environmental hazards. This waste can also be used as a potential feedstock for biochar production (Theeba et al. 2012).

In view of the above literature, the present study was designed to produce biochar from different agricultural wastes viz. farmyard manure, sugarcane filter cake, and rick husk and study their physicochemical, compositional, surface, structural, and functional properties with respect to the type of feedstock used for their preparation. Moreover, the changes in the stability and C sequestration potentials of biochars produced from these waste materials were also investigated.

Materials and methods

Material preparation

Sugarcane filter cake (SF) and rice husk (RH) wastes were collected from the agricultural farms while the farmyard manure (FM) was collected from the dairy farms located around Rawalpindi, Pakistan. The materials were dried, placed in the crucibles, covered with aluminum foil and pyrolyzed (5 °C per minute) at 350 °C for 4 h in a muffle furnace. The resultant

biochars were cooled in a desiccator, ground, sieved using 2-mm screen, and stored in plastic bottles. The biochars derived from SF, FM, and RH were labeled as SF-BC, FM-BC, and RH-BC, respectively.

Biochar characterization

Yield, proximate, and physicochemical analysis

The yield of the produced biochar was calculated by using Eq. 1 as follows:

$$Yield\% = \frac{\text{Weight of biomass} - \text{Weight of biochar}}{\text{Weight of biomass}} \times 100 \quad (1)$$

The proximate analyses such as moisture content, ash content, and volatile matter were performed by following the standard method of ASTM D1762-84. The standard method of ASTM D3172-13 was used for the calculation of fixed carbon (American Standard of Testing Material 2001). Briefly, the samples were dried at 105 °C up to a constant weight, the weights were recorded after cooling, and the moisture contents were analyzed by using Eq. 2:

$$Moisture\% = \frac{A-B}{B} \times 100 \quad (2)$$

where A is the mass of the air-dry sample and B is the mass of sample after drying at 105 °C.

For the determination of ash content, biochar samples were placed in the muffle furnace at 750 °C for 6 h and the percent ash content were calculated by Eq. 3:

$$Ash\% = \frac{D}{B} \times 100 \quad (3)$$

where B is the mass of the sample after drying at 105 °C and D is mass of the residue.

The volatile matter was calculated by Eq. 4 after heating the sample in a muffle furnace at 950 °C.

$$Volatile\ matter\% = \frac{B-C}{B} \times 100 \quad (4)$$

where B is the mass of the sample after drying at 105 °C and C is mass of the sample after drying at 950 °C.

The fixed carbon was calculated by difference method as given in the Eq. 5:

$$Fixed\ carbon\% = 100 - (moisture\% + \text{ash}\% + volatile\ matter\%) \quad (5)$$

The bulk density was determined by core method (Blake and Hartge 1986), and the particle density was measured using a helium pycnometer (Lowell et al. 2004; Kassama and Ngadi 2005):

$$Vs = Vc + \frac{Vr}{1 - P1/P2} \quad (6)$$

where Vs is sample volume, Vc is the volume of the empty sample chamber, Vr is the volume of the reference, P_1 is first pressure (i.e., in the sample chamber), and P_2 is second (lower) pressure after expansion of the gas into the combined volumes of the sample chamber and the reference chamber. Porosity was calculated by following the Eq. 7:

$$\epsilon = 1 - \frac{\rho b}{\rho s} \quad (7)$$

where ϵ is porosity; ρb is bulk density and ρs is particle density (Villegas et al. 1998).

The surface hydrophobicity of the biochar samples was determined by using the molarity of an ethanol drop (MED) test (Letey et al. 2000). The pH, electrical conductivity (EC), and dissolved salts of the biochar were determined in a 1:5 (*w*/*v* ratio) solid/water suspension (Leite and Freeman 1991; McLaughlin 2010). The organic carbon of the biochar samples was burnt to ash in the muffle furnace at 500 °C for 4–5 h and calculated by using Eq. 8 (Brake 1992):

$$Organic\ C\% = \frac{100 - \text{Ash}\%}{1.724} \quad (8)$$

Organic matter of biochars derived from different materials was calculated by using Eq. 9:

$$Organic\ matter\% = 100 - \text{Ash}\% \quad (9)$$

Cation exchange capacity (CEC) of the material was measured by the extraction method of ammonium acetate (Firestone et al. 1980; Mulvaney et al. 2004; Gaskin et al. 2008). Acid and base titration method was used for the measurement of total surface basicity and acidity (Jindarom et al. 2007). For oxygen-containing functional group determination, back-titration method with HCl was used (Bandoz et al. 1993; Boehm 1999).

Elemental composition

A portion of each biochar sample was digested in a digestion block by adding catalyst mixture and H_2SO_4. After digestion, the extract was distilled by using H_3BO_3 and NaOH, and the total nitrogen (N) was determined through titration (Kjeldahl 1883). Grinded biochar samples were digested by a mixture

containing Se powder, K_2SO_4, and H_2SO_4. Digested solution was filtrated and used for analysis of P with ammonium heptamolybdate-ammonium vanadate method, while the K with flame photometer (115 VAC, 50/60 Hz) and Ca, Mg, micronutrients (Fe, Cu, Mn, Zn), and heavy metals with atomic absorption spectroscopy (Enders and Lehmann 2012).

