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Development of biochar from different biological materials and its quality

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Abstract

Biochar, a stable form of carbon, is produced from pyrolysis of biological materials. It is attracting growing interest because of its potential to improve soil nutrients status, increase crop yield and sequester carbon (C) in the soil. Biochar serve as a source of reduced carbon compounds (organic molecules adsorbed to the particle's matrix) for any biochar colonizing soil bacteria. Therefore, C entering the soil as charcoal is a significant sink for atmospheric CO_2 and may be important for global C sequestration. The biochar proves to be stable and effective carbons sink. The carbon locked in them do not release as CO_2 due to the microbial activity. The carbon in the biomass is subjected to easy degradation since they contain low grade carbon. But in biochar, pyrogenic carbon is formed by pyrolysis. Hence they remain in the soil for long periods. Biochars were produced from the pyrolysis of a variety of biological materials *viz.*, paddy straw, maize stalk, coconut shell, groundnut shell, coir waste and prosopis wood, in a specially designed pyrolysis-stove. The Biochars differed much in their characteristics.

Keywords: Biochar, pyrolysis, biomass, carbon

Introduction

Biochar is a term reserved for the plant biomass derived materials contained within the black carbon continuum. This definition includes chars and charcoal, and excludes fossil fuel products or geogenic carbon (Lehmann *et al*. 2006) [1]. The unique characteristics of the biochar is its effectiveness in retaining most nutrients and keeping them available to plants than other organic matter such as for example common leaf litter, compost or manures. The chemical structure of charcoal is characterized with poly-condensed aromatic groups, providing prolonged biological and chemical stability that sustains the fight against microbial degradation; it also provides, after partial oxidation, the highest nutrients retention. Biochar is a stable form of carbon and may last in the soil for thousands of years. Thus it is possible, as part of a shift to organic farming practices, to use biochar to turn agriculture from a net emitter of carbon to a tool for drawing carbon back out of the atmosphere.

Materials and Methods

Biochar samples were prepared from the pyrolysis of various biological materials *viz.*, paddy straw, maize stover, groundnut shell, coconut shell, coir waste and prosopis.

Collection of Materials

Paddy straw and maize stovers were collected from the Department of Farm Management. Groundnut shells were collected from the Department of Oil Seeds, TNAU, Coimbatore. Coconut shells were collected from a farm in Vadavalli, Coimbatore. Coir dust samples were collected from the coir industry in Vedappatti village of Coimbatore District. Prosophis was collected from a private firm in Ramanathapuram, Coimbatore.

Fabrication of pyrolysis stove

The pyrolysis stove consists of a cylindrical drum made up of zinc alloy sheet fabricated by the Safire Scientific Company, Coimbatore. It consists of combustion chamber, ventilation cone, outer tin and lid. The diameter of combustion chamber and outer chamber were 15 cm and 28 cm, respectively and the height of the cylinder was 38 cm. The volume of combustion and outer chamber were 6726 cm^3 and 16, 682 cm^3, respectively. The distance between combustion and outer chamber was 13 cm. The height of the ventilation cone was 10 cm.

Process of pyrolysis

The combustion chamber was filled with fuel materials (wood pellets, dry twigs, etc.) which were used for lightening purpose. The biological waste raw material was placed in the gasifier space (space between combustion chamber and outer chamber). A rag soaked with kerosene was used as a fire starter. The lid was placed on the stove, when the fire was started burning. After 10 – 15 min the fuel material was burnt hotter, which showed the flame in yellow colour whereas; the waste biomass in the outer chamber began to burn after 30 min. At that time it released gases and the flame was turned blue with little smoke. This implied that there was a complete burnt of the fuel. This process was completed within 2 hr and the stove was cooled down after 1 hr. At the end of the process all the biomass was turned into char.

Characterization of Biochar

The Biochar samples were collected from the pyrolysis stove sieved (< 0.25 mm) and their important characteristics were analysed.

Result

Some important characteristics of Biochar samples produced from the pyrolysis of paddy straw, maize stover, coconut shell, groundnut shell, coir waste and prosopis are presented in Table 1. The pHs ranged from 7.57 to 9.68 and EC from 0.39 to 4.18 dSm^{-1}. Biochar sample from paddy straw, maize stover, coconut shell, groundnut shell and coir waste had higher pHs (> 9.0) than the Biochar from prosopis. The Biochar from groundnut shell recorded the lowest EC (0.39 dSm^{-1}) than rest of the samples. Maize stover, followed by coir waste resulted in higher EC of Biochar.

