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Molecular understanding of biochar aging on their properties and environmental significances

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Abstract
Biochar can be applied in various fields, such as carbon sequestration, pollution control, and soil restoration. Biochar unveiled a newly boulevard for sequestration of carbon has presented potential to enhance the productivity of agriculture. Biochar aging process changes its chemical and physical properties, with the formation of a variety of biochar derived organic materials. These changes have important effects for transport and bioavailability of contaminants and nutrients. In this review, render an overview on biochar aging, centering on its structural and chemical properties, and its impact on agriculture productivity and environment. After aging, biochar underwent chemical and structural alteration, such as the introduced functional groups, increased negative charge on surface, higher O: C ratio and enhanced cation exchange capacity. These alterations particularly formation of functional groups and high specific surface area substantially improve nutrient retention and soil fertility by increasing the amount of exchangeable cations in the soil. Therefore, a clear understanding of biochar aging process and their potential impacts on physiochemical and molecular properties of biochar as well as on soil can help to manage soil health in a better way without significantly affecting the surrounding environment.

Keywords
biochar aging, soil, environment, functional groups, productivity

Introduction

Biochar is a combusted product of biological residues under the low O_2 considerations, representing a porous, lower density C rich material. Surface area and cation exchange capacity of biochar are largely influenced by feedstock materials and pyrolysis temperature. Biochars prominent surface areas and the capacities of cation exchange, influenced to a high extent through origin materials and pyrolysis temperature, alters increased

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sorption of inorganic and organic both contaminants to their surfaces, reducing the mobility of pollutants while applied for amendment of contaminated soil (Beesley et al., 2011). Biochar has the ability to sequester the carbon; therefore it is highly useful in soil contamination mitigation (Pandit et al., 2018). The biochar applied to soil induce modifications in physical and chemical properties like rise in capacity of cation exchange, pH and water retention (Martinsen et al., 2015). Biochar also changes the biological properties of soil including enzyme activity and microbial biomass; these types of changes in the soil properties affect growth of crops on amended soils by biochar (Duku et al., 2011; Jeffery et al., 2017). Studies on the effects of fresh biochar on soil and crop pattern might not be applicable for evaluating how biochar impacts on agronomic performances and longtime sustainability system (Kookana, 2010). Contempt cognizance of mechanism of biochar aging and recognition of significance of aged-biochar effects on soil environment (Wang et al., 2012). A large number of studies have recognized the impact of fresh biochar on agronomic systems. Just few studies have examined how agro-ecosystem functions are affected with aged-biochars (Borchard et al., 2014; Rajapaksha et al., 2016). An increase in cation exchange capacity (CEC) due to surface oxidation of the pyrogenic carbon is responsible for aging process. Addition of fresh biochar in soil experiences similar changes and results in better nutrient retention with improved crop productivity. Biochar physiochemical properties potentially affect mobility, transfer and bioavailability of nutrients in the soil (Ameloot et al., 2013). Majority of studies have been published on various aspects of pyrogenic C and biochar, many of them centered on C stability and biochar mineralization in soils; e.g. the role of soil microbial stability has been reviewed, instancing the various mechanism of mineralization by abiotic and biotic processes (Hiemstra et al., 2013). In many literatures, components controlling the transport of pyrogenic C and stabilization have reported (Czimczik et al., 2007). Up to now, a detailed assessment procedure of biochar-aging has not been undertaken. In this particular review, have analyzed the studies carrying information regarding physiochemical traits of biochar and biochar molecular structure change during the aging as well as effects on agriculture and environment. In the last section, will highlight the impact of biochar aging on agriculture and environment.

Aging of Biochar

Biochar aging refers to changes in the biochar traits (Physical and chemicals) by a variety of time dependent actions occurring in the soil environment. Aging not only changes biochar properties but it also affects its biogeochemical functionalities. Normally chemical oxidizing agents are used to escalate the aging process for example (Lawrinenko et al., 2016) in a study did biochar oxidation with alkaline hydrogen per oxide (H_2O_2) for a period of four months and found that aging enhanced the presence of alcoholic and carbonyl groups while declined the exchange capacity of anions in biochars generated at 500°C. Biochar, a burnt biomass highly rich in carbon formed under limited supply or complete absence of oxygen. In the pyrolysis process of biochar, aliphatic carbon chains present in biochar feedstock are changed into aromatic carbons carrying a variety of intermediate products called poly-aromatic hydrocarbons (Spokas et al., 2011). Rising of temperature more than 270° C and increasing residence time condenses the aromatic carbons yielding aromatic moieties or planes. Aromatic moieties having different sizes joined together or connected via aliphatic chains constitute interconnected carbon planes called fixed carbons (Keiluweit et al., 2010). Production of volatile organic compounds occurs when some of the intermediate products are entangled between the planes of fixed carbons. These volatile organic compounds are considered very fragile. Moreover, the ratio of fixed carbons and volatile organic compounds highly depends on pyrolysis temperature, quality of feedstock and residence time (Wiedner et al., 2013). Consequently, Biochar for particular target adhered implementation like as agricultural amendment or carbon sequestration can be developed. The fixed carbon and structures of biochar has been represented in detail literature (Preston et al., 2006). Now we draw a model of char from published studies (Figure1). Heavy metals retention in soil controlled by the Carboxyl functional groups of biochar and stimulates the aging process if the biochar oxidized through Nitric acid (HNO_3) and sulfuric acid (H_2SO_4) (Uchimiya et al., 2012). A lot of literature presented that biochar applied to soil undergo change ascribable to actions of soil biological, physical and chemical agents (Fang et al., 2014). The changes due to aging process in biochar are discoursed under subheadings following sections.