Brunauer, Emmett, and Teller; scanning electron microscopy; Fourier transform infrared spectroscopy; and thermogravimetric analyses

The surface area of the produced biochars was measured via the Brunauer, Emmett, and Teller (BET) method using surface area and porosity analyzer (TriStar II 3020, Micromeritics, USA (Brunauer et al. 1938).The surface morphology of the biochars was studied by scanning electron microscopy (SEM; EFI S50 Inspect, Netherlands). Samples were adhered to aluminum stubs using graphite and nickel cement (Ted Pella, Redding, CA, USA) (Prakongkep et al. 2013). Images were taken in the range of × 2000–300 magnification at an acceleration voltage of 30 kV under high vacuum. The structural and functional groups composition of the biochar material was determined by using Fourier transform infrared spectroscopy (FTIR, Bruker Alpha-Eco ART-FTIR, Bruker Optics Inc.) (Dutta et al. 2015). Thermal stability of the biochar samples was analyzed using thermogravimetric analyzer (TGA: DTG-60H, Shimadzu, Japan). The weight loss of the materials were recorded with the rise in temperature 0–1100 °C.

Thermal stability calculation

Relative thermal degradation of biochar derived from different feedstock was measured using thermogravimetric analysis data by calculating recalcitrance index (R_{50}) (Harvey et al. 2012) using Eq. 10:

$$R_{50} = T_{50,x}/T_{50,graphite} \tag{10}$$

where $T_{50,\,x}$ and $T_{50,\,graphite}$ are the moisture and ash-corrected TG thermograms (weight loss due to C oxidation only) at 50% weight loss by volatilization or oxidation of the materials and graphite respectively. To correct the TG thermograms for moisture and ash content, the following equation was used:

$$W_{i,cor} = 100 + \left[100 \times \left(W_{i,uncor} - W_{200,uncor}\right)/\left(W_{200,uncor} - W_{cutoff,uncor}\right)\right] \tag{11}$$

where $W_{i,cor}$ is corrected percent weight loss of initial sample, $W_{i,uncor}$ is uncorrected percent weight loss of initial sample, $W_{200,uncor}$ is percent weight loss of the initial sample at 200 °C (corresponding to water loss in the sample), and $W_{cutoff,uncor}$ is weight loss at the temperature where no more oxidation takes place.

Percent carbon sequestration potential (CS) was calculated by the Eq. 12 as given by Zhao et al. (2013):

$$CS\% = \frac{Yield\% \times C\%Biochar \times R50}{C\%Feedstock} \tag{12}$$

where C is percent carbon content.

Effective particle size

The effective particle size (EPS) of the produced biochars was calculated by following the Eq. 13 (Lowell et al. 2004; Ahmad et al. 2017):

$$Effective\ particle\ size\ (\mathrm{EPS}) = \left[\frac{3}{\rho \times S}\right] \times 2 \tag{13}$$

where S is surface area analyzed by BET and ρ is the density of each material analyzed using core method. The dried material was filled in a cylinder of known volume and weight. The weight of the material was calculated by subtracting cylinder weight from the total and volume of the material taken equivalent to the volume of a cylinder. The density of the material was obtained by dividing weight by the volume.

Results and discussion

Changes in biochar composition

Yield and proximate analyses

The proximate composition and yield analyses of the produced biochars are presented in Table 1. On the basis of mass loss during the process of pyrolysis, SF-BC exhibited highest yield (42.18%) followed by RH-BC (37.14%), while FM-BC showed the lowest yield (30.98%), suggesting that up to 70% of mass was lost during the conversion of biomass into biochar and the biochar yield reduced significantly (30–50%). The effects of feedstock type on the biochar yields have already been reported (Jindo et al. 2014). The loss of mass might have occurred due to changes in the organic matter and C-related structure (Zhao et al. 2014). The SF-BC, FM-BC, and RH-BC did not differ significantly in moisture content. Results showed that the moisture contents of biochar decreased after drying (Taherymoosavi et al. 2016). The RH-BC showed higher ash content (61.19%) in comparison with SF-BC and FM-BC (52.36% and 39.24% respectively). The higher ash content of RH-BC was probably due to higher decomposition (Abrishamkesh et al. 2015), removal of

