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Lignin recovery, Biochar Production and Decolourisation of Coir pith Black Liquor

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Abstract

Coir pith black liquor obtained as a dark brown filtrate from oxidative delignification needs to be decolourised before releasing to open environment. From this liquor industrially valuable lignin was recovered using acid precipitation method. 'Biochar' was produced by slow pyrolysis of coir pith at 500°C and 600°C. Water holding capacity and pH of the biochar were estimated. CHNS analysis was carried out to identify the nutrient profile. Structural characterization was done using FTIR and SEM Studies. Biochar produced at 600°C was found to be more suitable for decolourisation of the coir pith black liquor. FTIR analysis indicated peak changes while SEM analysis indicated surface area and porosity changes. Biochar decolourisation experiments were carried out on crude coir pith black liquor and also on lignin recovered coir pith black liquor.

Key words: Coir pith, black liquor, lignin recovery, biochar

Introduction

Coir pith, an agro industrial residual, is resistant to natural degradation; polyphenol leaching makes it unfit for the normal landfill practices either. It also pollutes the nearby receiving water body by changing the physio-chemical properties. Sustainable management of coir pith can be achieved by converting it into useful products through suitable techniques. Several investigations are advancing aiming at utilization of coir pith for various applications such as adsorption[1], biomanure production[2], in horticulture[3], lignocellulolytic enzyme production[4], bio energy generation[5] etc. These applications altogether can utilize only a small percentage of the total annual production of coir pith and the rest remains still as waste material leading to environmental deterioration. This scenario emphasises the need for advancement of research for further product development.

Physical and chemical structural binding of coir pith is the primary hindrance that has to be addressed during the initial phase of product development process. Pretreatment is the widely used method to loosen the lignocellulosic binding[6] and oxidative delignification has been accepted as an effective pretreatment step[7]. Lignin and hemicelluloses shall be solubilised due to this treatment. Solubility of lignin and its derivatives by oxidative delignification generates highly coloured filtrate rich in phenolic compounds[8] termed as 'Black Liquor' which has to be treated before discharging into open environment[9]. Black liquor also contains industrially valuable products such as lignin, hemicelluloses, poly phenols, etc which can be recovered[10]. Acid precipitation is an accepted method for lignin recovery[11]. Lignin recovered can be further processed for the development of various products such as activated carbon, vanillin, benzene, dispersant, emulsifying agents, etc [12]. In the present study black liquor generated due to oxidative delignification is termed as coir pith black liquor (CBL).

Adsorptive property of coir pith has been explored by various researchers for effluent treatment and to generate activated carbon[13]. However, 'biochar' production from coir pith is a relatively new area of investigation. Biochar is the porous carbonaceous solid produced by thermo chemical conversion of organic materials in an oxygen depleted atmosphere which has the physiochemical properties suitable for safe and long-term storage of carbon in the environment and, potentially useful for improvement of soil quality. Biochar has the potential to adsorb toxic and colouring compounds from aqueous solutions. Usage of biochar as a precursor for activated carbon also was previously reported[14]. Biochar production technologies include pyrolysis[15] or gasification[16]. Fourier Transformation Infra Red (FTIR) Spectroscopy and Scanning Electron Microscope (SEM) are common tools used for structural characterisation of the biochar produced.

This paper reports the conversion of coir pith into biochar by slow pyrolysis and its characterisation and application for decolourisation of coir pith black liquor. The work includes oxidative delignification of coir pith and attempts lignin recovery from the coir pith black liquor and its consequent decolourisation.

Material and Methods

Substrate and Oxidative Delignification: Coir pith collected from a coir processing unit at Alleppey (Dt), Kerala was washed, air dried and utilised for biochar production. Oxidative delignification was performed by 2 % hydrogen peroxide treatment on coir pith at pH 11.5 with substrate to solution ratio 3g: 100ml. Coir pith black liquor obtained after the oxidative delignification of coir pith was stored in an amber coloured bottle and used for lignin recovery and subsequent decolourisation.

Lignin recovery and decolourisation: Aliquots of 0.1, 0.2, 0.3 and 0.4ml H_2SO_4 were added respectively to each tube containing 20 ml Coir pith Black Liquor (CBL) and pH measured. The solution was centrifuged at 4000 rpm for 15 minutes. Lignin obtained as residue was dried at 60°C and stored for further analysis. Supernatant obtained by centrifugation was maintained at 4°C for 24hrs and then centrifuged again at 4000rpm for 15 minutes. The supernatant thus obtained was subjected to spectroscopic analysis within a scan wavelength of 400 to 800nm. pH of the supernatant was also recorded.