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Decomposition of volatile and aliphatic carbons

Biochar may comprise variable ratios of aliphatic and volatile C depending on production circumstances and feedstock. After addition of char to soil, volatile and aliphatic carbons are mineralized through soil micro-organism, evident from decrease in aliphatic carbon with aging (Kuzyakov et al., 2014). Similarly in another study by (Uchimiya et al., 2012) reported biochar microbial decomposition was examined through application of ^{14}C tracer element. Aliphatic component associate aromatic moieties in biochar or confront of aromatic layers as side branches (Figure 1). Hence, microbe assisted decomposition of aliphatic carbon releases dispersed moieties. These aromatic moieties as a result of oxidation produce functional groups, like carboxyl groups at breaking point.

Generation of functional groups forces oxidized biochar to intermingle with soil nutrients, minerals and other soil contaminants. Deterioration of biochar associated aliphatic part might occur simultaneously with deterioration of soil organic matter at same timescales. Even though, quick decomposition was proposed for mineralization through labile organic matter in natural environments (Keith et al., 2011). Hence, biochar associated aliphatic carbons can change in a very short duration of time 0-25y leaving behind oxidized but complete aromatic moieties (Hilscher et al., 2009).

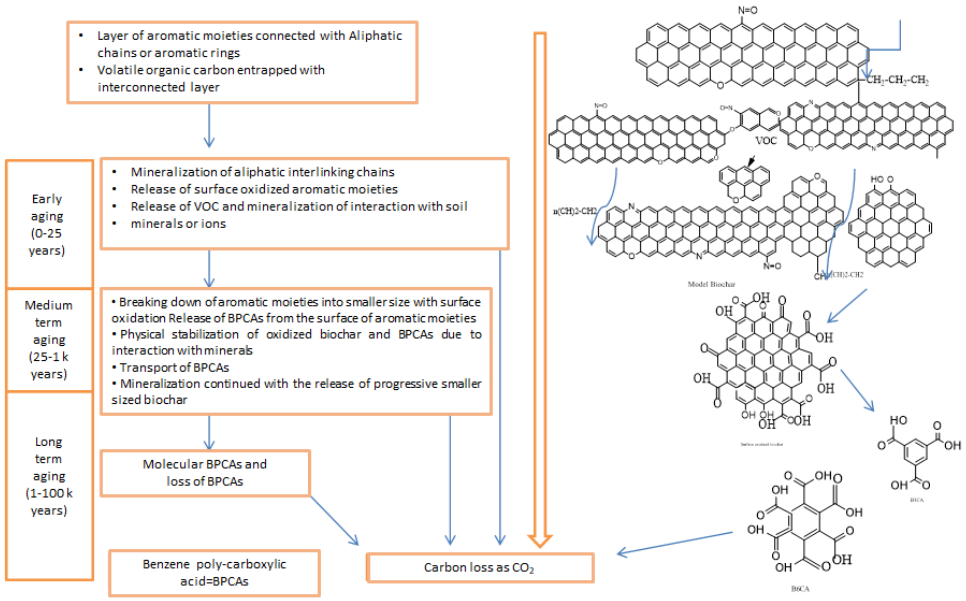

Figure 1. *Schematic demonstration of biochar aging and production of BDOMs letting in BPCAs (Benzene poly carboxylic acid and structure of biochar redrawn with adoption later.*

Disintegration of Aromatic moieties

As the aging process proceeds large sized aromatic moieties either entangled or disintegrated connection will experience chemical, physical, microbial, or may be photochemical disintegration (Joseph et al., 2018). Fundamentally, biochar aromatic moieties contain benzene rings. Benzene rings at corners of the biochar contain less number of bonds which connect them to large aromatic moieties in comparison to the rings present in the center of moieties. Therefore, biochar decomposition first takes place at the edges and releases some aromatic rings from edges that leads to the formation of functional groups at disintegrating points. Consequently, formation of surface oxidized biochar along with benzene poly carboxylic acids occurs (Rasmuson et al., 2019). Surface oxidized biochar then shows a continuous resilience to decomposition because it loses greater proportion of labile part and association with soil minerals (Xia et al., 2019). With progression of aging, a continuous decomposition of biochar will occur and small sized aromatic moieties are produced. Continuation of this process drops the size of aromatic moieties that they carry less number of benzene rings with more functional groups. On this such transformation of large sized aromatic moieties to many fused rings in soil might require hundreds to thousands of years' time span (Chen et al., 2017). Yet for a condensed biochar may be a longer time span is required, while a biochar having low aromatization may achieve this condition within 25–100 years timespan.