A wide variation, ranging from 3.2 to 16.0 cmol (+) kg $^{-1}$ in CEC was observed in Biochar s prepared from a variety of biomass. The Biochar from prosopis had higher CEC than the other samples. The CEC was lower (3.2 cmol (+) kg $^{-1}$) in Biochar from coir waste. The exchangeable acidity varied from 9.5 to 49 mmol kg $^{-1}$. While prosopis resulted in greater exchangeable acidity (49 mmol kg $^{-1}$), the groundnut shell resulted in relatively lesser exchangeable acidity (9.5 mmol kg $^{-1}$).

The C content of Biochar varied widely, from 540 to 940 g kg^{-1}. The prosopis – Biochar had the largest amount followed by the coconut shell – Biochar. The lowest amount was found in paddy straw – Biochar. Similarly the C/N ratio also varied significantly, between 51.4 and 96.8. The highest C/N ratio (96.8) was found in coconut shell – Biochar and the lowest (51.4) in paddy straw – Biochar.

The NPK contents of Biochars varied from 8.5 to 1.12 g kg^{-1}, 0.6 to 3.2 g kg^{-1} and 2.4 to 29 g kg^{-1}, respectively. The coconut shell – Biochar had higher amount of P followed by maize stover – Biochar. The amount of Na, Ca and Mg contents were also varied markedly in different Biochar samples. While the Na content ranged from 5.2 to 38 g kg^{-1}, the Ca content ranged from 1.8 to 11 g kg^{-1}. The prosopis - Biochar had relatively higher amount of both Na and Ca. The Mg content of Biochar samples ranged between only 0.36 and 6.2 g kg^{-1}, the highest was found in paddy straw – Biochar and the lowest in prosopis – Biochar.

Prosopis-biochar

The prosopis is widely grown in many parts of Tamil Nadu, particularly in dry tracts and wastelands. It is available in large quantities. The physical, chemical and biological characteristics of Biochar produced from the pyrolysis of prosopis are presented in Table.1. The Biochar had a bulk density and particle density of 0.45 Mg m^{-3} and 0.54 Mg m^{-3}, respectively, with a porespace of about 48%. It had very low moisture content (1.21%), but high water holding capacity (131%). The results showed that the pH of Biochar was near neutral (7.57). It had an EC of 1.3dSm^{-1} and CEC of 16 cmol (+) kg $^{-1}$. Significance relationship was observed between CEC and Total organic carbon content in biochar. (Fig.1). The sample was high in exchangeable acidity (49 mmol kg $^{-1}$). The C content was very high (940 g kg^{-1}), but total N content was low (1.12 g kg^{-1}). The Biochar contained only low amounts of total P (1.06 g kg^{-1}). However,

relatively higher amount of total K (29 g kg^{-1}) was found in the Biochar. Major and micro nutrient content in different biochar produced from different waste is presented in Fig.2 and 3. The Biochar contained relatively higher amount of Na (38 g kg^{-1}) than Ca (11 g kg^{-1}). Only a small amount of Mg (0.36 g kg^{-1}) was present in the Biochar.

Discussion

Pyrolysis is the chemical decomposition of an organic substance by burning in the absence of oxygen. The high temperatures used in pyrolysis can induce polymerisation of the molecules within the feedstocks, whereby larger molecules are also produced (including both aromatic and aliphatic compounds), as well as the thermal decomposition of some components of the feedstocks into smaller molecules.

Biochar from biological wastes

Biochars were produced by pyrolysis of a variety of biological materials *viz.*, paddy straw, maize stover, coconut shell, groundnut shell, coir waste and prosopis wood. The Biochars differed much in their characteristics. The pH measured in 1:5 solid: water suspension, varied from 7.57 to 9.68. The prosopis-Biochar had the lowest pH and the paddy straw-Biochar had the maximum pH. Wide variation in EC was also observed as the values vary from 0.39 to 4.18 dSm^{-1}. Maize stover – Biochar was found to have higher EC, followed by coirwaste-Biochar.

Cation exchange capacity of Biochar ranged between 3.2 and 16 cmol (+) kg^{-1} and the highest CEC was with prosopis-Biochar. The coirwaste-Biochar had a lower CEC. These values are much lesser than those reported by Liang *et al.*, (2006) [2] and Lehmann, (2007) [3]. The exchangeable acidity ranged from 9.5 to 49 mmol kg^{-1}, and the prosopis-Biochar had the maximum value. It is comparable to the value reported by Cheng *et al.* (2006) [4].

