



Cellulose Crystallinity Change Assessment of Biochar Produced by Pyrolysis of Coir Pith

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Abstract

Biochar production from biomass is a globally adopted strategy for carbon sequestration and also for integrated agricultural applications. In the present study biochar was produced at 600°C by slow pyrolysis of lignocellulosic agro industrial residue coir pith. Chemical and structural transformation of coir pith happened due to pyrolysis process. Changes in cellulose crystallinity was analysed by XRD and FTIR method. XRD analysis indicates cellulose crystallinity index change. FTIR analysis shows several characteristic peak changes indicating structural transformations of cellulosic components.

Keywords: Coir pith, Biochar, Cellulose crystallinity, XRD, FTIR.

Introduction

Conversion of biomass into biochar is an effective method for carbon sequestration. Carbon stored in biomass can be locked within soil for many years by addition of converted biochar into the soil¹. Immediate agricultural carbon foot print reduction can be attained by this process. Biochar also have significant agricultural applications^{2, 3, 4} such as improving water retention capacity of soil, reduced quantity of fertilizer input, crop yield improvement⁵, ability to absorb plant nutrients⁶, heavy metal adsorption of contaminated soils⁷, etc. Studies have reported that amendment of biochar to soil reduces emission of potent green house gases methane and nitrous oxide^{8,9,10,11}. Biochar can be a habitat for soil microbes also¹². Sorptive property of biochar has also been explored¹³ for several applications. Common methods of biochar production¹⁴ are pyrolysis¹⁵ and gasification¹⁶. Pyrolysis can be categorized into fast and slow and the physical properties of biochar are dependent on the pyrolysis process and the charring temperature. Lignocellulosic components of biomass undergo several chemical changes during pyrolysis process. Cellulose components may undergo depolymerisation during biochar formation. As the biochar composition varies according to the biomass source, it is of significance to characterize the physical properties of biochar. Crystallinity of the biochar has impact on its sorptive property and hence the study of crystalline nature of biochar is important. Also biochar crystallinity may have effects in the accessibility of microbial population.

Coir pith is a lignocellulosic agro industrial residue generated during the coir defibering process which is heaped in bulk quantities near the coir defibering units. It creates several environmental issues such as poly phenol leaching, pollution of nearby receiving water bodies, resistance for natural degradation

etc. Coir pith which is usually perceived as a waste can be utilised for the production of biochar which offers a means of waste management and valuable product development. Biochar production from coir pith and its application for decolourisation of coir pith black liquor has been already reported¹⁷. Biochar coir pith can be used as an environmental sorbent and the sorptive property of biochar can be explored to treat industrial effluents as well. Sorptive efficiency of biochar coir pith may be influenced by cellulose crystallinity. X-ray diffraction (XRD) analysis is an effective method to assess the cellulose crystallinity change while FTIR analysis can be used for structural change analysis¹⁸. Earlier paper reports cellulose crystallinity assessment of coir pith using XRD method¹⁹.

This paper reports the cellulose crystallinity change occurred by the conversion of coir pith into biochar.

Material and Methods

Materials: Coir Pith (CP) samples were collected from a coir defibering unit at Alleppey district, Kerala, India. Collected substrate was washed with tap water, dried and stored in air tight containers. Biochar production was done using this stored coir pith.

Methods: Biochar Production: Biochar was produced by slow pyrolysis of coir pith in a muffle furnace at 600°C for 30 minutes. The resultant Biochar Coir Pith (BCP) was cooled in a decicator and used for crystallinity analysis.

XRD Analysis: Coir pith and biochar coir pith produced by slow pyrolysis were used for analysis of cellulose crystallinity change. Rigaku X – Ray diffractometer was used to perform the crystallinity study. The radiation used was of Cu α radiation at a

wavelength of 1.5418 Å. The samples were scanned at a scan rate of 1° per minute with scan angle (2θ) from 7° to 40° and the sampling rate was 0.02° (2θ).

The cellulose crystallinity index was calculated using the equation

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad \text{(equation 1)}$$

where CrI indicates the relative degree of crystallinity, I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and I_{am} is the intensity of diffraction in the same units at $2\theta = 18^\circ$.

FTIR Analysis: Comparison of crystallinity changes of coir pith and biochar coir pith was achieved by Fourier Transformation Infrared (FTIR) analysis. FTIR spectrum of the coir pith and biochar coir pith was taken with a resolution of 4 cm^{-1} and 32 scans per sample. The absorbance spectra were recorded at wave numbers from 500 – 4000 cm^{-1} .