Table 1 Physical and chemical characteristics of SF-BC, FM-BC, and RH-BC

Parameters	SF-BC	FM-BC	RH-BC
Yield (%)	42.18 ± 1.45	30.98 ± 0.852	37.14 ± 1.62
Moisture content (%)	4.69 ± 0.157	4.59 ± 0.01	4.47 ± 0.169
Ash content (%)	52.36 ± 0.815	39.24 ± 3.65	61.19 ± 6. 09
Volatile matter (%)	21.27 ± 1.66	8.33 ± 1.155	15.90 ± 1.015
Fixed Carbon (%)	21.68 ± 2.423	46.83 ± 2.77	18.44 ± 7.25
Bulk density (g cm^{-3})	0.131 ± 0.014	0.213 ± 0.001	0.254 ± 0.006
Particle density (g cm^{-3})	0.583 ± 0.0005	0.823 ± 0.003	0.813 ± 0.001
Porosity (%)	76.56 ± 1.96	74.047 ± 0.111	68.71 ± 0.713
pH	7.34 ± 0.046	8.446 ± 0.025	7.23 ± 0.08
EC (dS m^{-1})	0.0335 ± 0.0007	0.626 ± 0.058	0.027 ± 0.003
TDS (mg L^{-1})	22.27 ± 0.55	420.67 ± 38.55	18.767 ± 1.85
TOC (%)	25.63 ± 3.93	35.24 ± 2.12	22.51 ± 3.54
OM (%)	47.65 ± 0.824	60.76 ± 3.65	38.81 ± 6.1
CEC (cmol kg^{-1})	23.45 ± 0.78	16.39 ± 1.395	28.24 ± 0.35

The mean ± standard deviation for three determinations

EC electrical conductivity, *TDS* total dissolved salts, *TOC* total organic carbon, *OM* organic matter, *CEC* cation exchange capacity

volatiles, and accumulation of inorganic contents (Tag et al. 2016). Cantrell et al. (2012) and Cao and Harris (2010) reported that the higher ash content indicated higher concentrations of minerals and organic matter loss from feedstock during pyrolysis. Similar to percent yield, the volatile matter was high in SF-BC (21.27%). With pyrolysis, the enrichment of biochar with volatile matter composition occurred (Jindo et al. 2014). Mishra et al. (2017) reported similar results in rice husk-derived biochar, i.e., 4.25% moisture content and 15.64% volatile matter. High volatile matter and low ash contents were reported in sugarcane bagasse as compared to rice husk, suggesting that as the temperature increased, volatile matter decreased and ash content increased in feedstocks (Kameyama et al. 2017). It has been reported that the manure-derived biochar was high in ash content as compared to crop residue-derived biochar (Zhao et al. 2013). The comparison of sawdust biochar and rice husk biochar showed that rice husk biochar that showed higher ash content (50.94%) contained more functional groups on the surface but low contents of volatile matter, i.e., 13.11%. Zhang et al. (2017) also reported higher ash content in rice straw biochar than the walnut shells, corncobs, and corn straws under similar conditions. Similar findings were investigated in previous studies (Manolikaki et al. 2016).

Fixed carbon was higher in FM-BC (46.83%) and lower in RH-BC (18.44%). Ash particles hinder the formation of aromatic structures that contribute greatly to fixed carbon content (Cely et al. 2015). The content of fixed carbon is a potential measure for estimating biochar recalcitrance (Enders et al. 2012; Crombie et al. 2013) which is moderately dependent on temperature but strongly on the feedstock (Zhao et al. 2013). Feedstocks with relatively higher ash contents produced relatively lower fixed carbon biochars, which attributed to the high ash content inhibiting the formation of aromatic carbon forms (Enders et al. 2012). At 300 °C, 60.77% volatile matter and 32.50% fixed carbon were reported (Zhao et al. 2017). Fixed carbon content represents the degree of aromaticity and stability of biochar (Joseph and Lehmann 2015). Hence, the FM-BC in this study possesses relatively higher stability and recalcitrance potential, compared to other types of biochars.

Physicochemical analyses

The SF-BC exhibited lower bulk density and particle density (0.131 g cm^{-3} and 0.583 g cm^{-3}, respectively), while higher porosity (76.56%) as compared to FM-BC and RH-BC (Table 1). The average bulk density of all biochars reported less than 1 g cm^{-3}(Yargicoglu et al. 2015). Biochar contains macro and micro pores (Downie et al. 2009), which greatly reduced the bulk density of biochar and can hold air or water (Brewer et al. 2009). Generally, the bulk densities lie between 0.09 and 0.5 g cm^{-3}(Karaosmanoglu et al. 2000;Ozcimen and Karaosmanolu 2004; Bird et al. 2008; Spokas et al. 2009). The SF-BC and RH-BC showed slightly neutral pH, while FM-BC showed alkaline pH, i.e., 8.44. The magnitude of pH increments depended on the composition of feedstock (Cantrell et al. 2012; Cely et al. 2015; Li et al. 2017a, b). Usually, it is considered that pH increases with pyrolysis temperature; however, this increment depends on the characteristics of the raw material (Cantrell et al. 2012).Charring at temperatures of lower than 400 °C was selected to avoid excessive increment of pH (Zornoza et al. 2016). The pH of RH-BC reported almost neutral (i.e., 7.14) (Ndor et al. 2016). Similarly,