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Small sized aromatic moieties containing few benzene rings may experience further deterioration and in hard conditions production of molecular benzene could happen. However such formation may require a long time of approximately 1000 years. Benzene rings released from aromatic moieties may carry different number of carboxylic acids, lies between 2–6. It is the number of bonds attached to other aromatic rings that decides the carboxylation level. At the beginning of aging, benzene rings having few carboxylic groups (3-4) will be released by the aromatic moieties, these benzenes rings can be disintegrated easily because they are attached to aromatic moieties edges with less number of bonds. At more advanced levels of biochar aging five to six carboxylic functional groups will be accompanied the benzene rings, because benzene rings are detached from the core. The BCPA release pattern shows the following order of B2CA > B3CA > B4CA > B5CA > B6CA representing the level of aging (Yang et al., 2017). Increased solubility of BPCA helps in its leaching and transportation through the soil. Moreover, a subsequent portion of BPCA might be sorbed into soil organic matter and biochar (Enders et al., 2012; Kalbitz et al., 2000). The number of functional groups such as carboxylic and phenolic increases on the surface of oxidized biochar with progression of aging, while BCPAs produced from aged biochar also carry a large number of carboxylic groups. This will result in higher negative surface charge in BDOMs and aged biochar.

Approaches used to accelerate biochar aging

Although natural oxidizing agents as well as soil microbes play a vital role in biochar aging under natural environment. Yet aging process can be speed up by using following methods discussed below.

Aging of biochar by chemical agents

Several oxidizing agents are used to oxidize biochar attacking different fractions like acid soluble fraction (FAs, fulvic acid), acid insoluble fraction and oxidized biochar fragment. A large number of oxidizing agents are used for oxidation purpose such as H_2SO_4, $(NH_4)S_2O_8$, H_2O_2 and HNO_3. Moreover, different oxidant ratios, temperature and exposure time to variable bichar are also used for accelerating the aging process. Different oxidizing agents show variable strengths but HNO_3 appeared to be the stronger agent among all (Azargohar et al., 2014; Yakout, 2015). A gradual rise in the concentration of oxidizing agent and oxidation duration can result in a higher extent of oxidation along with decline in biochar weight (Wang et al., 2015). Adsorption ability cation exchange ability (CEC), functional groups of surface, pH and significant chemical and physical attributes will modify the chemical aging process (Tang et al., 2014).

Chemical aging of biochar will surely affect the capacity of production function. A number of biochar characteristics such as element distribution are crucial and pour structure is also the concentrate in the study of process of aging. Pore structure always affected biochar pore size and particular surface area and then damaged the adsorption capacity of surface. Samples of biochar were oxidized with the 3:1 v/v H_2SO_4:HNO_3 mixture for imitating the process of aging in acidic surroundings which could noticeably raise biochar carboxylic content (Cho et al., 2010). After the treatment of aging with H_2SO_4:HNO_3 there were vital modifications in adsorption capacity and surface morphology of biochar. The O content and (O+N)/C increased at two temperatures of preparations that resulted in enhanced polar oxygen carrying functional groups. Also ash content and pH of aged biochar were lower as compared fresh biochar (Wang et al., 2019). Aging treatments with chemicals may modify the sorption ability of adsorbent.

Pore structure of biochar might be decreased since the micro pores on surface of biochar were blocked with thin soil particles. In addition the process of aging might induce the introduction of functional groups like hydroxyl, phenolic and carbonyl on the surface of biochar, affecting its adsorption quality (Zhang et al., 2016; Khorram et al., 2017). After biochar aging few changes -occur in surface functional groups, there were broad absorption peaks at 3430 cm^{-1} and 3244 cm^{-1} ascribable to the extending vibration of O-H. The stretching vibrations about the band at 2988 cm^{-1} and 2840 cm^{-1} were -CH_2 aliphatic (Zhang et al., 2018; Zhang et al., 2011). Thus, intrinsic chemical attributes of biochar like as oxidizing agent strength, aromaticity, oxidation duration and temperature can influence the oxidation magnitude oxidized biochar production (Humic acids, fulvic acid). It's not clear which char part - aromatic or aliphatic should be oxidized through specific kind of chemicals. a very specific target, like agriculture it is important to find what type of oxidizing agents or their combination can help to enhance CEC without decreasing original biochar weight Since the greatest challenge would be to search out cost effective

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methods for purification of oxidizing materials to be used in agriculture and to reduce deleterious residual effects of oxidizing agents used in biochar on human health and overall environment.

