

## Review Article

# Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants: An Overview

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This paper provides an updated review on the subjects, the available alternative to produce biochar from biomass, quantification and characterization of biochar, the adsorptive capacity for the adsorption of contaminants, and the effect of biochar addition to agricultural soils on contaminant bioavailability. The property of biochar produced is much dependent upon the composition and type of biomass and the conditions at which biomass is carbonized. The physical and chemical characterizations are necessary to identify the basic structure and property of biochar and to predict its potential in various environmental application. Biochar is a promising alternative to remedy the soils contaminated with heavy metals and organic compounds through adsorption and immobilization due to its large surface area, charged surface, and functional groups. Overall, the bioavailability of heavy metals and organic compounds decreases when biochar is amended into soils.

## 1. Introduction

Biochar (BC) is the carbon-rich product obtained when biomass, such as wood, manure, or leaves, is heated in a closed container with little or no available air. In more technical terms, BC is produced by so-called thermal decomposition of organic material under limited supply of oxygen ( $O_2$ ) and at relatively low temperature ( $<700^\circ C$ ) [1]. The term “BC” is a relatively contemporary development, evolving in conjunction with soil management, carbon sequestration issues, and immobilization of pollutants [2].

Addition of BC to agriculture soils has been projected as a means to improve soil fertility and mitigate climate change [3–7]. Recently, it is reported that conversion of biomass into BC can not only result in the renewable energy (synthetic gas and biooil), but also decrease the content of  $CO_2$  in the atmosphere, which reveal more research on the effect and behaviour of BC in soil [8–11]. It is indicated that amending BC into soil improves the structure and properties of soil, such as the water-holding capacity, organic matter content, aeration condition, pH value, cationic exchange capacity (CEC), and the formation of aggregates of soil [7, 12–15]. The leaching losses of nitrogen and phosphorous in soil and the

releases of greenhouse gases ( $N_2O$  and  $CH_4$ ) from soil could be decreased in the presence of BC [4–6, 16]. In addition, BC has porous structure, charged surface, and surface functional groups (such as carboxyl, hydroxyl, phenolic hydroxyl, and carbonyl groups). These properties are the important factors that influence the migration, transformation, and bioavailability of contaminants in soil.

Figure 1 shows a schematic process diagram for the factors affecting BC production and application. This paper reviews the literature available for the production of BC from different category of biomasses, quantification and characterization of the resultant BC, adsorptive capacity, and the progresses made on experimental work and the importance in the environment.

## 2. Production of BC

*2.1. Category of Biomasses.* BCs are made from range of biomasses that have different chemical and physical properties. The properties of each biomass feedstock are important in thermal conversion processes, particularly the proximate analysis (ash and moisture content), caloric value, fractions

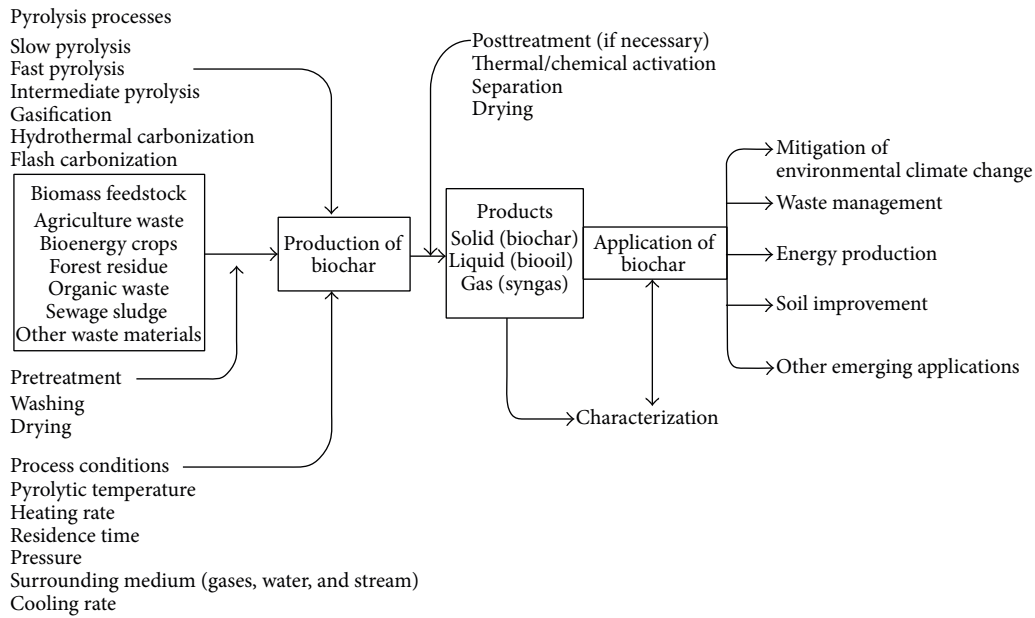


FIGURE 1: Schematic process diagram for the factors affecting BC production and application.