Abrishamkesh et al. (2015) also reported 7.4 pH in rice husk-derived biochar. Electrical conductivity and total dissolved salts (TDS) were also considerably higher (0.626 and 420.67 mg L^{-1}, respectively) in FM-BC than the other agricultural feedstocks. The concentration of TDS was higher in FM-BC, subsequently resulting in higher EC. The cationic and anionic contents of the feedstock mostly remained in the biochar (Tan et al. 2014), and this increment in the ash content connected with increments in EC. Thus, the soluble salts in ash contents become responsible for the increment of EC (Zornoza et al. 2016). By comparing the TOC and OM of different biochars, it was determined that FM-BC had 35.24% of TOC and 60.76% of OM, which is higher than the other biochars (SF-BC and RH-BC). The higher ash contents result the lower the carbon content of the biochar (Windeatt et al. 2014). Lowest TOC and OM were reported in rice husk biochar by Windeatt et al. (2014), i.e., the lowest carbon content was seen in rice husk biochar which has the highest ash content; conversely, the highest carbon content was seen in the coconut shell biochar which has the lowest ash content. In the analyses of TOC, the highest value was recorded in bamboo chip biochar, i.e., 81.2%, while lowest TOCs were recorded in rice husk biochar and rice straw biochar, i.e., 57.2% and 49.5%, respectively (Mandal et al. 2017). Total organic carbon, fixed carbon, and mineral elements of biochar were mostly the affected parameters by feedstock properties (Zhao et al. 2013). The CEC of RH-BC was considerably higher (28.24 cmol kg^{-1}) than the SF-BC and FM-BC (23.45 cmol kg^{-1} and 16.39 cmol kg^{-1}, respectively). The variability in CEC was due to variable concentrations of different cations such as Ca, Mg, and K, and cation amount varies greatly with the type of feedstock (Zhao et al. 2013).

Elemental composition

The elemental compositions (C, H, N, and O) and the content metals, P and K, in the biochars prepared from different feedstock are shown in Table 2. Significant differences in the elemental contents were observed. Zhang et al. (2017) reported that feedstock types significantly affected the elemental composition of the biochars. Highest total N content (0.56%) was observed in SF-BC followed by FM-BC (0.42%) and RH-BC (0.28%). The FM-BC showed the maximum percentage of total P (1.93%) as compared to other feedstocks. It has previously been reported that manure-derived biochar contains more plant-available P as compared to the biochars derived from crop residues and grasses (Laird et al. 2010).The animal waste such as poultry litter and swine manure-derived biochar contains a higher concentration of K (1.6–5.9%) as compared to biochar from other materials (Subedi et al. 2016). Manure-derived biochars possess high levels of Ca, K, Mg, and Na (Ender et al. 2012). The FM-BC showed highest total K contents (0.557%) while total K was not detected in SF-BC and RH-BC. The FM-BC contained the highest concentration of Ca, Mg, and Na (0.96, 0.32 and 0.053%, respectively) as compared to SF-BC and RH-BC. The higher contents of these basic cations resulted in higher EC and TDS of the FM-BC (Table 1).

Table 2 Total nitrogen (N), phosphorus (P), potassium (K), micronutrients, and metals contents of SF-BC, FM-BC, and RH-BC

Parameters	SF-BC	FM-BC	RH-BC
Total N (%)	0.56 ± 0.0153	0.42 ± 0.015	0.28 ± 0.006
Total P (%)	1.297 ± 0.095	1.93 ± 0.02	0.53 ± 0.015
Total K (%)	ND	0.557 ± 0.025	ND
Ca (%)	0.68	0.96	0.36
Mg (%)	0.21	0.32	0.09
Na (%)	0.010	0.053	0.009
Cu (mg kg^{-1})	114.93	15.08	ND
Zn (mg kg^{-1})	401.85	132.42	105.13
Fe (mg kg^{-1})	13,393.46	4469.84	471.37
Mn (mg kg^{-1})	681.21	166.82	130.799
Co (mg kg^{-1})	ND	ND	ND
Cr (mg kg^{-1})	24.75	3.77	ND
Cd (mg kg^{-1})	ND	ND	ND
Li (mg kg^{-1})	20.55	15.08	10.86
As (mg kg^{-1})	ND	ND	ND
Ni (mg kg^{-1})	ND	ND	ND
Pb (mg kg^{-1})	ND	ND	ND
Se (mg kg^{-1})	12.58	ND	ND
V (mg kg^{-1})	ND	ND	ND

The concentration of micronutrients and heavy metals determined in the biochar samples is presented in Table 2. Among the four main micronutrients, the Cu was not detected in RH-BC. Highest values of Cu, Zn, Fe, and Mn were observed in SF-BC (114.93, 401.85, 13,393.46, and 681.21%, respectively) followed by FM-BC and RH-BC. In the analyses of metals, Co, Cd, As, Ni, Pb, and V were not found in all the types of biochars while Se was observed only in SF-BC sample (12.58 mg kg^{-1}). The Cr was determined in SF-BC and FM-BC (24.75 mg kg^{-1} and 3.77 mg kg^{-1}, respectively) while not detected in RH-BC. The Li contents in SF-BC, FM-BC, and RH-BC were 20.75 mg kg^{-1}, 15.08 mg kg^{-1}, and 10.86 mg kg^{-1}, respectively. The high nutrients and low heavy metal concentrations in SF-BC showed its suitability to be used as soil amendment.