Nitrogen content in the Biochars varied from 1.1 to 10.5 g kg^{-1}, and the prosopis-Biochar recorded the lowest value. The N content was relatively higher in groundnut shell-Biochar, closely followed by paddy straw-Biochar. Total P and K were found higher in coconut shell-Biochar followed by maize stover. The concentration of Na, Ca and Mg varied significantly between the Biochar samples. One of the important characteristics of Biochar is its carbon (C) content which decides its agricultural and environmental benefits. The total organic carbon (TOC) content varied from 540 to 940 g kg^{-1}. Such variation was commonly reported for a variety of Biochar produced from different feed stocks (Novak *et al.*, 2009; Rondon *et al.*, 2007) [6, 8]. The maximum C content (940 g kg^{-1}) was found in the prosopis-Biochar followed by the coconut shell-Biochar (910 g kg^{-1}) and maize stover-Biochar (830 g kg^{-1}). Higher content of C in these Biochar samples resulted in greater C/N ratio which ranged from 51.4 to 96.8. The coconut shell-Biochar was found to have the highest C/N ratio than the rest. The C/N ratio of the prosopis-Biochar was 83.9. These values are closely similar to those reported for other carbonized Biochar (Novak *et al.,* 2009; Rondon *et al.,* 2007; Cheng *et al.*, 2006) [6, 8, 4].

Characteristics of prosopis-biochar

The prosopis – Biochar had a bulk density of 0.45 Mg m^{-3} and a particle density of 0.54 Mg m^{-3}. It had a very high water holding capacity (131%). The pH was neutral (7.57), but the exchangeable acidity was high (49 mmol kg^{-1}). The EC an index of salt loading, indicates that the Biochar contained a very low amount of salt.

The Biochar had a very poor nutrients content, which followed: K > N > P. sodium content was relatively higher in the Biochar than Ca and Mg. The temperature, the time a material is held at a given temperature and the heating rate during pyrolysis directly influence the chemical constituents of Biochar (Lima and Marshall, 2005) [10]. Individual elements are potentially lost to the atmosphere, fixed into recalcitrant forms or liberated as soluble oxides during the heating process. For example, in the case of wood based Biochar formed under natural conditions, C begins to volatize around 100 °C, N above 200 °C, S above 375 °C, and K and P between 700 to 800^0C (Neary *et al.*, 1999) [7].

During the pyrolysis or oxidation process that generates Biochar, heating causes some nutrients to volatilize, especially at the surface of the material, while other nutrients become concentrated in the remaining Biochar. Nitrogen is the most sensitive of all macronutrients to heating; thus the N content is low (Tyron, 1948) [12]. Therefore, Biochar is likely more important as a soil conditioner and a driver of nutrient transformations and less so as a primary source of nutrients (Glasser *et al.*, 2002; Lehmann *et al.*, 2003) [5].

As has already been mentioned the prosopis-Biochar had a very high C content (940 g kg^{-1}) with a C/N ratio of 83.9. Biochemical analysis has shown that the cellulose content was relatively higher (36%) than the hemicelluloses (31%) and the lignin (22%). Charred biomass consists not only of recalcitrant aromatic ring structures, but also of more easily degradable aliphatic and oxidized C structure (Schmidt and Noack, 2000) [9]. The SEM image of prosopis biochar is presented in Fig.4. The range of C forms within a Biochar particle may depend on the C properties (Lehmann, 2007) [3]. Studying the ^{13}C NMR spectral pattern of pecan–Biochar, Novak *et al.* (2009) [6] found that most of the Biochar – C was distributed in aromatic structures (58%), with less amounts of C having single bonds to O (29%) and in carboxyl (13%) groups, but little carbohydrate – C. In general, the C 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%, but increased the C content from 56 to 93% (Sohi *et al.*, 2009) [11].

Table 1: Characteristics of Biochar from different Biomass

S. No	Characters	Paddy straw	Maize stover	Coconut shell	Groundnut shell	Coir waste	Prosopis wood
1.	pH (1: 5 solid water suspension)	9.68	9.42	9.18	9.30	9.40	7.57
2.	EC (dSm^{-1}) (1: 5 soil water extract)	2.41	4.18	0.73	0.39	3.25	1.3
3.	Cation Exchange Capacity (cmol(+) kg^{-1})	8.2	6.5	12.5	5.4	3.2	16
4.	Exchangeable Acidity (mmol kg^{-1})	22	27	32	14	9.5	49
5.	Total organic carbon (g kg^{-1})	540	830	910	770	760	940
6.	Total Nitrogen (g kg^{-1})	10.5	9.2	9.4	11	8.5	1.12
7.	C:N Ratio	51.4	90.2	96.8	70	89.4	83.9
8.	Total Phosphorus (g kg^{-1})	1.2	2.9	3.2	0.6	1.5	1.06
9.	Total Potassium (g kg^{-1})	2.4	6.7	10.4	6.2	5.3	29
10.	Sodium (g kg^{-1})	14	21.5	16.8	5.2	9.6	38
11.	Calcium(g kg^{-1})	4.5	5.6	8.5	3.2	1.8	11
12.	Magnesium (g kg^{-1})	6.2	4.3	5.8	2.1	1.4	0.36