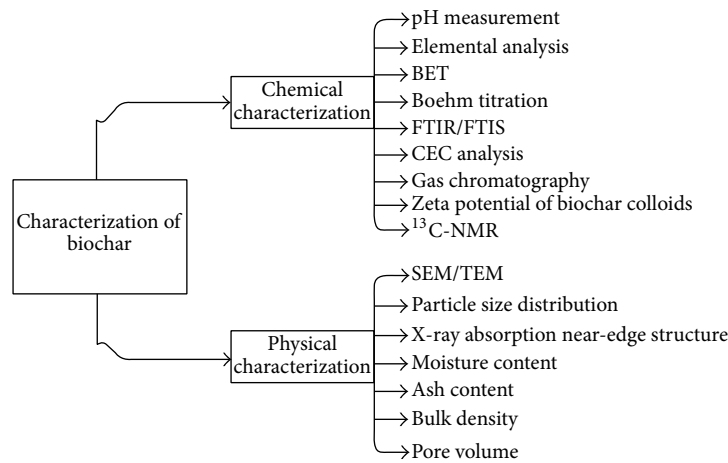


FIGURE 2: Overview of proposed characterization of BC.

of fixed carbon, and volatile components [17]; percentage of lignin, cellulose, and hemicelluloses [18]; percentage and composition of inorganic substance, bulk, true density, particle size, and moisture content. Extensive feedstock biomasses have been used in the production of BC [17], such as bioenergy crops (willows, miscanthus, and switchgrass) [19, 20], forest residues (sawdust, grain crops, and nut shells) [21], organic waste (green yard waste and animal manure) [22, 23], agricultural waste [24–29], kitchen waste, and sewage sludge [30]. It was again found that the following temperature-dependent structure transition was proposed: (1) transition BC having crystalline nature of the biomass feedstock or material preserved; (2) amorphous BC that is a random mixture of thermally changed molecules and emerging aromatic polycondensates; (3) composite BCs having poorly structured graphene stacks fixed in their amorphous phase; and (4)

turbastic BC dominated by chaotic graphite crystallites [31]. In general, a high yield of BC derived from this biomass which has more lignin and less cellulose can be expected. Meanwhile, the porosity of BC increases with the content of lignin in biomass. In addition, the volatile component, water content, and particle size and shape of biomass will affect the property of BC obtained. BCs formed at higher temperatures (lower oxygen to carbon ratio) are expected to be  $\pi$ -donors, while BCs formed at lower temperatures are expected to be  $\pi$ -acceptors [32]. BC produced from agricultural waste biomasses does not cause any notable life cycle based greenhouse gas (GHG) emissions [33].

**2.2. Preparation of BC.** Carbonised organic matter can essentially have different physical and chemical properties based on the technology (e.g., torrefaction (a pyrolytic

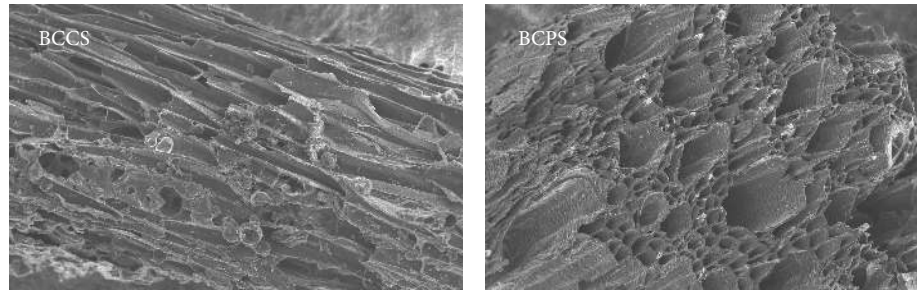


FIGURE 3: Photomicrograph from SEM.

TABLE 1: Biomass feedstock products of different types of pyrolysis.

| Process   | Liquid<br>(biooil)<br>(%) | Solid<br>(BC)<br>(%) | Gas<br>(syngas)<br>(%) |
|---|---------------------------|----------------------|------------------------|
| Fast pyrolysis: moderate temperature (600°C), short hot vapour residence time                     | 75                        | 12                   | 13                     |
| Intermediate pyrolysis: low moderate temperature, moderate hot vapour residence time              | 50                        | 25                   | 25                     |
| Slow pyrolysis: low moderate temperature, long residence time                                     | 30                        | 35                   | 35                     |
| Gasification: high temperature (>700°C), long vapour residence time                               | 5                         | 10                   | 85                     |
| Hydrothermal carbonization: elevated temperature (200–250°C) and elevated pressure.               | NRA                       | NRA                  | NRA                    |
| Flash carbonization: (350–650°C), residence time below 30 minutes, at elevated pressure (1–3 MPa) | NRA                       | 50                   | 50                     |

\*NAR = not readily available.

process primarily at low temperature), slow pyrolysis, intermediate pyrolysis, fast pyrolysis, gasification, hydrothermal carbonization (HTC), or flash carbonization) used for its production [34]. In contrast to considerable research, this has already been carried out to assess the value of BC as soil amendment [35]. No publication was identified which looks at the use of BCs from modern pyrolysis as soil amendment and immobilization of both inorganic and organic contaminants in the soil and water systems. BC can be produced both in traditional earthen charcoal kilns, where pyrolysis, gasification, and combustion process are carried out in parallel below the earthen kiln layer, and in modern BC retorts, where pyrolysis and combustion processes are physically separated by a metal barrier [36]. Papers have been published on the suitability of BC for the stabilization of organic carbon [3] and on the suitability of BC for the improvement of soil properties and immobilization of contaminants in both soil and solution systems [37].

