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Characteristics of biochar: A review

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Abstract

A carbon-rich substance with great environmental stability, biochar is mostly made from biomass. The direct use of biochar as a renewable energy source, as a soil additive to increase soil fertility and reduce soil greenhouse gas emissions, and as a filter medium for wastewater treatment. Making biochar results in less air pollution than burning agricultural waste outside, which can release noxious gases (CO, SOx, NOx), as well as smoke particles that contain carcinogens. In addition to the particle pollutants, open burning of agricultural waste in fields produces a 16 polyaromatic hydrocarbon that is harmful to human health. Mostly carbon-based chemicals make up biochar. Additionally, there are traces of hydrogen, oxygen, sulphur, nitrogen, and ash. The type of biomass employed, the reactor design, and the production conditions all have an impact on the composition and properties of biochar.

The most important factors affecting the adsorption qualities of biochar are its chemical composition, porosity, quantities of inorganic metals initially present in the feedstock, and the process conditions. Similar to activated carbon, biochar has a surface heterogeneity. Because of its large surface area, higher carbon content, high cation and anion exchange capacity, and stable structure, biochar reportedly outperforms activated carbon in the removal of a variety of contaminants, including pathogenic organisms, organic matter, surfactants, nitrogen (N), micropollutants, heavy metals, and other pollutants. The pore network of biochar is evenly distributed and has a vast surface area, with micropores as large as 2 nm, macrospores as small as 50 nm, and micropores ranging from 2 to 50 nm. It has a specific adsorption effect on heavy metals and organic ammonia nitrogen in the water because of its huge specific surface area. In other instances, the biochar's surface area was found to be less than activated carbon, although it had a greater capacity for adsorption. This is owing to the fact that the adsorption of water causes swelling within the biochar, increasing the internal surface area, and as a result, increasing the adsorption capacity.

Keywords: Biochar, pyrolysis, biological nitrogen fixation, *Prosopis juliflora*

Introduction

Characterization of biochar

The properties of biochar vary substantially depending on the source of biomass, the rate at which it is heated, the maximum temperature of heating, and the extent to which volatiles produced during pyrolysis are separated from the biochar prior to cooling. The level of aromaticity directly influences the stability of biochar in soil environments. Other properties of biochar that influence soil quality are particle size, porosity, surface area, the density and types of surface functional groups, concentrations of biologically available and biologically active compounds in the biochar, and concentrations and forms of inorganic bases that are admixed with the biochar (David and Novak. 2012) [8].

Carbon

Biochar contains about 65 to 90 per cent carbon, with the balance being volatile matter and mineral matter (Antal and Gronli, 2003) [1]. The carbon content of biochar is inversely related to biochar yield. Increasing pyrolysis temperature from 300 to 800°C decreased the yield of biochar from 67 to 26 per cent and increased the carbon from 56 to 93 per cent (Tanaka, 1963 and Sohi *et al*., 2009) [25, 24]. With increasing temperature, the recovery of biochar commonly decreases, whereas the carbon content increases (Daud *et al*., 2001; Demribas, 2001 and Katyal *et al*., 2003) [7, 10, 14]. Although carbon is the major constituent of biochar, exact composition and physical properties depend upon the starting material and the condition under which it is produced (Brown, 2009) [2]. The range of carbon forms within a biochar particle may depend on the carbon properties (Lehmann, 2007) [17].

Novak *et al.* (2009) [20] observed that most of the biochar carbon was distributed in aromatic structures (58%), with less amounts of carbon having single bonds to oxygen (29%) and in carboxyl (13%) groups but little carbohydrate carbon and also observed that carbon content of biochar is inversely related to biochar yield. Shenbagavalli and Mahimairaja (2012) [23] reported that the *Prosopis* biochar had very high carbon content (940 g kg^{-1}) with a C/N ratio of 83.9. In biochemical analysis revealed that the cellulose content was relatively higher (36%) than the hemicelluloses (31%) and the lignin (22%).

Biochar from wood has very low ash content, typically less than 2 per cent, whereas the ash content of tyre-derived char is often over 10 per cent. The proportion of biochar comprised of ash increased from 0.67 to 1.26 per cent between 300° C and 800° C (Kuwagaki and Tamura, 1990) [15].