Values are mean of triplicate sample

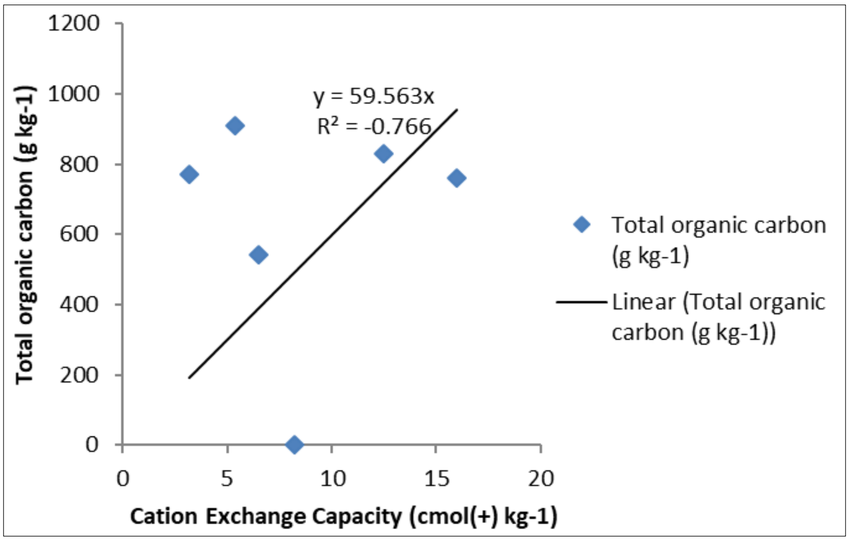

Fig 1: Relationship between total organic carbon and cation exchange capacity

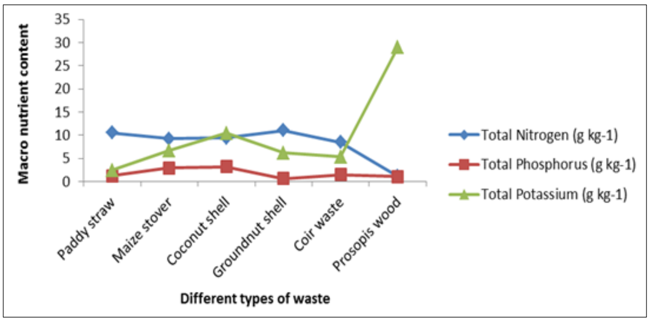

Fig 2: Macronutrient content of various biochar from different waste

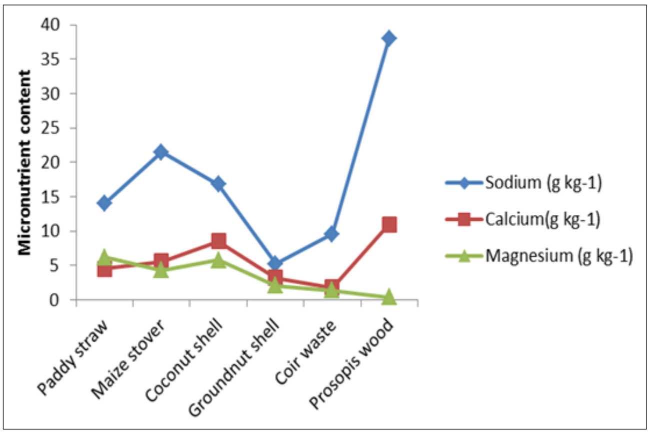

Fig 3: Micronutrient content of various biochar from different waste

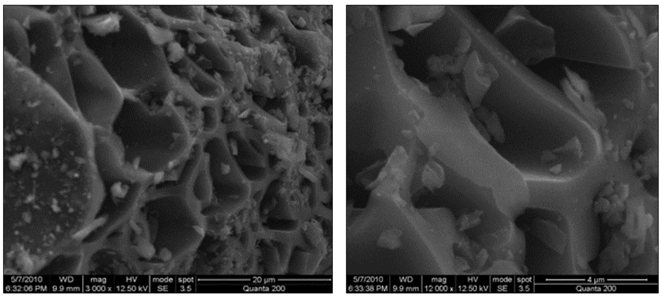

Fig 4: Scanning Electron Microscope (SEM) images of Biochar

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