Pyrolysis technology can be distinguished by the residence time, pyrolytic temperature of the pyrolysis material (e.g., slow and fast pyrolysis process), pressure, size of adsorbent, and the heating rate and method (e.g., pyrolysis started by the burning of fuels, by electrical heating, or by microwaves). Asensio et al. and IEA Bioenergy differentiate pyrolysis technology according to the pyrolytic temperature and the residence time of the pyrolysis or carbonization process as can be seen from Table 1 [36, 38].

Slow pyrolysis (heating for seconds or minutes) may be described as a continuous process, where purged (oxygen-free) feedstock biomass is transferred into an external heated kiln or furnace (gas flow removing volatile BC emerging at the

other end); “fast” pyrolysis on the other hand depends on very quick heat transfer, typically to fine biomass particles at less than 650°C with rapid heating rate (ca 100–1000°C/s) [39]. The characteristics of the BC product are heavily affected by the extent of pyrolysis (pyrolytic temperature and residence pressure) and entirely by biomass size and kiln or furnace residence time [36]. The rate at which volatile and gases are removed in a kiln or furnace determines the vapour residence time [39]. Prolonged residence time results in secondary reactions, notably the reactions of tar on BC surfaces and charring of the tar rather than additional combustion or processing outside the kiln or furnace [40]. For gasification in pyrolysis, the biomass feedstock to some extent is oxidized in the gasification chamber at a temperature of about 800°C at atmospheric or elevated pressure [40, 41]. As already pointed out by its name, the main product of this process is gas; only few or no BCs, liquids, or the likes are formed.

The hydrothermal carbonization of biomass is obtained by applying high pyrolytic temperature (200–250°C) to a biomass in a suspension with liquid under high atmospheric pressure for several hours. It yields solid, liquid, and gaseous products [42]. Libra et al. refer to hydrothermal carbonization as a “wet pyrolysis” [43]. Because no oxygen is applied to the reactor with the biomass liquid suspension, this explanation is readily accepted.

On the other hand, with flash carbonization of biomass, a flash fire is lights up at an elevated pressure (at about 1–3 MPa) at the underneath of a packed bed biomass. The fire travels in an upward direction through the carbonization bed against the downward flow of air supplied to the process. A total of about 0.8–1.5 kg of air per kg of biomass is injected

TABLE 2: List of some notable chemical characterizations of BC.

| Characterization   | Determination  | Results and remarks   | References   |
|--------------------|--|---|--------------|
| Elemental analysis | C, H, O, S, and N associated ratios  | H/C, O/C, and N associated ratios are used to determine the degree of aromaticity and maturation  | [56, 60, 61] |
| BET                | Surface area, pore structures, average pore diameter, pore volume, and average pores of BC             | $1057 \text{ m}^2 \text{ g}^{-1}$ ; macroporosity and microporosity; 5.2 nm; $0.24 \text{ mLg}^{-1}$ ; 3.3 nm   | [63, 125]    |
| Boehm titration    | Acidic and basic functional groups   | Functional groups determined include carboxylic, lactonic, and phenolic   | [45, 65]     |
| FTIR/FTIS          | Changes that occur in BC preparations as well as chemical functional groups present on the original BC | Changes include dehydration, pyrolysis, graphene nucleation, and finally carbonization; O–H ( $3600\text{--}3100 \text{ cm}^{-1}$ ), C=C and C=O stretching ( $1740\text{--}1600 \text{ cm}^{-1}$ ), C–O–C symmetric stretching ( $1097 \text{ cm}^{-1}$ ), –COOMe ( $1400\text{--}1500 \text{ cm}^{-1}$ ), and so on | [66–68]      |
| CEC                | Measure of the surface charge in soil or BC  | At aging 278 to $518 \text{ mmol}_c \text{ kg}^{-1}$ , $10.2$ to $69.2 \text{ mmol}_c \text{ kg}^{-1}$ , at neutral pH and $16.2 \pm 6.0$ and $21.0 \pm 17.2 \text{ mmol}_c \text{ kg}^{-1}$ for BC produced at 400 and $600^\circ \text{C}$  | [19, 69]     |

TABLE 3: Organic contaminants adsorbed by BC produced from different biomass precursors.

| Source of BC   | Organic pollutant sorbed   | References |
|--|--|------------|
| Pine needle  | Naphthalene, nitrobenzene, and m-dinitrobenzene from waste water | [83]       |
| Bamboo   | Pentachlorophenol  | [29]       |
| Bamboo, Brazilian pepper wood, and sugarcane bagasse | Sulfamethoxazole from waste water                                | [94]       |
| Wheat straw  | Hexachlorobenzene  | [25]       |
| Hardwood, softwood, and grass                        | Catechol and humic acid  | [19]       |

to the process. The residence time of the process is below 30 min, and the pyrolytic temperature in the reactor is in the range of  $330\text{--}650^\circ \text{C}$  [40]. The process results mainly in gaseous and solid products such as BC. In addition to that, a limited number or no number of condensates are formed [44]. While oxygen supplied to the carbonization process is a feature of gasification technologies, both process temperature and the product spectrum (delivery between solid, liquid, and gaseous output) of flash carbonization are exceptional for gasification processes [45].