Chemical properties

In general, biochar had a very poor nutrients content in the order of K > N > and P. Sodium content was relatively higher than Ca and Mg in the biochar. The huge variation in the chemical composition can be attributed to the differences in feed stocks and conditions under which the various types of biochar are produced. The operating conditions of production also influence the nutrient content of biochar. When comparing the biochar produced from poultry litter by Lima and Marshall (2005) [18], the operating conditions during pyrolysis determine to a significant extent the N contents. The total N contents of biochar from poultry litter produced by Chan *et al.* (2007) [4] was 20 g kg^{-1} compared to 7.5 and 6.0 g kg^{-1} for two types of biochar made from different poultry litter reported by Lima and Marshall (2005) [18], such large differences in total N are a result of either different poultry litter quantities or different pyrolysis conditions. Lima and Marshall (2005) [18] reported that the temperature, the time and a material are held at in a given temperature and the heating rate during pyrolysis directly influences the chemical constituents of biochar. They have also reported that the individual elements are potentially lost to the atmosphere fixed into recalcitrant forms or liberated as soluble oxides during the heating process. A much higher temperature (700°C) was used by Lima and Marshall (2005) [18] as compared to the 450° C reported by Chan *et al.* (2007) [4] which may suggest greater N loss at higher pyrolysis temperatures.

During low temperature (< 500° C) slow pyrolysis, P, K and S typically accumulate on the biochar product in a bio-available form (Hossain *et al*., 2007) [13]. Where pulp and paper sludge is pyrolysed, the ash content contains considerable quantities of $CaCO_3$ and bentonite, originally used in the paper making process. These materials provide valuable liming properties when applied to acid soils, but would be undesirable contaminants if the same biochar was applied as a metal reductant (Van Zwieten *et al*., 2007) [26].

Chan and Xu (2009) [3] summarized the pH and nutrient (N, P and K) composition of biochar produced from various feed stocks. The carbon contents of biochar ranged between 172 and 905 g kg^{-1}. The ranges were even larger in the case of total N (1.8 to 56.4 g kg^{-1}), total P (2.7 to 480 g kg^{-1}) and total K (1.0 to 58 g kg^{-1}). The most important measures of biochar quality include adsorption, cation exchange capacity, mobile matter (tars, resins, and other short-lived compounds) and type of organic matter feedstock used. Over time, adsorption capacity of biochar decreases, whereas its cation exchange capacity increases (Cheng *et al*., 2008 and McLaughlin *et al*., 2009) [6, 19].

Physical properties

The chemical structural aspects of biochar can be characterized spectroscopically (e.g. 13C-NMR, ESR, Raman), chemical/thermal analysis (TGA-MS, Py-GCMS) or microscopically (SEM, TEM). Chemical characteristics of biochar can be assessed using standard agricultural soil testing, although some methods require modification.

Eco toxicological testing such as earthworm avoidance assays and plant germination inhibition assays can be used to test the ecological safety of the biochars. Scanning electron microscopy (SEM) is often used to describe the physical structure of biochar and the architecture of cellulosic plant material is clearly retained. It has been suggested that the porous structure of biochar can explain its impact on soil water holding and adsorption capacity (Yu *et al*., 2006) [29] process temperature greatly affects the surface area of pyrolysis products. Surface area was shown to increase from 120 m^2 g^{-1} at 400 °C to 460 m^2 g^{-1} at 900 °C. This effect of temperature has led to suggestions that biochar created at low temperature may be suitable for controlling the release of fertilizer nutrients (Day *et al*., 2005) [9] whilst high temperature biochars would be more suitable for use as activated carbon (Ogawa *et al*., 2006) [21]. The surfaces of low temperature biochar are hydrophobic and this may limit the capacity to store water in soil.