Surface composition

Oxygen-containing functional group Oxygen-containing functional groups present on biochar surface provide sites for the binding of metal ions and pollutants (Uchimiya et al. 2011). With the closer inspection of the data in Table 3, it was seen that the surface of biochars derived from different

feedstocks contained three classes of acidic surface oxides (phenolic, lactone and carboxylic) as determined by Boehm titration. Separation of feedstock type was distinct for oxygen-containing functional groups. Highest values of carboxylic and phenol groups were determined in SF-BC, i.e., 0.0017 mol dm^{-3} and 0.0146 mol dm^{-3}, respectively, followed by FM-BC and RH-BC. While highest value of lactones was observed in RH-BC (0.0048 mol dm^{-3}). Suliman et al. (2016) concluded that most of the oxygenated surface functional groups (carbonyl, carboxyl, and hydroxyl groups) present in different biochars removed as the pyrolysis temperature increased. It was also reported that the CEC of biochar was affected by the surface oxygen groups and the surface area.

Total surface basicity and acidity The surface acid/base chemical activity of different biochars was determined (Table 3). The surface acidity and basicity comparison of three feedstocks showed a slight difference from each other. In general, surface acidity of SF-BC (0.017 mol dm^{-3}) was greater than for all the other biochars while the surface basicity was higher in FM-BC (0.02 mol dm^{-3}). Moreover, the pH, EC, and TDS were high in FM-BC, due to which the surface basicity was high. The H and O contents both are important in determining surface acid/ base chemical activity (Mukome et al. 2013). The biochars prepared at low pyrolysis temperature have more surface acidity than that prepared at high temperature. While, increasing pyrolysis temperature increases total surface basicity (Yakout 2017). As the pyrolysis temperature increases, biochar converted into a stable component, which becomes more resistant to decomposition (Zhang et al. 2012; Sun et al. 2014; Yao et al. 2014). Thermal treatments were also used to study the structure of biochar materials (Kalderis et al. 2014; Mimmo et al. 2014). Regarding the structure, biochar has a porous structure with a carbon backbone, whereas, chemically, biochar contains several functional groups (hydroxyl, aliphatic, etc.) on its surface (Das et al. 2015). The feedstock nature significantly affects the surface functionality of biochar (Yadav et al., 2016). To control the quantity of surface functional groups of biochar, the feedstock is a key factor and controls the number of mineral elements of biochar (Li et al. 2017a, b). The amount of K, Ca, Mg, Na, and P in biomass enhances the formation of oxygen-containing functional groups on the surface of biochar resulting in high CEC (Meszaros et al. 2007).

Hydrophobicity Biochar hydrophobicity varied from extremely hydrophobic to hydrophilic (< 1 S). Molarity of ethanol drop test (MED) showed that FM-BC and RH-BC were more hydrophobic as compared to SF-BC (Table 4). At the level of 8, FM-BC and RH-BC were extremely hydrophobic, while the SF-BC was slightly hydrophobic. As the molarity of ethanol increased, the materials became hydrophilic. MED values 1–2 indicate hydrophilic samples, values of 3–4 are slightly to moderately hydrophobic, while 5–7 indicated extremely hydrophobic materials (Hale et al. 2015). Liu et al. (2016) used MED test and reported that samples start absorbing the ethanol solution within 3 s. The hydrophobicity nature of biochar might have been due to the presence of aliphatic functionality (Gray et al. 2014). Das et al. (2015) also stated that biochars made at low pyrolysis temperatures have less affinity towards water due to the low surface area, fewer pores, and presence of aliphatic functional groups that promote hydrophobicity. Zornoza et al. (2016) observed that all the biochars they produced at 300 °C were highly hydrophobic.

Fourier transform infrared spectroscopy The FTIR spectra of biochars contained a number of structural-functional groups including O–H, C–H, C=C, C=O, and C–O (Fig. 1). It is obvious from the spectra that as the pyrolysis temperature increased, the spectra of FTIR became less complex. A band at 800 cm^{-1} was designated as Si–O, which was present in all the biochars. A band with high absorbance at 1000–1100 cm^{-1} in all biochars was assigned to C–O–C stretches with little shift in peaks, and sharp peaks indicated the presence of polysaccharide cellulose. The shift in band location of three materials was due to complexation in composites. Absorption peaks at 1400 cm^{-1} were assigned to CH_4 and CH_3. The research work based on textile sludge biochars also reported small band at 1350 ≈ 1460 cm^{-1} assigned to CH_2 and CH_3 (Sohaimi et al. 2017). The absorption wavelengths that appeared in the range 1550–1600 cm^{-1}were assigned as –COOH, indicating the presence of carboxylic groups such as ketones, esters, and carboxyl. The peak at 1700 $cm^{-1}$was ascribed as C=O stretching. The small bands at 2800 ≈ 3000 cm^{-1}were designated as C–H, OH, and C–H stretching. At the range of 2800 ≈ 3000 cm^{-1}, the absorption wavelengths were assigned to the stretching vibration mode of hydroxyl groups (Sohaimi et al. 2017). A broadband around 3300–3400 cm^{-1} indicated the presence of –OH stretches of H-bonding water molecules and other volatile functional groups which were lost during pyrolysis and disappeared in the biochars. In previous research, N–H functional groups from phenol, alcohol, and water were characterized by 3000–3800 cm^{-1} adsorption bands (Keiluweit et al. 2010; Chen et al. 2011).