Biochar production and characterization: Biochar was produced by slow pyrolysis of coir pith in a muffle furnace at 500°C and 600°C for 30 minute. Water holding capacity of the biochar was measured by transferring 1g of substrate into a conical flask containing 100ml distilled water. The solution after agitation for 30 minutes was filtered and the difference in the initial and final volume gave the water holding capacity of the substrate. pH of the biochar produced was measured. Nutrient profile was assessed by CHNS analysis. Morphological analysis was carried out by scanning electron microscopy (SEM). Functional group analysis was done by recording FTIR absorbance spectra at wave numbers from 400 to 4000cm^{-1} with scan resolution of 4cm^{-1}. FTIR and SEM images of raw coir pith were also taken for comparison.

Decolourisation by Biochar: Decolourisation was carried out with respect to coir pith black liquor (CBL) and also with lignin recovered coir pith black liquor (LCBL). A quantity of 1g biochar was added respectively to each conical flask containing 100ml CBL and 100ml of LCBL. It was kept in a rotary shaker at 75rpm for 24 hours. The solution was filtered and absorbance measured using a spectrophotometer within a scanned wavelength of 400 to 800nm.

Results and Discussion

Lignin Recovery and Decolourisation: Addition of concentrated H_2SO_4 caused lignin precipitation which was recovered as residue after centrifugation. Reduction of pH below 3 is the reason for precipitation of lignin from black liquor. Further pH variation of the filtrate after lignin recovery was observed as shown in the Table-1.

Table-1
pH Comparison: Before and after lignin recovery

Volume of H2SO4 added (ml)	pH of solution after addition of H_2SO_4	pH of solution after lignin recovery
0.1	3.21	3.05
0.2	2.2	2.05
0.3	2.04	1.80
0.4	1.65	1.70

Lignin recovery changed the colour of black liquor from dark brown to pale yellow which indicated the removal of lignin from solution. Spectrophotometric reading indicated that decolourisation was achieved to a greater extent by lignin recovery. Reduction in colour led to the inference of the removal of chromophores. Treatment with 0.4ml of H_2SO_4 / 20 ml of CBL favoured maximum decolourisation by way of lignin recovery.

Biochar Production: Slow pyrolysis proved to be a feasible method in product conversion process. Optimum conditions for biochar production were found to be 600°C and 30 minutes of pyrolysis. Water holding capacity of biochar produced at 500°C was found to be 7 times greater than its weight while it was found to be 9 times greater than its weight in case of biochar produced at 600°C. Accordingly 1 g of biochar can hold 9 ml water. It has to be pointed out that raw coir pith holds water only 4.5 times greater than its weight suggesting doubling the water holding capacity of biochar. This property of the biochar could be effectively utilised to improve water retention capacity of soil. pH of the biochar along with the data on CHNS analysis are given in the Table-2.

Table-2
Comparison of pyrolysis profile of biochar

S. No.	Pyrolysis Temperature in deg C	Water Holding Capacity	pH	C %	H %	N %	S %
1	500	7	6.5	62.24	4.82	0.27	0.13
2	600	9	7.4	63.14	3.62	0.64	0.21

The nutrient profile of the biochar produced at 600°C was found to have increased. However, decrease in H value was observed for the biochar produced at 600°C. Increase in the C value indicated more carbon sequestration potential of the produced biochar. This suggests the conversion of lignocellulosic components to carbon during the process.

Biochar FTIR analysis: FTIR Images indicates peak changes and helps identification of functional groups. Observed prominent peaks and its associated functional groups are given in Table-3.

Table-3
FTIR Peak Assignment for coir pith biochar

Peaks	Functional Group
3420	0-H
2920	Aliphatic C-H Stretch
1610	C=C; C=N (Aromatic Structures)
1501	C-H, Lignin
1450	C-H, Lignin
1373	C-H, Lignin
1247	C-O
1110	C-O
1040	C-O
586-891	C=C-H (Aromatic -H)

Comparison of FTIR images as shown in Figure-1 indicates significant changes in peak heights of associated functional groups. Change in polysaccharide characteristic peaks around 3430 and 1040 indicates dehydration and depolymerisation of cellulose and hemicellulosic components[9]. Change in aromatic peak around 1610 may be due to transformation of lignin related products. FTIR Spectrum of biochar produced at 500°C and 600°C are given in figure-2 and figure-3 respectively.