Table.1. *Chemical aging of biochar with various agents (Mia et al., 2017).*

		Oxidation			Targeted material			
Oxidizing Agent	Pyrogenic Material	POM:OA (w/v)	Temperature (°C)	Duration (h)	Biochar Oxidation	FAs	HAs	Reference
H_2O_2 (1-30%)	Biochar	33.3	25	24	+	_	_	(Sun et al., 2016)
HNO_3	Biochar	45	100	4	_	_	+	(Guimaraes et al., 2015)
H_2SO_4 (2%)	Biochar	_	150	24	+	_	_	Yakout,2015
KOH	Biochar	_	100	2	+	_	_	Yakout,2015
H_2O_2 (0-30%)	Biochar	400	60	24-240	+	_	_	(Guo and Chen, 2014)
HNO_3 (65%)	Biochar	1	100	3	+	_	_	Yakout,2015
H_2O_2	Biochar	70	80	2	+	_	_	Cross and Sohi, 2013
HNO_3 (25%)	Biochar	30	90	4	_	_	+	(Hiemstra et al., 2013)
HNO_3 (65%)	Biochar	10	80	48	+	_	_	(Liu et al., 2013)
H_2O_2 (15-30)	Biochar	10	25-30	100	+	_	_	(Wang et al., 2015)
HNO_3 and H_2SO_4(1:3)	Biochar	80	70	6	+	_	_	(Qian et al., 2015)
H_2O_2	Biochar	6.3	22	2	+	_	_	(Xue et al., 2012)
H_2O_2 (1-30%)	Biochar	20	25	2	+	_	_	(Huff et al., 2016)

Acceleration of biochar aging by soil microbes

Biochar aging can be speed up through soil microbes, as their working can be accelerated by energizing them with carbon rich compounds such as fresh biomass or glucose (Keith et al., 2011). Information about fundamental microbial mechanism (microorganism) is limited because biochar amendment into soil has variable impact on microbial actions (Biederman and Harpole, 2013). Nowadays, biochar used as feed for animals and bulking agents for compost and in these schemes char was got to be aged or oxidized (Joseph et al., 2015). Current scientific developments have contributed to examine of biochar would increase efficiency of composting (Mondini et al., 2016; Sanchez-Monedero et al., 2018; Vandecasteele et al., 2016). Composting is microbial treating that needs favorable condition for growth and development in the presence of microorganism. Inclusion of biochar to composting batch hypothetically can change vital fundamental physicochemical attributes parameters and gives a most proper habitat for micro-organism involved and enhance the growth of microorganism. These favorable conditions help to increase the formation of organic matter and microbial activity. The modifications

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experienced through surface of biochar during biochar activation also have gains in conditions of avoiding damages during leaching nutrient retention and during composting volatilization. These modifications may highly improve the agronomical quality of compost enriched biochar when applied as a soil amendment (Wu et al., 2017). Microorganisms potentially play vital role in aging process of biochar. Recently, more attention has been described to the environmentally safe less persistent free radicals in the biochar which can generate oxygen reactive species for efficient degradation of pollutants accelerate aerobic (Oxidative) stress in the vicinity of microorganism (Masiello et al., 2013; Ruan et al., 2019). For example; the loss of carbon from abiotic research laboratory biochar incubations was 60-90% lower than that of microbial immunized incubations (Zimmerman et al., 2010). (Hamer et al., 2004) Investigated that maize biochar aged with microbes for 60 days at 20° C also revealed that approximately 0.4% of wood biochar carbon and 0.9% corn biochar carbon was mineralized in the absence of glucose addition, and only 0.6% to 1.2% carbon of aged biochar mineralized with microbial accelerating glucose addition. Although it is experienced that pyrogenic carbon in biochar is approachable to microorganism, however studies regarding microbial effects on aging particularly microbe induced changes in the chemistry of biochar are very scanty.

Biochar aging with physical methods

Biochar aging can be performed by physical methods, but this kind of aging is not effective as compared to chemical and microbial aging in terms of chemical effectiveness of biochar. Alternate wetting and drying technique with variable moisture contents, freezing and thawing process and partial surface oxidation of biochar are some examples of physical methods used for biochar aging in different studies used for biochar aging in many studies (Kammann et al., 2015; Naisse et al., 2015; Zhang et al., 2016).

Properties of biochar and biochar-derived organic matter after chemical aging

Alterations in structure and surface traits of char along with their derived organic matter are normally visualized using different spectroscopic methods like as XPS, FTIR, NEXAFS, NMR or some chemical analysis methods like cation exchange capacity are also used to detect these changes (Mikutta et al., 2009). For analysis of variations occurred in biochar properties due to aging, characteristics of fresh biochar, naturally aged biochar, artificially aged biochar, humic acid obtained from biochar treated soils are compared to reference humic acid and soil organic matter in the sections given below.

Functional and structural composition

^{13}C Nuclear magnetic resonance technique has been widely employed to analyze various components of carbon species including carboxylic, aromatic, carbonyl and aliphatic in PyC. NMR Spectroscopy is the most laboratory method for the structural characteristics of carbon in biochar and black carbon because of its power to recognize various carbon nuclei. Figure 2 represents about some examples of ^{13}C Nuclear magnetic resonance spectra used in various studies regarding artificially-aged, naturally aged char, biochar derived humic acid, fresh biochar, humic acid from non-biochar treated soil. Nuclear magnetic resonance (NMR) signal from 0-45ppm represents aliphatic (CH*x*), 45-110ppm indicates O-alkyl (OCH_3), at 110-160ppm for aromatic, and finally, 160-220ppm for carbonyl carboxyl carbon species (Hilscher *et al.,* 2009). More intense signals were seen in aromatic region (130ppm) representing all biochar associated materials but not for soil organic