Brunauer, Emmett, and Teller surface area The variations in the BET surface area of SF-BC, FM-BC, and RH-BC are represented in Table 5. Results showed that the RH-BC exhibited highest surface area (130.5 m^2 g^{-1}), followed by FM-BC (49.25 m^2 g^{-1}) and SF-BC (42.1 m^2 g^{-1}). Few studies reported that the surface area of manure and biosolid-derived biochars was smaller (5.4–94.2 m^2 g^{-1}) than the plant-derived biochar (112–642 m^2 g^{-1}). Larger surface area (78.45 m^2 g^{-1}) in rice husk biochar has been reported previously (Wang et al. 2014). In biochar, the progressive degradation of the organic

Table 3 Acidity, basicity, and oxygen-containing functional groups of SF-BC, FM-BC, and RH-BC

Parameters	SF-BC	FM-BC	RH-BC
Acidity (mol dm^{-3})	0.0173 ± 0.0012	0.0073 ± 0.0011	0.01 ± 0.00058
Basicity (mol dm^{-3})	0.017 ± 0.002	0.02 ± 0.001	0.01 ± 0.0025
Carboxylic (mol dm^{-3})	0.0017 ± 0.00015	0.0016 ± 0.00013	0.0014 ± 0.00012
Lactones (mol dm^{-3})	0.0028 ± 0.00021	0.0048 ± 0.00015	0.0014 ± 0.00019
Phenols (mol dm^{-3})	0.0146 ± 0.00116	0.0025 ± 0.00074	0.009 ± 0.00043

materials (hemicelluloses, cellulose and lignin) and the formation of vascular bundles or channel structures may increase the surface area (Kim et al. 2013; Li et al. 2013).

Structural and mineral composition

Scanning electron microscopy The surface morphology of biochar as analyzed by SEM is shown in Fig. 2. The surface of biochar was porous with channels. Due to thermalization, organic matter becomes volatilized and new pores were created. Likewise, volatilization of organic matter during pyrolysis resulted in increased porosity, subsequently creating channels and pores on the surface of biochars (Usman et al. 2015; Ahmad et al. 2017).

Effective particle size Figure 3 presents the results of effective particle size (EPS), which showed that EPS was significantly higher in RH-BC while lower in farmyard manure biochar. In comparison to the biomass, the average EPS reduced in biochar because of pyrolysis (Ahmad et al. 2017).

Changes in stability of biochar

Recalcitrance potential of biochars

The aromatic structure of biochar resists degradation resulting in higher recalcitrance (Keiluweit et al. 2010; Zhao et al. 2013), consequently increasing C sequestration in soil. The stability of C in the biochar largely depends on feedstock type and composition (Ahmad et al. 2017). For the estimation of stability and recalcitrance of biochar, an index is required in relation to graphite, which is considered as the most stable form of C (Windeatt et al. 2014). Therefore, recalcitrance index (R_{50}) (Harvey et al. 2012) has been used to evaluate the recalcitrance potential of biochars using thermogravimetric analyses. Thermal analyses were extensively used to test the stability of organic matter. When the process of pyrolysis started, the mass of all biochars decreased slightly due to temperature increase (Fig. 4). The thermogravimetric curves of three different biochars revealed similar behaviors regarding the weight loss (in wt.%) on a decreasing trend with increasing temperature. The weight loss started at 250 ≈ 300 °C, and two general regions of weight loss were identified on the thermograms: (i) around 300 °C for biomass due to thermal degradation of hemicelluloses and cellulose compounds (Yang et al. 2007) and (ii) around 600–1000 °C due to lignin degradation

Table 4 Hydrophobicity of SF-BC, FM-BC, and RH-BC

MED	SF-BC	FM-BC	RH-BC
2	12.3 s	ND	ND
4	5.86 s	ND	ND
6	3.66 s	ND	ND
8	1.47 s	33 s	5 s
10	< 1 s	< 1 s	< 1 s
12	< 1 s	< 1 s	< 1 s
16	< 1 s	< 1 s	< 1 s

MED molarity of ethanol drop, *ND* not detected

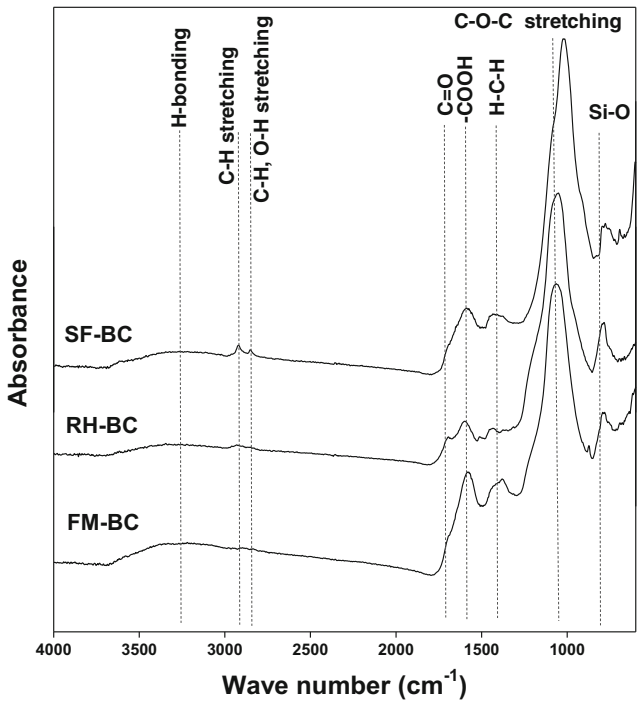

Fig. 1 FTIR spectra of SF-BC, FM-BC, and RH-BC

Table 5 The surface area of SF-BC, FM-BC, and RH-BC

Sample	Surface area (m^2 g^{-1})
SF-BC	42.1 ± 0.6
FM-BC	49.25 ± 0.85
RH-BC	130.5 ± 1.5