It can be observed that typical solid products yields obtained by gasification and fast pyrolysis process are significantly lower as compared to the solid product yields of slow pyrolysis, flash carbonization, hydrothermal carbonization, and torrefaction [39]. Recent studies by Dowie et al. revealed the experimental pyrolysis conditions performed at the heating rate of about 10 k/min up to the press cubed pyrolytic temperature ranging from 673 to 973 K [46]. The yields of the resulting BC products are in the range of 25–40 wt%. The yield was observed to decrease slightly at higher pyrolysis temperature, which should be attributed to the volatilization of other volatile products from the component of the biomass.

Pellera et al. [47] also deduced that the BC yields of rice husk and compost derived after hydrothermal pyrolysis were about 62.5%, while olive pomace and organic waste were quite lower at 37.5%. Concerning the BCs produced through pyrolysis, the increase of pyrolytic temperature leads to a decrease in the yield for all produced materials. Specifically, the yields at  $300^\circ \text{C}$  and  $600^\circ \text{C}$  were 32.8% and 31.9% for rice husks, 39.3 and 26.7% for olive pomace, 39.6% and 32.8% for orange waste, and 78.7% and 46% for compost, respectively. The development of integrated systems that produce BC at higher efficiency by slow pyrolysis is still, therefore, mainly on the research scale with technology commercially deployed only at a handful of research centres and locations.

### 3. Quantification and Characterization of BC

**3.1. Quantification of BC.** The major aim of quantification is to distinguish BC from soil organic matter and from other forms of black carbons produced from varieties of biomasses. Many of the potential techniques depend on spectroscopic characteristics rather than physical separation or isolation. Some of the techniques that most effectively distinguish different types of BC can also be used to characterize individual BC wastes (or collection of fragments) recovered from both soil and solution systems. An assessment of pure samples removes the matrix effects, but where function of a recalcitrant component depends on its surface characteristics or those of accessible pores, separation of active and inactive components presents a significant challenge [29].

Classifying BC is principally problematic on the basis of its chemical complexity and diversity, yet characteristically uncreative nature. Due to its recalcitrance nature, BC cannot eloquently be extracted from soil using chemical methods, though potential biomarkers may be. The results from studies using the physical location of BC within a soil matrix [40, 48] suggest that usefulness of physical separations using density or means other than hand sampling approach (which is restricted to very small samples) is susceptible to site factors.



Until recently, the most practical methods have sought to remove nonblack components (i.e., oil organic matter and mineral carbonates) with subsequent evaluation of the residue. However, for quantifying BC, particularly this type of quantification may be affected by the presence of the more frequent recalcitrant black carbon forms, as well as by the presence of highly resistant organic carbon compounds, such as those stabilized on the biomass not incompletely removed, which in some cases are estimated alone [4].

Different technical methods differentiate components of increasing minimum stability incompletely charred biomass, BC, charcoal, activated carbon, soot, and graphitic black carbon [49]. Leaching method in this grouping includes removal of nonblack carbon by chemical oxidation (e.g., sodium chlorite and potassium dichromate), using ultraviolet radiation, or by a thermal approach [50]. Hydrolysis pyrolysis (HyPy) is an alternative way to the removal of nonblack carbon [51], which evolved gas analysis from the character of the varied gaseous products of thermal decomposition. A combined chemothermal oxidation method, with a temperature of threshold [34], forms the foundation of a benchmark procedure for the determination of fixed carbon, which is composed of the most stable fraction of black carbon and has the more stable component of BC.

Virtual separations have conventionally been based on spectroscopic techniques in combination with pretreatment (or other allowance) for numeral interference, for example, using hydrofluoric acid [52], pyrolysis gas chromatography mass spectroscopy (PyCG/MS), and solid state  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$ NMR) spectroscopy with cross-polarization, block deterioration, and combined with magic angle spinning (MAS) [49] or chemically extracted and purified biomass products, particularly benzene polycarboxylic acid (BPCA) [53] and laevoglucose [54]. A further approach well thought of in this class is matrix-assisted laser desorption ionization (MALDI-TOF) [55].

The utilization of these methods depends on the purpose of the analysis and the specific nature of the target fraction, so even though all have been evaluated for a set of environmental and black carbon samples in a ring trial [56], there remains comparatively little agreement as to a widespread paradigm. Since most methods depend on progressive segregation which are based on increasing recalcitrant soil organic matter, graphitic and soot fraction, it is easy to know the content of relatively less condensed (stable) charcoal or BC fractions [57]. On the other hand, UV or chemical oxidation with elemental and  $^{13}\text{C}$ NMR analysis of residues, thermal analysis [50, 56], and PyHy [51] were identified as the most promising techniques.