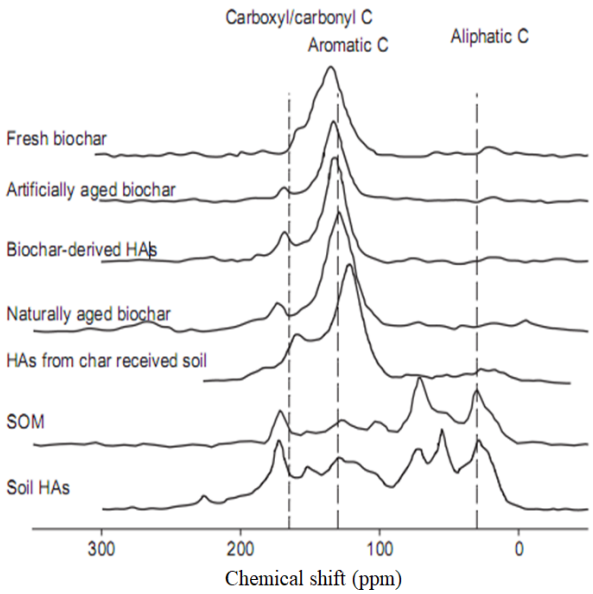

Figure 2. *^{13}C Nuclear magnetic Resonance (NMR) spectra of fresh biochar produced at 4000 °C, BC 400 and artificially-aged biochar (oxidation of BC 400 by Nitric acid), biochar derived humic acid from BC 400 and naturally aged biochar (Sultana et al., 2011). Humic acid collected from biochar received soil, a soil organic matter and a soil humic acid without biochar (Ikeya et al., 2004; Shindo et al., 2004; Mia et al., 2017).*

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matter and humic acids thus clearly indicating higher proportion of aromatic carbon in biochar and biochar derived humic acids. Artificial-aged biochar and derived humic acid derived from biochar expressed a sign of carboxylation when signal appeared near at 165 ppm (Sultana et al., 2011).

These outcomes propose a higher level of aging in naturally-aged biochar as compared to artificially aged biochar. Contrary to that, soil organic matter and soil humic acids showed more strong signals from 20-40ppm and near to 70 ppm, which means they had higher content of O-alkyl and aliphatic carbon (Ikeya et al., 2004). Fourier transforms infrared spectroscopy (FTIR) used to recognize various functional groups contained by different organic compounds. Fourier transforms infrared (FTIR) spectra of artificially-aged biochar, fresh biochar, naturally-aged biochar and biochar derived humic acids from many investigations has been analyzed to clearly understand the variations occurring in functional groups due to biochar aging (Figure 3) the designation of stretching signal for various functional groups is shown in (Table. 2) Like other pyrogenic C materials, all four biochar derived humic acids and expressed clear stretching of signal against aromatic C-H at 3200cm^{-1} and for C=C aromatic at 1600cm^{-1} (Ghaffar et al., 2015; Liu et al., 2013; Jimenez-cordero et al., 2015; Qian et al., 2015; Singh et al., 2016).

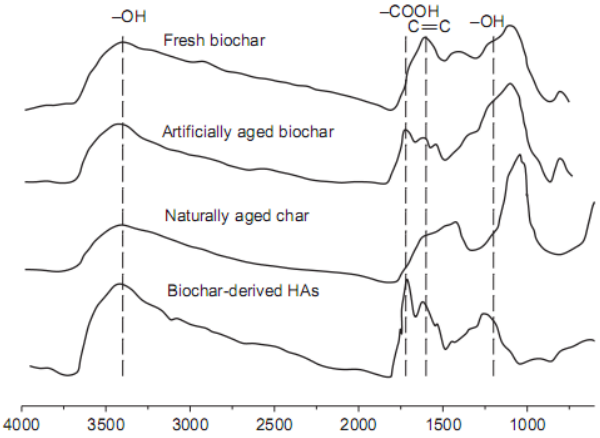

Figure 3. *Fourier transforms infrared spectroscopy (FTIR) of artificially and fresh aged-biochars (Liu et al., 2013). Terra preta (Archanjo et al., 2014) and biochar derived humic acid (Trompowsky et al., 2005; Mia et al., 2017). Dotted streaks symbolize bands for various functional groups.*

Biochar humic acids from artificial aging indicated stretching bands regarding ketone or carboxyl at about 1700 cm^{-1} and for hydroxyl group at 1210 cm^{-1} but these singles were more intense indicating greater proportion of detected functional groups (Ghaffar et al., 2015; Trigo et al., 2014; Yakout, 2015). Further, there was a more intense stretching band of –OH at 3400cm^{-1} for biochar with aging treatment (Liu et al., 2013; Trompowsky et al., 2005).