(Ahmad et al. 2017). The weight loss in SF-BC took place from 300 to 1000 °C and after that, weight loss becomes stable. While in the case of FM-BC and RH-BC, weight loss started from 300 and 268 °C and became stable at 600 and 700 °C, respectively. With increase of temperature, biochar lost weight slightly due to the release of moisture and light volatiles. Weight loss began to reduce gradually due to decomposition and then become stable.

The ash and moisture-corrected TGA thermograms are presented in Fig. 5. Depending on R_{50}, biochars can be categorized into three categories:

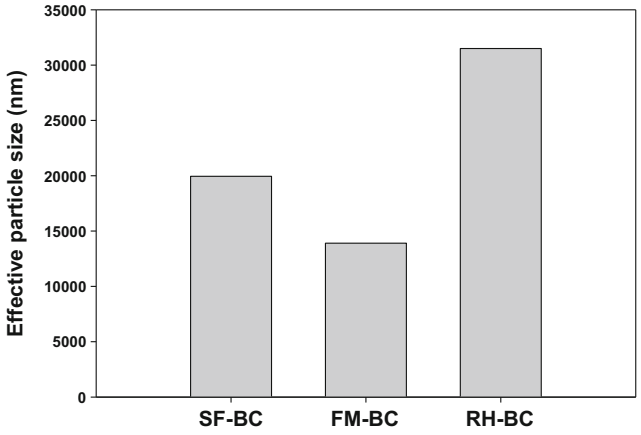

Fig. 3 Effective particle size (EPS) of SF-BC, FM-BC, and RH-BC

1. $R_{50} \geq 0.7$ = highly recalcitrant
2. $0.7 > R_{50} \geq 0.5$ = minimal degradable
3. $R_{50} < 0.5$ = highly degradable

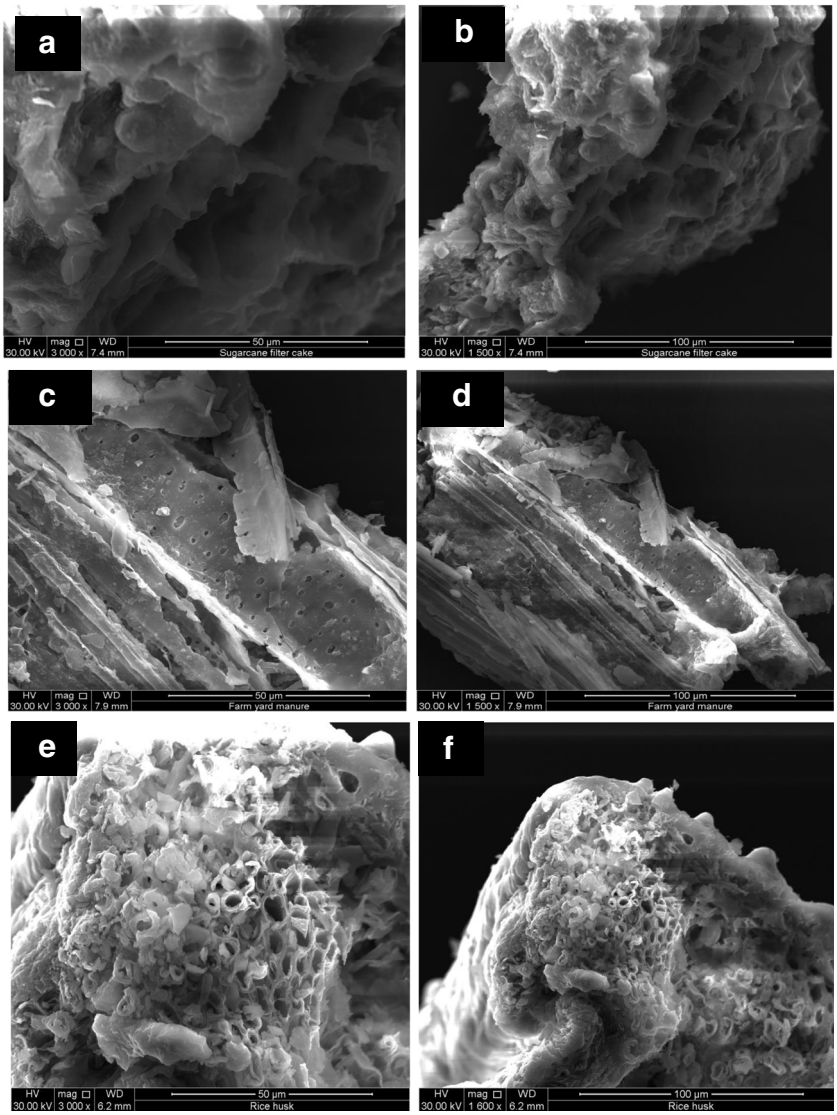

Fig. 2 Scanning electron microscopy (SEM) images of SF-BC, FM-BC, and RH-BC. Scales for SF-BC, **a** 50 μm, **b** 100 μm; for FM-BC, **c** 50 μm, **d** 100 μm; and for RH-BC **e** 50 μm, **f** 100 μm