A partial new development in the quantification of BC has been the use of correlative techniques based on mid-infrared (MIR) spectroscopy. Initially evaluated for the estimation of organic carbon content of bulk soil and solution samples, among other key properties, algorithms have been utilized for relating MIR response spectrum to BC, using a calibration set assessed using UV-oxidation method. The method has also been employed to evaluate charcoal content in region evaluation using archived soil [17] and holds potential for comparable assessments in the worldwide contexts.

**3.2. Chemical Characterization.** The original biomass feedstock and its BC can be subjected to a range of analyses in order to provide the basic physicochemical characteristics of each raw and pyrolyzed material. These physicochemical characterizations are displayed in Figure 2.

The chemical characteristics of individual feedstock species and therefore of BC derived from the feedstock have always been shown to vary significantly both spatially and temporarily [34]. BC production is often assessed through changes that might occur in the elemental concentrations of C, H, O, S, and N and associated ratios [49]. It is well known that fixed carbon is the solid combustible residue that remains after a particle sample is carbonized and volatile matter is expelled [58, 59]. Thus, it is used as an estimate of the number of carbonaceous substances that will be yielded from a solid sample. Particularly, H/C and O/C ratios are used to determine the degree of aromaticity and maturation, as is often described in Van Krevelen diagrams [56]. Yu et al. on their recent work [60], where they used BC-based catalyst in the transesterification of canola oil, found out that the elemental analysis showed a decrease in the H/C and O/C ratios with increasing temperature of pyrolysis. Elemental ratios of O/C, O/H, and C/H have been found to provide a reliable measure of both the extent of pyrolysis and level of oxidative adjustment of BC in the soil and solution systems and are relatively straightforward to be determined [60, 61].

BET (Brunauer, Emmett, and Teller) areas increased with an increase of carbon burn-off, irrespective of the pyrolytic temperature [56]. This indicates that the burn-off of the carbon has the most significant consequence on the increase of the surface area. In general, the surface area, pore volume, and average pore size increased with residence time and pyrolytic temperature [62]. Qiu et al. determined the BET surface area of BC ( $1057\text{ m}^2\text{ g}^{-1}$ ) which was slightly higher than that of AC ( $970\text{ m}^2\text{ g}^{-1}$ ). The micropore volume of BC ( $0.24\text{ mL g}^{-1}$ ) was again smaller than that of activated carbon ( $0.32\text{ mL g}^{-1}$ ), dependable with the average pore diameter of the former (5.2 nm) being larger than the latter (3.3 nm) [63]. Cheng et al. worked extensively on the magnetic BC for the sorption of organic pollutants and phosphates determined that the surface areas (internal and external surface areas) of BCs were fewer than other BCs, whereas the average pore radius use of the former was larger than the latter [64]. This might be due to the magnetic BCs containing substantial amount of the iron oxide, which have smaller surface areas and plentiful temporary pores. Table 2 shows few chemical characterizations of BC from the paper reviewed.

Operational determination of acidic and basic functional groups on BC can be performed by Boehm titration [65] in which the BC is equilibrated in the presence of consecutively strong bases ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , and ethoxides) or strong acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ ) followed by titration of the extract with strong acid or base to estimate the fraction that reacted. Differences in the number of the acids or bases needed are used to estimate their relative amounts of carboxylic, lactonic, phenolic, and carboxylic functional groups (base equilibration) or basic functionalities (acidic equilibration) [45]. Characterization of BC used as soil

amendment and, the ethoxides equilibration is commonly omitted as it measures functional groups that are dissociated only at a very high pH, while immobilization of pollutants occurs at moderately low pH [64]. The Boehm titration operates well for hydrophobic BC but a major shortfall appears when a significant number of biooils or mineral surfaces are present [47].

In carbonization of biomass feedstock for the preparation of BC four regions of changes are normally observed at nonhydrothermal conditions [31]. They include dehydration, pyrolysis, graphene nucleation, and finally carbonization. These changes can be observed when BC is subjected to Fourier transform infrared spectroscopy (FTIS/FTIR). Again FTIS/FTIR can also be used to identify the chemical functional groups present on the original BC [66]. As enumerated by Lee et al., their recent work [67] showed that samples used in preparing gasification BC (700°C) and fast pyrolysis BC (450°C) showed characteristic bonds similar to those of cellulose. It is clear between the baseline corrected FTIR spectra of the sample that with increase in temperature, there is a remarkable decrease in features associated with O–H (3600–3100 cm<sup>-1</sup>), C=C and C=O stretching (1740–1600 cm<sup>-1</sup>) and aromatic C=C and C–H deformation modes of alkenes (1500–1100 cm<sup>-1</sup>), and the C–O–C symmetric stretching (1097 cm<sup>-1</sup>) characteristics of cellulose and hemicelluloses. In the combined sorption of Pb<sup>2+</sup> and its mechanism case study by Qiu et al. [66], BC was found to contain an abundant amount of carboxyl and hydroxyl groups through FTIR spectra analysis of their sludge-derived BC (SDBC). Again, the band for the complexed carboxyl (–COOMe) shows no clear change effect after being replaced by lead at the range of 1400–1500 cm<sup>-1</sup>, possibly due to the corresponding substitution of the cations. The remarkable shift of the band at 3404–3406 cm<sup>-1</sup> (pH = 2.0), 3420 cm<sup>-1</sup> (pH = 3.0), 3429 cm<sup>-1</sup> (pH = 4), and 3422 cm<sup>-1</sup> (pH = 5.0) supported the proposed complexation between Pb<sup>2+</sup> and hydroxyl as well as carboxyl functional groups [68]. Additionally, the band at 1032 cm<sup>-1</sup> was shifted to 1034 cm<sup>-1</sup> (pH = 4.0) and 1035 cm<sup>-1</sup> (pH = 5.0); they again concluded that it is an indication of coordination of Pb<sup>2+</sup> with carboxylate groups.