Charred biomass consists not only of recalcitrant aromatic ring structures, but also of more easily degradable aliphatic and oxidized carbon structures (Schmidt and Noack, 2000) [22]. The range of carbon forms within a biochar particle may depend on the carbon properties of the plant cell structure, on the charring conditions, and on the formation process (by either condensation of volatiles or by direct charring of plant cells). The consequence of this heterogeneity is that some portions of biochar may indeed be mineralized very rapidly, as are aliphatic carbon forms (Cheng *et al*., 2006) [5]. An extrapolation from relatively easily mineralizable carbon forms to the entire biochar may therefore lead to erroneous projections.

Biochar's particulate form also clearly distinguishes it from other stable forms of organic matter, which are commonly perceived as macromolecules or macromolecular associations entrapped in fine pores adsorbed to mineral surfaces, or occluded in aggregates. Particulate organic matter is mostly unprotected by mineral association and is therefore easily mineralizable (Golchin *et al*., 1994) [12]. Biochar exists as particulates, biotic or abiotic decay must be initiated on its surface. Such surface oxidation may be initiated quite rapidly (Cheng *et al*., 2006) [5], but is restricted to the outer areas of a particle, even after several hundred years in soils (Lehmann *et al*., 2005) [16]. Although biochar is present in particulate form, it is very recalcitrant to microbial decomposition (Schmidt and Noack, 2000) [22]. The particulate form may serve in itself as a protection mechanism against decay for the interior of the biochar particle, by compartmentalization; this is similar to the mechanism proposed for the protection of organic by aggregation (Yin *et al*., 2000) [28]. Although the vascular structure of plant materials contributes to large pores in biochar, most of the surface area derives from nonporous created during the heating process (Brown, 2009) [2].

Mobile matter can block porosity and initial adsorption but is highly susceptible to biological decay, which can mitigate those effects. The physical structure of the feedstock, mainly its pore size, which greatly determines surface area, water retention, and biological utilization of the biochar produced, is essentially locked into form during "thermal modification." While a greater proportion of micro-pores may yield a higher surface area, and thus greater nutrient retention capability, many soil microorganisms are too large to utilize such small spaces and benefit from some amount of larger pore sizes (Warnock *et al*., 2007) [27]. In terms of increasing plant growth, biochar with various pore sizes may be best suited to enhance the physical, chemical, and biological characteristics of soils. The process by which a biochar is produced is an important factor influencing its quality. While some methods have consistently produced low-quality biochar, other processes, when done properly, can yield high quality biochar.

A notable characteristic of biochar is its high porosity. Downie *et al.* (2009) reported that the bulk density of biochar made from plant biomass is lower than that of the corresponding feedstock. In general biochar retains the cell wall structure of the biomass feedstock as observed in scanning electron microscope. Levine (2009) reported that at a smaller scale biochar consists largely of amorphous graphene sheets, which give rise to large amounts of reactive surfaces where a wide variety of organic (both polar and non-polar) molecules and inorganic ions can sorb.

Downie *et al.* (2009) [11] reported that the pore space of biochar in many orders of magnitude greater than that of uncharred biomass. The low density of biochar and its property to float before it is fully imbibed result in more water being required. In the case of standard fuel charcoal analysis techniques, some methods need to be modified to produce results which relate to the effect biochar will have in soil. For example, "volatile matter" in charcoal is measured at 950° C, and it is difficult to relate this "volatile matter" to functions of biochar in soil.

Characteristics of *Prosopis juliflora* L. biochar

Prosopis is widely grown in many parts of Tamil Nadu and it is available in large quantities particularly in dry tracts and wastelands. Shenbagavalli and Mahimairaja (2012) [23] reported that the biochar had a bulk density and particle density of 0.45 and 0.54 Mg m^{-3} respectively with a pore space of about 48 per cent. It had very low moisture content (1.21%) but high water holding capacity (131%). The pH and EC of the *Prosopis* biochar were near neutral (7.57) and non-saline (1.3 dS m^{-1}) respectively with CEC of 16 cmol (p+) kg^{-1}. It was high in exchangeable acidity (49 m mol kg^{-1}). The carbon content was very high (940 g kg^{-1}) but total N content was very low (1.12 g kg^{-1}).