Biochar SEM Analysis: SEM images indicate structural changes between raw coir pith and biochar. Surface area increase was observed in biochar which was comparatively higher in the case of the one produced at 600°C. Fragmentation of structure favoured increased adsorptive properties for biochar with increased porosity due to slow pyrolysis. SEM Images of raw coir pith, biochar produced at 500°C and biochar produced at 600° C are shown in figure-4, 5 and 6 respectively.

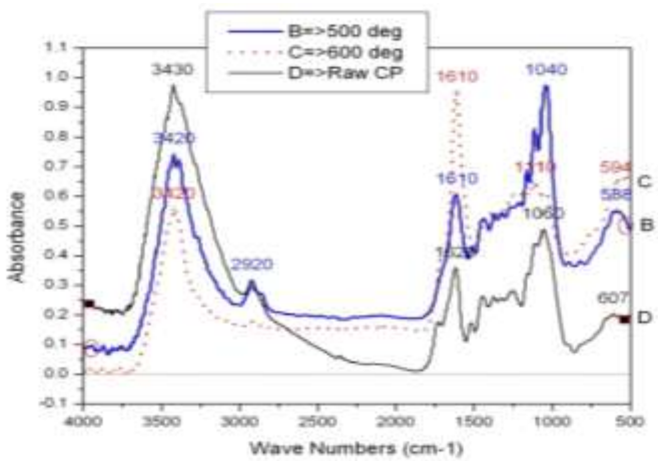

Figure-1
Comparison of FTIR spectrum of raw coir pith, biochar produced at 500°C and 600°C