Results and Discussion

Cellulose Crystallinity Change Assessment: A graph was plotted with XRD data of coir pith as shown in figure1 and another one was plotted with XRD data of biochar produced as shown in figure.2 Equation 1 and graph values along with XRD data helped to calculate the cellulose crystallinity index values. Calculated values of crystallinity index of coir pith and biochar are given in table 1

Table-1
Crystallinity Index values of Coir pith and Biochar

Sample	I_{002}	I_{am}	CrI
Coir pith	622	379	39.06
Biochar Coir Pith	108	102	5.55

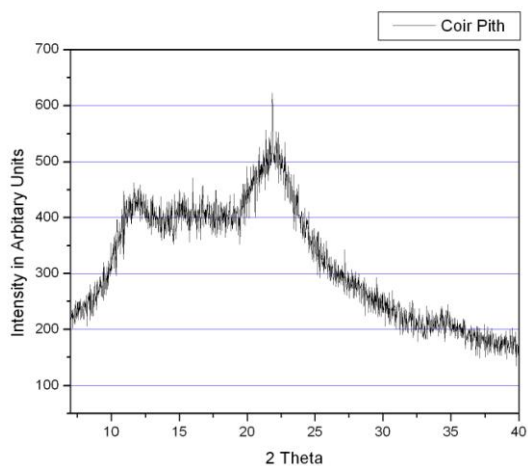


Figure-1
XRD Graph of Coir pith

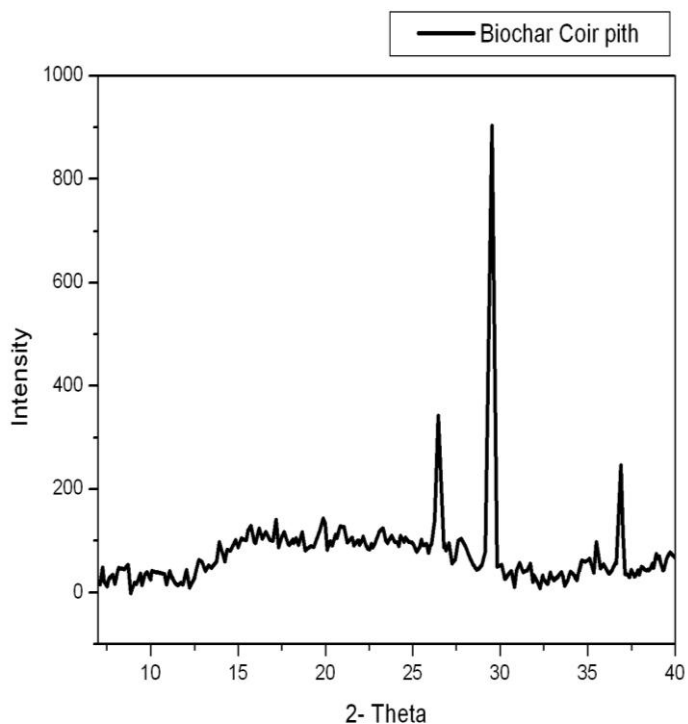


Figure-2
XRD Graph of Biochar Coir pith

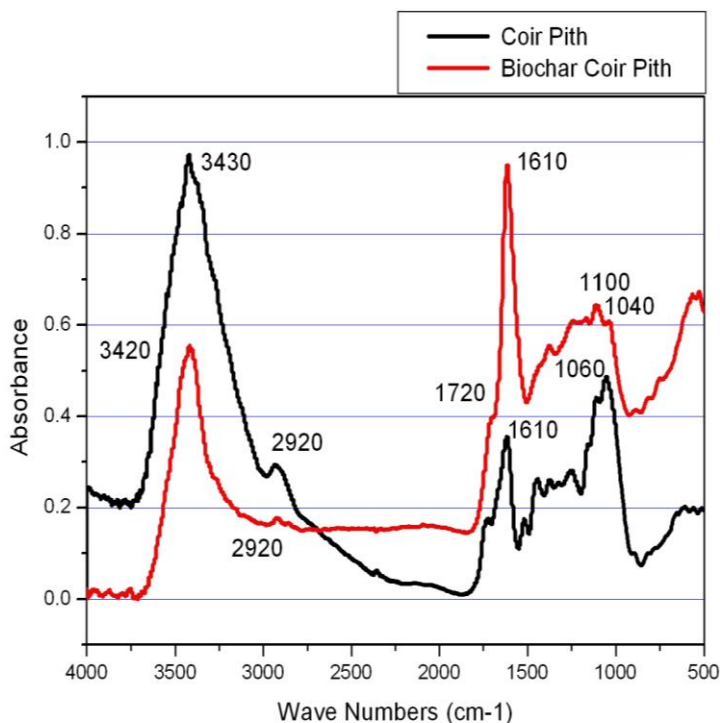


Figure-3
FTIR Spectrum of Coir pith and Biochar Coir pith

Comparison of FTIR spectrum of coir pith and biochar coir pith is shown in figure 3. Peak change at 1040 cm^{-1} indicates cellulosic transformations. Characteristic polysaccharide peak change at 3430 cm^{-1} also indicates cellulosic depolymerisation. Peak intensity change at 1610 cm^{-1} can be attributed to the dehydration. In product development perspective and in agricultural application perspective information regarding cellulose crystallinity of biochar shall be of significance.