Cationic exchange capacity (CEC) as widely known in agronomical sector is the measure of the surface charge in soil or BC, which increases as the BC ages [34] and has been ascribed to an increase in some oxygenated functional groups on the surface of the BC [64]. The most distinct change in any absolute CEC values was observed for the BC as a result of time where it increased from 278 to 518 mmol<sub>c</sub> kg<sup>-1</sup>, most likely because oxidation process created hydroxyl and carboxylic acid functional groups [69].

Biomass feedstock is a major factor governing the status of such physicochemical properties; pyrolytic temperature is the most significant process parameter; carbon content of BC is nondirectly related to BC yield, increasing from 53 to 83% and from 300 to 800°C in one study, while yield of BC decreased from 67 to 26% [19].

**3.3. Physical Characterization.** Scanning electron microscopy (SEM) is a microscopic technique in determining

the image macroporosity and physical morphology of solid substances [17]. The macroporous structure (pores of approximately 1 μm diameter) of BC produced from cellulose plant material depends upon the intrinsic architecture of the feedstock, and it is potentially important to water-holding and adsorptive capacity of pollutant in soil and solution systems [17, 70]. SEM micrographs of BCCS (cotton (*Gossypium herbaceum*) straw) and BCPS (potato (*Solanum tuberosum*) straw) obtained in our previous study are shown in Figure 3 [71]. The BCs produced at different pyrolytic temperature had a distinguishable honey-comb-like structure due to the presence of tubular structures originally emanating from plant cells. As a result of these well-developed pores, the BCs possessed a high BET surface area. The significance of pyrolytic temperature leads to the suggestion that BC produced at low pyrolytic temperature may be appropriate for regulating release of fertilizer nutrients [72], while high temperatures would lead to a material analogous to AC in environmental remediation [70]. It can also be detected that the surfaces of low temperatures BC can be hydrophobic, and this may reduce its capacity to store water in soil as well as adsorb pollutants. The form, type, preliminary preparation steps and size of the biomass feedstock, and type of pyrolysis product may affect the characteristics, nature, quality, and potential use of BC [73]. Initially, the ratio of exposed to total surface area of BC will be affected by its size. Additionally, although low pyrolytic temperature BC is stronger than high temperature products, it is brittle and pores are abraded into fine fractions once incorporated into the soil.

In explaining the relationship between the mechanism of heavy metal sorption and SEM, Qiu et al. proposed a vivid explanation [66]. They observed bright zones on the pores surface of Pb-loaded BC at pH = 5 in the SEM photography. Its EDX spectrum represents the red surface and additionally established the occurrence of silicon and phosphorus, which might exist in the form of 5PbO·P<sub>2</sub>O<sub>5</sub>·SiO<sub>2</sub> (lead phosphate silicate) precipitates which was again identified by XRD spectra. They concluded that the precipitates should be an important means of modelling the mechanism for Pb<sup>2+</sup> removal from soil system and again can be related to solution system.

## 4. Sorptive Properties of BC

Unlike any other carbonaceous fuel, BC is generally used as a soil amendment and in water treatment. The physicochemical properties of BC such as surface area, charged surface, and functional group vary appreciably based on the biomass source and pyrolysis condition, which affect the adsorptive capacity of BC to heavy metals and organic compounds.

**4.1. Sorption of Heavy Metals.** In cases of BC nature, the most appropriate and effective method for heavy metal or trace metals removal has been proven to be adsorption using BC [26, 30, 74–76]. The adsorption mechanisms mainly include electrostatic interaction, ionic exchange, chemical precipitation, and complexation with functional groups on BC surface [26, 34, 74, 76]. Mechanisms of heavy metal sorption