It contained only low amounts of total P (1.06 g kg^{-1}) and relatively higher amounts of total K (29 g kg^{-1}). It also contained higher amount of Na (38 g kg^{-1}) than Ca (11 g kg^{-1}) and only a small amount of Mg (0.36 g kg^{-1}).

Biological Nitrogen Fixation

The effect of biochar application on biological nitrogen fixation was studied. They studied the potential, magnitude and causes of enhanced biological N_2 fixation (BNF) by common beans (*Phaseolus vulgaris* L.) through biochar additions. Biochar was added at 0, 30, 60, and 90 g kg^{-1} soil, and BNF was determined using the isotope dilution method after adding 15 N-enriched ammonium sulphate to a Typic Haplustox cropped to a potentially nodulating bean variety in comparison to its non-nodulating isoline, both inoculated with effective *Rhizobium* strains. The proportion of fixed N increased from 50 per cent without biochar additions to 72 per cent with 90 g kg^{-1} biochar added. Although total N derived from the atmosphere (NdfA) was significantly increased by 49 per cent and 78 per cent with 30 and 60 g kg^{-1} biochar added to soil respectively, NdfA decreased to 30 per cent above the control with 90 g kg^{-1} due to low total biomass production and N uptake.

Biological fixation of atmospheric N by common beans was found to be enhanced by the addition of biochar to a highly weathered savannah soil, most likely through the mechanism of greater micronutrient availability. It was reported that the higher BNF with biochar additions was due to greater B and Mo availability. Increase in K, Ca and P availability, as well as higher pH and lower N availability and Al saturation, might also have contributed to a lesser extent. Enhanced mycorrhizal infections of roots did not contribute to better nutrient uptake and BNF. Bean yield increased by 46 per cent and biomass production by 39 per cent over the control at 30 and 60 g kg^{-1} biochar respectively. However, biomass production and total N uptake decreased when the biochar applications were increased to 90 g kg^{-1}. Results demonstrate the potential of biochar applications to improve N input into agro-ecosystems while pointing out the need for long-term field studies to better understand the effects of biochar on BNF. Research indicates that both biological nitrogen fixation and beneficial mycorrhizal relationships in common beans (*Phaseolus vulgaris*) are enhanced by biochar applications (Warnock *et al*., 2007) [27].

Biochar additions not only affect microbial populations and activity in soil, but also plant –microbe interactions through their effects on nutrient availability and modification of habitat. *Rhizobia spp*. living in symbiosis with many legume species is able to reduce atmospheric N_2 to organic N through a series of enzymatic reactions.

This BNF is regarded as an important opportunity to mitigate N deficiency in cropping systems worldwide. BNF significantly decreases, however, if available NO_3 concentrations in soils are high, and if available Ca, P and micronutrient concentrations are low. With large biochar concentrations, available NO_3 concentrations are usually low and available Ca, P and micronutrient concentrations are high, which is ideal for maximum BNF. Indeed, BNF by common beans, as determined by 15 N dilution, increased from 50 to 72 per cent of total N uptake with increasing rates of biochar additions (0, 31, 62, and 93 t C ha^{-1}) to a low-fertility).

Conclusion

Currently, biochar is employed as a soil addition to improve the soil's nutrient fertility. Recently, a lot of studies have also looked into the use of biochar made from agricultural waste as an environmentally friendly, locally accessible adsorbent for the removal of organic compounds, metals, nutrients, and pathogens. Since biochar has a higher calorific value than raw biomass, it is also now utilised to make briquettes as an alternative fuel in rural areas. Numerous functional groups, such as -CHO (aldehyde), -COOH (carboxyl group), and -OH are frequently found in modified biochar (alcohol or phenol). It achieves remarkable outcomes in the removal of organic pollutants and toxic metals from the environment. Modified biochar operates on both physical and chemical adsorption during the adsorption processes. Nevertheless, the primary adsorption mechanisms may vary based on the nature and characteristics of the adsorbate. Benefits for structure can be obtained by increasing the number of pores and the precise surface area of the biochar produced by the addition of iron oxides. Based on the various physical, chemical and biological properties the biochar can be highly recommend for various aspects like soil health improvement, bioremediation of heavymetals, carbon sequestration etc., in the environment.

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