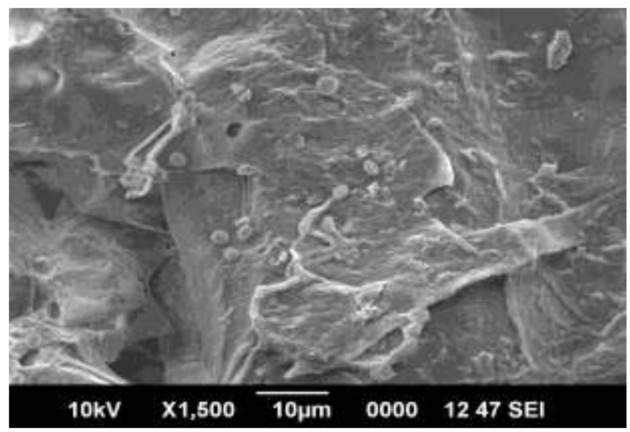

Figure-1
SEM image of raw coir pith

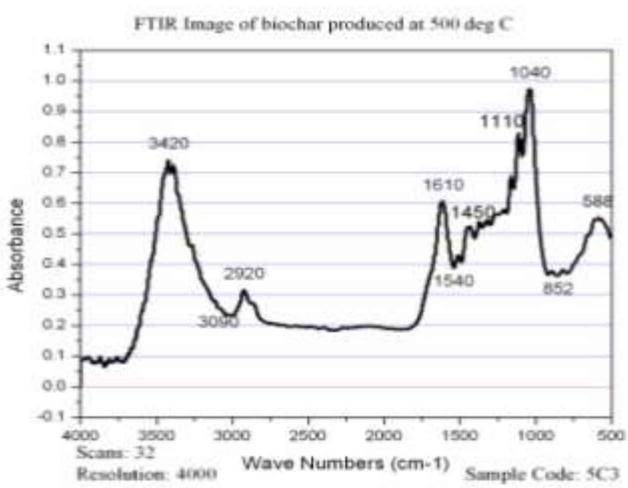

Figure-2
FTIR spectral analysis of biochar produced at 500°C pyrolysis

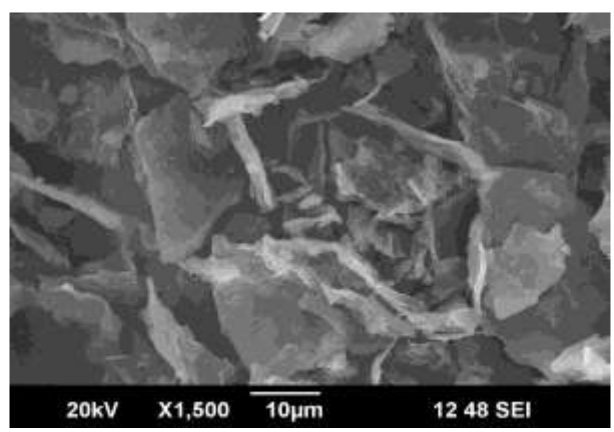

Figure-2
SEM Image of Biochar produced at 500°C pyrolysis

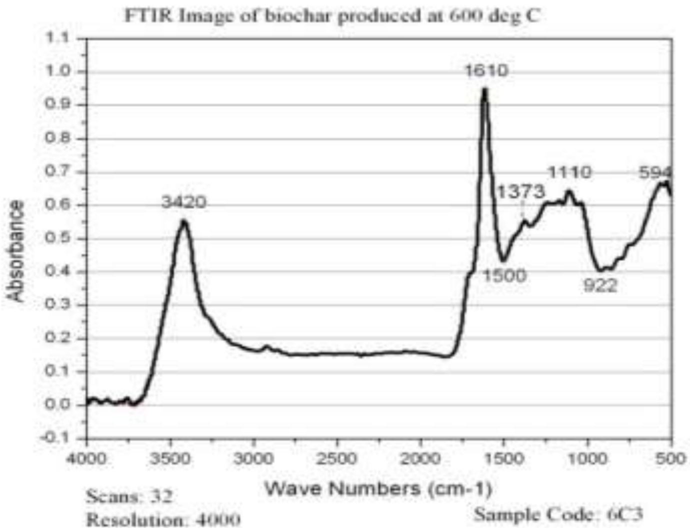

Figure-3
FTIR spectral analysis of biochar produced at 600°C pyrolysis

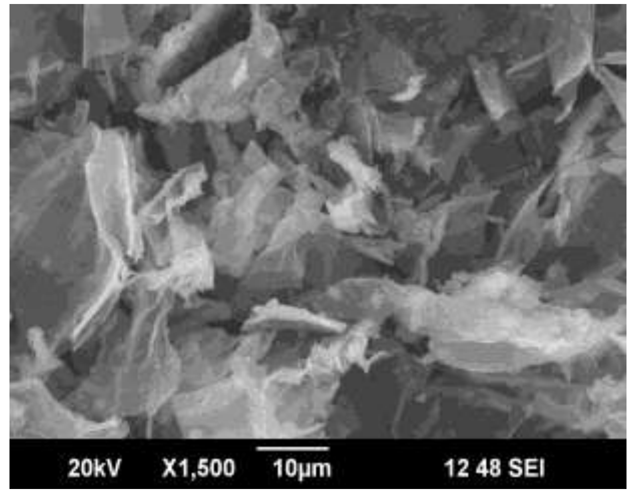

Figure-3
SEM Image of biochar produced at 600° C

Biochar Decolourisation: Decolourisation of CBL was observed after 24 hr treatment with biochar. Increase in surface area and porosity helps to adsorb more colouring reagents of CBL to biochar. However, the decolourisation doesn't happen to that extent as occurred by lignin recovery process. In the case of LCBL treatment with biochar, increase in absorbance was observed. This slight increase in colour may be due to the colour imparting reactions of biochar with LCBL. Lignin transformed residues present in the biochar might have induced colour to LCBL. In case of CBL treatment the colour induced by biochar might have been lesser than the adsorption of more coloured compounds initially present in the CBL, and hence the decolourisation.

Conclusion

Lignin recovery and biochar production upholds the sustainable concepts of waste management and product development of coir pith. Lignin recovery and subsequent decolourisation of the coir pith black liquor helps to minimize the further treatment of the effluent. Decolourisation experiments with biochar suggest that biochar has the potential to decolourise crude black liquor but is not effective in decolourising lignin recovered coir pith black liquor (LCBL). However, biochar is a valuable product developed from coir pith which can be used as a means of carbon sequestration and shall be suitable for agricultural and environmental applications. Increased water holding capacity of biochar exhibits its suitability as an amendment to improve the water retention capacity of soil. Coir pith biochar application can be extended for decolourising highly coloured industrial effluents as well.

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