Table 2. *Demonstrations of FTIR spectral signal stretching to various functional groups (Mia et al., 2017).*

Function Groups	Wavenumber cm^{-1}	Reference
Phenolic –OH	3400cm^{-1}	(Liu et al., 2013; Trompowsky et al., 2005)
Aromatic C-H	3050cm^{-1} , 3200cm^{-1}	(Singh et al., 2016)
Carboxylic, ketone C = 0	1690cm^{-1} and 1720cm^{-1}	(Ascough et al., 2011)
Aliphatic C - H	2850cm^{-1} and 2920cm^{-1}	(Singh et al., 2016)
N - H amide and Heterocyclic N	1346cm^{-1} and 1534cm-1	(Qian et al., 2015)
Ca-phosphate	960cm^{-1}	(Archanjo et al., 2014)
Ca-C-O	1416cm^{-1}	(Archanjo et al., 2014)
Oxides sorbed to aged-char through -OH	3396cm^{-1}	(Singh et al., 2016)

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Chemical aging treatment with Nitric acid inserted a nitro group (-NO_2) at approximately 1540, 1346cm^{-1} (Qian et al., 2015), showing a turnover in physiochemical properties during aging with Nitric acid. Boichar natural aging also induced functionalization, indicating absorption peak at 1210 cm^{-1} for hydroxyl and 1700cm^{-1} carboxylic group (Nishimura et al., 2012; Trigo et al., 2014). Aging of biochar in soil can also ensue of Quinone functional groups development (Jindo et al., 2014). Hence these results propose that aging of biochar, either natural or artificial, produce O_2-comprising functional groups on surface having different types and quantities.

Elemental Polarity and composition

Dong et al., (2017) Found 49.1% carbon content in fresh char but it increased to 51.6% after aging of biochar in response of different treatments (B 30; B 60 and B 90) as shown in table 3. Hence, implementation of aging carbon content improved from 2.1-2.8%. Likewise, the amount of N and H in aged-biochar was more compared to fresh biochar, while oxygen content was lower in aged biochar (9.1%) compared to fresh biochar that contained 11.9% oxygen content. Furthermore, 41% reduction was noted in C content of aged biochar that its amount decreased from 10g kg^{-1} to ˜5.9g kg^{-1}.

Table.3. *Inorganic carbon and elemental content (%) (Mean) of aged and fresh biochar (Dong et al., 2017).*

Treatment	C	H	N	O	Inorganic C
B2009	49.1	1.8	1.2	11.9	1.0
B30	51.9	2.1	1.4	8.6	0.5
B60	51.6	2.0	1.4	9.1	0.6
B90	51.2	1.9	1.3	9.6	0.6

Continuous decrease of O/C and H/C proportions with rising of pyrolysis temperature, which was mainly employed for thermal changeover of organic to carbonized organic matter and suggestive of organization of structures comprising condensed C like as aromatic rings (Chen et al., 2008; Xu et al., 2013). Biochar aged with H_2SO_4 and HNO_3 the O/C proportions enhanced showing that O_2 comprising groups were put in on surface of biochar. O/C ratio increase was also examined when biochar aging was done with HNO_3/H_2SO_4 (Chen and Huang, 2011). The content of nitrogen in aged biochar improved because of increasing concentrations of Nitric acid and Sulfuric acid (HNO_3/H_2SO_4), nitrogen content of aged-char almost 3-fold improved than without aged biochar, this investigation is ascribed to the aged with HNO_3 (Qian and Chen, 2014; Seredych et al., 2008). The outcomes show that through aging, whether naturally or artificially, biochar oxidation increases progressively with the development of aging process and subsequently content of oxygen increases.

Transportation of organic molecules and their solubility generally depend on polarity with progression of aging functional groups on biochar-derived organic matter and biochar may enhance their mobility and polarity in the surroundings. Compare with humic acid and soil organic matter from soil without biochar, index of polarity of biochar-derived organic matter and biochar was calculated applying ^{13}C Nuclear magnetic resonance spectra in adopting this equation below (Mia et al., 2017).

Polarity index of fresh and aged biochar was same ~0.30 when it escalated to ~0.46 for char humic acid in (Fig. 4).

Naturally-aged biochar polarity index was higher ~ 0.79 than to artificially-aged and fresh biochar. Thus, both humic acids and soil organic matter had much higher polarity compared to aged or fresh biochars. Therefore, outcomes suggest that transport and mobility of char may enhance through aging treatments, as well as in case of naturally aged-biochar.

Specific surface area

Specific surface area (SSA) is the vital physical properties of biochar that indicates water holding capability, microbe's habitat and also influences metal sorption ability (Rajapaksha et al., 2016; Bagreev et al., 2001). A comparison of variations in SSA occurring due to natural aging or chemical oxidation is presented in table 4.