Conclusion

Slow pyrolysis is an effective method to convert coir pith into biochar. Pyrolysis induces chemical changes to the substrate. Cellulosic depolymerisation and degradation occurred during biochar conversion process and cellulose crystallinity index was significantly reduced. XRD and FTIR analysis also indicates structural transformations. Loss of cellulose crystallinity for biochar shall have its impact on its sorptive property. Information on cellulose crystallinity shall be useful while utilising biochar for bioremediation and agricultural applications. Biochar production from coir pith also serves as a sustainable method of waste to valuable product conversion.

References

1. Shrestha G., Traina S.J. and Swanston C.W. Black Carbon's Properties and Role in the Environment: A Comprehensive Review, *Sustainability*, **2(1)**, 294-320 (2010)
2. Atkinson C.J., Fitzgerald J.D. and Hips N.A., Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review, *Plant and Soil*, **337**, 1-18 (2010)
3. Lehmann J., Czimnik C., Laird D. and Sohi S., Stability of Biochar in the Soil. In: Lehmann J., Joseph S. (Eds.), *Biochar for Environmental Management*. Earthscan, London, 183 (2009)
4. Pramod Jha, Biswas A.K., Lakaria B.L. and Rao A. Subba, Biochar in agriculture – prospects and related implications, *Current Science*, **99**, (2010)
5. Catherine E. Brewer, Rachel Unger, Klaus Schmidt Rohr, Robert C and Brown, Criteria to Select Biochars for Field Studies based on Biochar Chemical Properties, *Bioenerg. Res.* (2011)
6. Claudia Maria B.F, Maia, Beata. E. Madari, Etelvino H and Novotony, Advances in biochar research in Brazil, *Dynamic soil, Dynamic plant*, **5(1)**, 53-58 (2011)
7. Baoliang Chen and Miaoxin Yuan, Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar, *J Soils Sediments*, **11**, 62–71(2011)
8. Kurt A. Spokas and Donald C. Reicosky, Impacts of Sixteen Different Biochars On Soil Greenhouse Gas Production, *Annals of Environmental Science*, **3**, 179-193 (2009)
9. Singh B.P., Hatton B.J., Singh B., Cowie A.L. and Kathuria A., Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils, *Journal of environmental quality*, **39**, 1224-1235 (2010)
10. Spokas K.A., Koskinen W.C., Baker J.M. and Reicosky D.C., Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil, *Chemosphere*, **77**, 574-581 (2009)
11. Yanai Y., Toyota K., Okazaki M., Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments, *Soil Science and Plant Nutrition*, **53**, 181-188 (2007)
12. Daniel D. Warnock, Johannes Lehmann, Thomas W. Kuyper and Matthias C. Rillig, Mycorrhizal responses to biochar in soil – concepts and mechanisms, *Plant Soil*, **300**, 9–20 (2007)
13. Xiaoyun Xu, Xinde Cao, Ling Zhao, Hailong Wang, Hongran Yu and Bin Gao, Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar, *Environ Sci Pollut Res*, (2012)
14. Brown R., Biochar Production Technology. In: Lehmann, J., Joseph, S. (Eds.), *Biochar for Environmental Management*, Earthscan, London, 127-146 (2009)
15. Van Zwieten L., Kimber S., Morris S., Chan K.Y., Downie A., Rust J., Joseph S. and Cowie A., Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility, *Plant Soil*, **327**, 235–246 (2010)
16. M. A. Mohd Salleh, Nsamba Hussein Kisiki, H. M. Yusuf and W. A. Wan Ab Karim Ghani, Gasification of Biochar from Empty Fruit Bunch in a Fluidized Bed Reactor, *Energies*, **3**, 1344-1352.(2010)
17. Rojith G. and Bright Singh I.S., Lignin recovery, Biochar Production and Decolourisation of Coir pith Black Liquor, *Res.J.Recent Sci.*, **1(ISC-2011)**, 270-274 (2012).

18. Sang Youn Oh, Dong I Yoo, Younsook Shinb and Gon Seo, FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide, *Carbohydrate Research*, **340**, 417–428 (2005)
19. Rojith G. and Bright Singh I.S., Delignification, Cellulose Crystallinity Change and Surface Modification of Coir Pith Induced by Oxidative Delignification Treatment, *International Journal of Environment and Bioenergy*, **3(1)**, 46-55 (2012)
20. Marco Keiluweit, Peter S. Nico, Mark G. Johnson and Markus Kleber, Dynamic Molecular Structure of Plant Biomass-derived Black Carbon (Biochar), *Environmental Science and Technology*, (2010)