by BC can be systematically investigated using different methods, including adsorption isotherms and kinetic models, desorption studies, and industrial analysis including XRD, FTIR, and SEM. Sorption may encompass the electrostatic attraction and innersphere complex with free and complexed carboxyl, alcoholic hydroxyl, or phenolic hydroxyl groups on BC surface (such as R-COOH, -COOMe, -ROH, and -ROMe, where Me represents the central metal atoms) as well as coprecipitation or superficial precipitation [66]. Carboxyl (R-COOH) and alcoholic or phenolic hydroxyl groups (R-OH) are usually acknowledged as the main groups contributing to coordination between heavy metals and sorbent surface [77]. Comparing with organic pollutants, inadequate information is available on the factors regulating the immobilization of inorganic contaminants on BC and the impact of BC on heavy metal retention in soils [78]. Studies utilizing ACs have suggested that, depending on the solution composition and the carbon type, the following mechanism predominates: (1) electrostatic interaction between metal cations and negatively charged carbon surfaces (above  $\text{pH}_{\text{pzc}}$  of carbon) and (2) ionic exchange between ionisable protons at the surface of the acidic carbonaceous adsorbent via proton exchange ( $-\text{C}\pi-\text{H}_3\text{O}^+$ ) [47, 79] or coordination of d-electrons [22]. Mineral impurities such as ash and basic nitrogen groups (e.g., pyridine) can serve as additional adsorption sites of the carbonaceous material. Interpretation of the thermodynamic parameters of metal sorption to BCs and activated carbons reveals that sorption is an endothermic physical process [26, 80, 81]. That is, an electrostatic interaction occurs between the positively charged metal cations and  $\pi$ -electrons associated with either C=O ligands or (more likely) C=C of a shared electron cloud on aromatic structures in BC [68, 74, 81, 82]. The authors suggested that BC reduces Pb mobility due to the precipitation of insoluble Pb-phosphates. BCs derived from manure have been reported to be rich in P [22]. Solution pH is an important parameter that affects both the surface charge density of the adsorbent and the metal ion speciation [83]. Chen et al. also observed that pH significantly affected the adsorption of Cu(II) and Zn(II) adsorption onto BC and was more pronounced for CS 600°C (corn straw based BC produced at 600°C) and HW 450°C (hardwood based BC produced at 450°C) [84]. They found out that the adsorption capacities  $q_e$  ( $\text{mg g}^{-1}$ ) of these BCs increased with increasing of pH values of the test solution until it attains its maximum at pH 5. Measurement of the change in solution pH after BC addition and adsorption equilibrium showed that both BCs had a buffering capacity that was distinguished from that of the electrolyte.

**4.2. Sorption of Organic Pollutants.** The adsorptive capacity of BC for organic contaminants depends upon the type of biomass and pyrolysis conditions. It has been found that BC has large adsorptive capacity for pesticide, persistent organic pollutant (PAHs, PCBs, etc.), chlorinated compounds, and dyes [63, 85–92]. Table 3 shows BC produced from different biomasses used in the adsorption of some organic pollutants. The sorption of organic contaminants of both wood and manure based BC was found to be assisted by  $\pi$ -electrons

interactions [83] and progressed with a pore-filling mechanism process [93]. Previous work has been done on plant-residue derived BC for sorbing organic contaminants. Chen et al. reported that pine-needle derived BC was effective in removing naphthalene, nitrobenzene, and m-dinitrobenzene from water [83]. Lou et al. showed that agricultural soil amended with bamboo derived BC improved the leachability and bioavailability of pentachlorophenol [29]. Yao et al. again reported that BCs derived from bamboo, Brazilian pepper wood, sugarcane bagasse, and hickory wood were successful in removing sulfamethoxazole from water [94] and De Wild et al. finally assessed the bioavailability assessment of hexachlorobenzene in soil by employing wheat straw based BC [25].

Addition of BC has been shown to increase sorption and to decrease the dissipation of pesticides in soils [95]. Finally, previous studies have demonstrated that carbonaceous materials, such as peat [24, 96], soya bean stalk [96], and coke [97] based BC, can effectively regulate organic contaminants and decrease the bioavailability of organic contaminants by repartitioning organic contaminants to carbonaceous adsorbents. However, it is still inexact if BC is suitable for the sequestration of organic pollutants. Furthermore, most researches on the likelihood of regulating organic pollution with carbonaceous materials have been performed by equilibrium adsorption experiments [29]. Yet, soil column leaching experiments were found to be more idyllic to simulate the actual situation of in situ soil organic pollution control and to understand the possibility of using carbonaceous materials to guard plant and groundwater [98].

In the collective sorption of pentachlorophenol (PCP) case study [99], the BC produced from rice straw (RC) and fly ash (FC) was found to have exhibited encouraging sorption ability. It was again found out that the sorption capacity of the BC supplemented sediments increased with an increase in BC content in the sediments. The parameters were well fitted by the Freundlich and dual mode models.

The sorption of both organic and heavy metal pollutants may be influenced by several factors, such as pH [100], specific surface area [101], particle size, time of exposure of pollutants, and soil moisture [99]. Some researches have indicated that the adsorptive competition occurs when multicontaminants are adsorbed onto BC. Inyang et al. prepared two BCs from anaerobically digested biomass. The adsorptions of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  onto BCs were investigated [102]. It was found that the BCs demonstrated a better ability to remove  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ . The competitive adsorption between Cu(II) and Zn(II) onto BCs produced from pyrolysis of hardwood and corn straw occurred when the ion concentrations were kept at 1.0 mM/L [84]. The results reported by Uchimiya indicated that the adsorption of deisopropylatrazine onto broiler litter BC was inhibited in the presence of Cu(II) in binary-solute experiments [82].