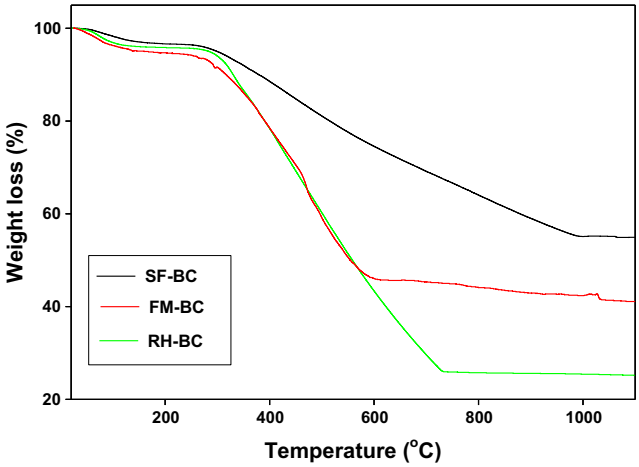

Fig. 4 Thermogravimetric analysis of SF-BC, FM-BC, and RH-BC

All the biochars in our research fall in class 2, which is minimally degradable with R_{50} values below 0.7 but higher than 0.5 (Table 6). The R_{50} gives a range of recalcitrance relevant to graphite; however, it does not tell the precise time-scale for C sequestration.

Carbon sequestration potential of biochars

The CS was calculated and presented in Table 6. Carbon sequestration potential was highest in SF-BC (43.68%) followed by FM-BC (25.03%) and RH-BC (24.06). The CS depends on (i) %C contents of biochar before and after pyrolysis, (ii) R_{50} values, and (iii) %yield of biochar. In general, due to the higher values of R_{50} and %yield of biochar, %CS increased. In previous studies, 40.49% CS was reported in date palm waste-derived biochar and categorized in class 2 (R_{50} = 0.62), which is minimally degradable (Ahmad et al. 2017). According to the classification of Spokas (2010), biochars

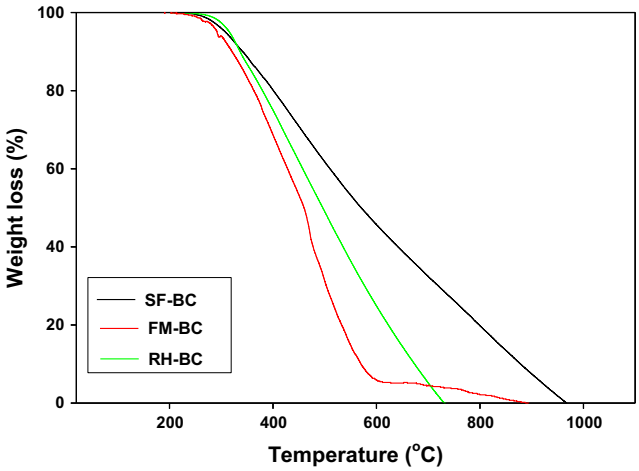

Fig. 5 Ash and moisture corrected thermograms of SF-BC, FM-BC, and RH-BC

Table 6 Ash free composites (*T50*), recalcitrance index (*R50*), and carbon sequestration potential (CS) of SF-BC, FM-BC, and RH-BC

Sample	T_{50}	R_{50}	*CS* (%)
SF-BC	571.14	0.64	43.68
FM-BC	459.72	0.52	25.03
RH-BC	496.21	0.56	24.06

formed at 350 °C have expected half-lives of 100–1000 years, while the biochars formed at 500 and 650 °C have half-lives of > 1000 years.

Conclusion

The agricultural waste such as sugarcane filter cake (SF), farmyard manure (FM), and rice husk (RH) were pyrolyzed at 350 °C (5 °C per min) and characterized to investigate the changes in surface, chemical, physical, and structural composition of the resultant biochars. Additionally, the recalcitrance potential and carbon sequestration potential of the produced biochars were compared. Results indicated significant variations in physicochemical, structural, and morphological characteristics; recalcitrance potential; and carbon stability of the biochars derived from different feedstocks. The SF-BC was found to be most appropriate biochar to be employed as soil amendment for soil carbon sequestration as compared to other biochars. The more suitability of the SF-BC was due to higher recalcitrance index (0.64) and carbon sequestration potential (43.68%). Hence, it was concluded that reusing the sugarcane filter cake waste may reduce surface waste pollution, and its thermal conversion may produce a highly stable biochar, which may serve as a sustainable technology to enhance soil carbon pool, and C sequestration.

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