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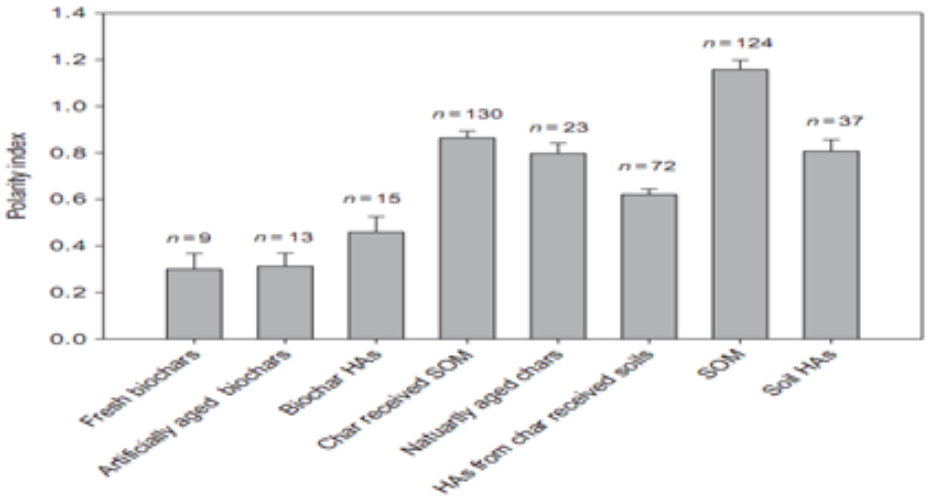

Figure 4. *Polarity index of biohar, biochar-derived humic acids, naturally aged-biochar, artificially aged char, and char received soil organic matter, humic acids from char received soils and reference soil SOM and humic acids without biochar. Error bar represents standard error for the observations showed in graph. Data are adopted from (Duarte et al., 2013; Hilscher et al., 2011; Knicker et al., 2013; Mastrolonardo et al., 2015; Novotny et al., 2007; Mia et al., 2017; Suarez-Abelenda et al., 2014; Sultana et al., 2011).*

Table 4. *Change in specific surface area of biochar after aging (Mia et al., 2017).*

Biochar	Temperature °C	Aging condition	Duration of aging	SSA (CO_2 m^2g^{-1})	SSA (N_2 m^2g^{-1})	% change in SSA(CO_2)	% change in SSA(N_2)	Reference
Oak BC oxidation	600	65% HNO_3, w/v-10 at 80°C	48 h		282		-24	(Liu et al., 2013)
Bamboo biochar	600	65% HNO_3, w/v-10 at 80°C	48 h		1		-99	(Liu et al., 2013)
Corn stover biochar	600	60 °C		190			+7	(Hale et al., 2011)
Peanut hull hydrocarbon (PHHC)	300	10% H_20_2,w/v-3 at 22 °C	2 h	114	1	+18	+8	(Xue et al., 2012)
Corn stover biochar	600	Freezing-thawing	19 h	181		+2		(Hale et al., 2011)
Cottonseed hull biochar	800	Conc. H_2SO_4 & HNO_3(3:1),w/v-80 at 70 °C	6 h	157	184	-43	-72	(Uchimiya et al., 2012)
Flax biochar	700	Conc. H_2SO_4 & HNO_3(3:1),w/v-80 at 70 °C	6 h	443	580	-14	-11	(Uchimiya et al., 2012)
Flax biochar oxidation (30%)	700	(30%)HNO_3-w/v-25 at 70 °C	1 h	145	182	-72	-72	(Uchimiya et al., 2012)
Nut shell biochar aged in soil(1year)		Soil	1 y		70		+7742	(Trigo et al., 2014)
Nut shell biochar aged in soil(1year)		Soil	2 y		6		+653	(Trigo et al., 2014)
Naturally aged biochar	~400	Soil	150 y		414			(Kupryianchyk et al., 2016)
Naturally aged biochar	~400	Soil	2000 y		404			(Kupryianchyk et al., 2016)

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Artificial moderate aging induced through air, steam or with chemical processes may raise SSA because volatile organic compounds are eliminated from biochar (Shi et al., 2015; Vithanage et al., 2015), on the other hand aging with strong acids (nitric acid, sulfuric acid and per-chloric acid) can reduce specific surface area due to damaging of structures (Liu et al., 2013). Despite the fact that less information is available about the specific surface area of naturally aged biochar, the SSA might be less as compared to artificially-aged and fresh biochar due to deterioration of structures and blockage of their pores. However, a contradiction found when Kupryianchyk et al., (2016) noted a comparatively large specific surface area for naturally-aged biochar.