## 5. Effect of BC on Bioavailability of Heavy Metals and Organic Pollutants in Soil

Soil is well known for its adsorption and CEC properties. The adsorption of heavy metals by soils and BC effect on the



mobility and fate of the heavy metals have been extensively studied in recent times [57, 91, 103–108]. The results showed that the addition of wood BC to soil did not have any significant effect on the dry matter yield of maize plants, even at the highest rate of application, but BC application decreased the concentration of As, Cd, and Cu in maize shoots, which depended upon amount of BC addition, pH values of soils, and ability of metal to adsorb on BC [105]. When BCs made from sludge and lignite were applied to soil, not only are the properties of the soil improved but also the mobility of the HMs in the mixtures, which is connected with the characteristics of the matrix, may be affected [82]. In their recent work [20], Beesley and Marmiroli found that there was an important negative relationship between pH and cadmium in eluates from soil when it had passed through BC, showing that raising the pH could be the mechanisms by which Cd movement was reduced by BC, considering the high soluble Cd concentration in the soil. Other notable researches have also indicated that increase in soil pH will subsequently lead to an increase of Cd in solution by adsorption [109].

The sorption of anthropogenic hydrophobic organic compounds (HOCs) (e.g., PAHs, polychlorinated biphenyls, PCBs, pesticides, and herbicides) in soil and sediments is generally described based on two coexisting and simultaneous processes, absorbing into natural (amorphous) organic matter (NOM) and adsorption into naturally occurring BC material [110]. Comparatively, to that of NOM, BC (including soot) generally holds up to 10–1000 times higher sorption affinity toward such compounds [111]. It has been estimated that BC can account for as much as 80–90% of total uptake of trace HOC in soils and sediments [110]. BC application is therefore expected and accepted to improve the overall sorption capacity of soil [112] and, consequently, influence toxicity, transport, and fate of trace contaminants, which may be already or are to be added to soils. Despite the fact that little is still known on the microscale process controlling sorption to BC [113] in soils and sediments, it has been suggested that it is mechanistically different from the conventional sorption model for NOM and that it is also a less reversible process. While adsorption onto BC has little or no concentration dependence, adsorption to BC has been shown to be strongly concentration dependent [114], with affinity decreasing for increasing solute concentration.

BC is applied to soil for the conditioning and fertilization purposes; application can also be favourable in reduction of toxic components. Recent studies have shown that BC is also capable of adsorbing heavy metals such as lead, cadmium, nickel, and some notable organic contaminants that contaminated soils which can cause harm to human, plants, and animals [115]. For that reason, BC as an additive to a soil can be expected to improve its overall adsorption capacity impacting toxicity because there is a decrease in transportability and depletion of the presence of metal or organic compounds. Due to its low cost and limited environmental impact, BC would be a promising strategy for remediation of polluted environment [116]. Recent studies have shown that BC in collaboration with activation have comparable adsorption and absorption abilities, which plays a great role in removal of contaminants such as lead (Pb) [115].

Considering recent experimental methods, results have shown that metal ions are strongly adsorbed onto specific active sites containing phenolic and carboxyl functionalities of the surface of BC [117]. Reviewing of BC application to wastewater treatment, contaminants such as heavy metal (lead) intake by BC, involves replacing already existing ions that might be present on the BC with the metal ion in solution system, suggesting a potential correlation between content of the BC and its remediation potential for metals [84]. With my research, monitoring, reviewing, and basic understanding of BC, proper or accurate application to benefit environment concerns will be in the near future the simplicity of production methods to the capability for integration into less developed countries.

Although amending soils with BCs will reduce the bioavailability and hence the toxicity of contaminants, it is also likely for them to reduce the rate at which organic compounds are degraded in the environment precisely due to this reduction in bioavailability [118]. A number of studies have shown that the presence of BC or black carbons can reduce the degradation of organic pesticides [104, 119] and other organic contaminants [103, 120, 121]. This should be considered when amending soils with BC, especially when soils contain organic compounds that would otherwise degrade relatively rapidly. Also, this decreased bioavailability can be detrimental in terms of reducing herbicide efficiency, resulting in the need for higher application rates of these chemicals [122]. In some occasions, BCs have been found to have a negative effect on some sediment and soil organisms, especially those that live in intimate contact and ingest large volumes of sediment and soil [123, 124].

## 6. Conclusions

BC can be derived from a wide range of sewage sludge, forest residue, organic and agricultural wastes biomass feedstocks, at different pyrolysis conditions and at a range of balances. The characteristics of BCs identified by physical and chemical methods reveal the basic structure and property of BC. Due to its large surface area, charged surface, and functional groups, BC is of great potential to adsorb heavy metal and organic contaminants. Addition of BC should decrease the bioavailability, toxicity, and mobility of organic and inorganic pollutants. This has the potential to be beneficial for immobilization of contaminants with high concentrations. However, the amending of BC also has negative effect on the efficacy of pesticides and herbicides, the degradation rate of organics and some sediment, and soil organisms.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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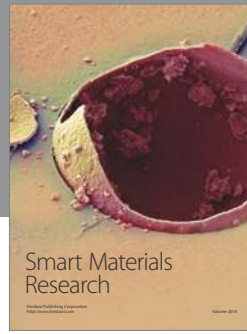
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