Characteristics of surface charge

Surface charge essentially effects the interactions among biochar-derived organic matters and biochar with soil contaminants, minerals and nutrients, however when biochar is artificially-aged, surface negative charge increases and stays negative up to pH 3.5 (Silber et al., 2010; Mia et al., 2017). Increment in surface negative charge occurs mainly due to increasing levels of aging or chemical oxidation. Following this pattern high surface negative charge is also noted in naturally aged biochar (Chen et al., 2008), relative to both artificially-aged and fresh biochar. An assay mark of the surface chemistry of chemical aged-biochar is the formation of oxygen-comprising functional groups, particularly phenolic and carboxylic those provide render sites for enhanced –ve charge (Nagodavithane et al., 2014; Cheng et al., 2009). A consequent reduction in surface +ve charge has been noticed. Evidences proposes that the sites of adsorption and carbon containing functional groups presents on biochar surface may affect its cation exchange capacity, which in turn, play a vital role in the composition of biochar trace elements complexes (Nagodavithane et al., 2014; Cheng et al., 2009; Cheng et al., 2008; Lee et al., 2010; Liang et al., 2006; Mia et al., 2017). Fresh biochar ion exchange capacity varied broadly ranging from cation exchange capacity of ~250 to an anion exchange capacity of ~120 $cmol_c kg^{-1}$ depending on conditions of production and feedstock applied for pyrolysis (Mia et al., 2017; Yuan et al., 2011). Average, fresh biochar have anion exchange capacity (~0.5 $cmol_c kg^{-1}$), artificially-aged biochar have substantial cation exchange capacity of ~27 $cmol_c kg^{-1}$and naturally aged-biochar had more higher cation exchange capacity of ~100 $cmol_c kg^{-1}$. Likewise biochar-derived humic acids have higher cation exchange capacity of ~485 $cmol_c kg^{-1}$, as compared to soil humic acids ~363 $cmol_c kg^{-1}$.Thus, with the aging of biochar, cation exchange capacity of biochar increases considerably (Lu et al., 2015; Mia et al., 2017; Yuan et al., 2011). The development level of surface charge or cation exchange capacity depends on the phases of aging. A higher level of aging, as in case of biochar-derived humic acids, expresses a broader surface charge, which is evident from a higher number of surface functional groups.

Impacts of biochar aging on environment and agriculture

The mobility and bioavailability of mineral nutrients and contaminants in environment are regulated by the soil's reactive surfaces. Reactive surface proliferation on biochar in soil by the composition of functional group with aging treatment may ease interaction of biochar-derived organic matter and aged-biochar with soil contaminants, minerals and plant nutrients. Consequently, the mobility, retention, and transportation of contaminants and nutrients could be affected substantially. Fresh biochar contains a large SSA and may bring net +ve surface charge. After aging when char oxidized in soils alterations occur in its chemical and physical properties. Particularly functional groups are formed e.g. hydroxyl and carboxylic groups. As a consequence –ve surface charge and CEC of biochar rise with aging treatment (Mia et al., 2017). Application of aged-biochar to soils can enhance nitrogen (N) retention and also plant uptake (Guerena et al., 2012; Major et al., 2009). The higher productivity and nutrient retention of various anthropogenic soils are mainly expressed with the raised cation exchange capacity induced by naturally-aged biochar, also like to anthropogenic soils an enhanced cation adsorption or retention was noticed in different examines with char that has aged into soils extra time (Wang et al., 2015; Nagodavithane et al., 2014). There are a bounded number of studies on aging of biochar impacts on the sorption mechanism of organic pollutants or contaminants (OCs) like pesticides, herbicides and Polycyclic Aromatic Hydrocarbons. While as the biochar become aged, some physical properties of biochar, especially pore volume and specific surface area can alter depending on chemical oxidation or degree of aging, accordingly having a distinction part to sorption (Rajapaksha et al., 2016; Inyang and Dickenson, 2015) e.g. utmost aging or oxidation can reduce specific surface area, consequently reducing organic contaminants sorption (Trigo et al., 2014; Kupryianchyk et al., 2016). Aging

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of biochar can enhances hydro-philicity. Hydrophilic diversion can frequently enhance sorption by increasing H-bonds among nitro or hydroxyl groups of organic contaminants electron ample functional groups of char, especially carbonyl group (Jing et al., 2014). Aging of biochar also eliminate minerals of soil and formation of organic mineral composites. Such organic contaminants and soil organic matter can be sorbed to char surfaces and a large proportion of pore spaces of biochar may be tenanted by soil organic matter. Formation of these biochar- soil organic matter complexes may enhance with time duration, thus aging of biochar can reduce organic contaminants sorption that contend for the same sites of biochar (Jones et al., 2011; Kumari et al., 2014). Sorption is the consequence of various prospective mechanisms and which procedure might be predominant is mostly dependent on both organic contaminants and biochar. Hence, it is hard to forecast the behavior of sorption without distinguishing the properties of specific biochar surface.

Aging is a cost effective or not

Aging process is a cost effective or not and its environmental risks are still unclear. Because the aging experiments are did on laboratory basis or small scale. But it's looking time consuming and costly process. Biotic and abiotic aging require more time and resources. Cost related problems will be resolve, when aging technique will be implementing at the large scale.

Conclusions

Application of biochar for environmental and agricultural benefits relies on various characteristics of biochar like surface charge and specific surface charge. Aging of biochar contributes to formation and breakdown of a range of biochar-derived organic matters and these biochar-derived organic matters differ from fresh-biochar in functionality perspective Continuous aging, leads to biochar size reduction biochar and elimination of functional groups like hydroxyl, carbonyl and carboxyl, that are developed on the surface of biochar. Resultantly, aged-biochar and other biochar-derived organic matters put a greater energy to hold cations and to enhance the availability of anions such as arsenate and phosphate. Interactions of organic contaminates, minerals and soil organic matter with biochar-derived organic matters may vary due to the changing mobility and availability of organic contaminants at various levels of aging. Aging of biochar in natural ecosystems and formation of important –ve surface charge and chemical oxidation by nitric acid and hydrogen peroxide or other oxidizing agents may enhance the useful effects of biochar.

Conflict of Interest

Authors have no conflict of interest.

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