



# Characterization and Application of Biochar from Spent Fermentation Sludge of Coir Wastes in Removing Malachite green from Effluent Water

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## Abstract

Lignin rich solid residues after saccharification during the production of ethanol from lignocellulosic substrates are major concern during past times. These solid residues left after the saccharification of Coir pith and Bit fiber waste are pyrolysed at 350 oC to yield biochar, which has been characterized and its potential for removal of Malachite Green, a dye present in the effluents from coir product manufacturing units are studied. FTIR and XRD spectra revealed the diverse functional groups present on the surface of biochar. SEM images showed the porous structure of the biochar. A maximum dye removal efficiency of 99.5% was achieved using Coir Pith Biochar (1 %) within 24 hours of treatment at a dye concentration of 100 mg/l. The removal efficiency was 99.4 % using Bit Fiber Biochar (0.8 %) in the same treatment period. The efficiency of removal was enhanced on adjusting the pH to 4 at which the dye removal of 99.6 % and 99.7 % was achieved using Bit fiber biochar and Coir pith biochar respectively. The residence time was significantly reduced to 2 and 4 hours respectively for bit fiber and coir pith biochar at pH 4 and hence the produced biochars are cost effective adsorbents for removal of dyeing effluents in wastewater. The adsorption fits into pseudo-second order kinetics and is well described by langmuir isotherm model. This would also facilitate the sustainable use of spent solid substrates left after lignocellulosic ethanol production in a more economical way.

**Keywords:** Adsorption, Pyrolysis, Dye removal, Wastewater, Malachite Green.

## INTRODUCTION

Coir fiber is a natural lignocellulosic substrate obtained from the plant *Cocos nucifera*, the most common natural fiber in the land of Kerala. The strong natural fiber extracted from coconut husks is spun & woven into elegant floor furnishing décor in coir units set up in many coconut growing states in India. These units cater to the domestic & export market for coir mats, mattings, rugs & carpets. Dyeing of the fiber is an important step in the coir industry in product manufacturing and finishing. The objective is achieved by use of various chemical dyes usually classified as acidic, basic, direct and indirect dyes (Benkhya et al., 2020; Raval et al., 2017). This method of dyeing coir uses large quantity of water and subsequently releases the effluent with high concentrations of the dye in it. Adsorption is a cost effective and easy method for the removal of dyes from effluents. Malachite green (MG) is a common dye in the effluents from coir and textile industry, whose toxicological effects include potent eye irritation and shows acute toxicity if orally swallowed. Malachite green is known for its carcinogenic, genotoxic and teratogenic effects which also inhibits microbes by disruption of cells through pore formation

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(Gopinathan et al., 2015). The toxicity of MG increases with exposure time, temperature and concentration. It is reported to cause chromosomal fractures, respiratory toxicity, organ damage and developmental abnormalities. This dye seems to get bioaccumulated in its reduced form 'Leucomalachite green' in serum, liver, kidney and tissues of fishes. (Srivastava et al., 2004).

At present in Kerala, one of the major environmental concerns posed by the small-scale coir and mat finishing units are the pollution caused by the release of untreated dyeing and bleaching effluents. Although treatment and biotransformation methods (Costa-Ferreira et al., 2007) have been developed, due to its high infrastructural & maintenance costs, they are absent in the small scale units. Even activated biochars are better known adsorbents for dye removal, the cost becomes a barrier for the small scale and cottage coir industry entrepreneurs.

Biochar is a carbon-rich solid product formed by pyrolysis of bio-organic materials at middle to low temperature under anoxic conditions. In recent years, biochar in the field of wastewater treatments has become a hot research topic, as a new type of adsorbent with high efficiency and environmental protection and has broad prospects in the field of adsorption treatment for typical pollutants in wastewater (Deng et al., 2017, Ghosh et al., 2020). Reports suggest that coir pith biochar is already being used in effluent treatment and acts as a powerful adsorbent for hexavalent chromium with a removal efficiency of 99.6 % at 32 °C (Vidhya et al., 2018). Previous studies report the use of various biochars for the removal of Malachite Green and other allied dyes from effluent solutions (Raval et al., 2017).

This work reports the simultaneous use of spent solid substrates from the fermentation of Coir pith and Bit fibre waste produced during lignocellulosic ethanol production. The use of this solid residue in production of Biochar, its characterization and the adsorptive removal of malachite green from waste water is studied. Most researchers focusing on the lignocellulosic ethanol production leave behind these solid residues rich in lignin without its effective utilization.

Coir pith and Bit Fiber Waste, are dumped in large quantities as waste in many parts of Kerala. The utilization of these wastes in an efficient manner for ethanol production and further use of the solid residue as a low cost adsorbent for dyes paves its path towards environment and water protection. This application would facilitate its economic utilization to benefit coir entrepreneurs in the coconut growing states in India, to be more environmental friendly. Thus, the method could be developed as a green and cost effective technology for treatment of dyeing effluents.

## MATERIALS AND METHODS

The substrates used are the spent solid residue left after the saccharification of Coir pith (CP) and Bit Fiber Waste (BF) during the production of ethanol. Both are lignocellulosic substrates obtained from coconut husk. Coir bit fiber is the waste obtained during the shearing or leveling of coir mats. The solid residue left after fermentation is washed and pressed to remove the water and dried in oven at 105 °C. These solid substrates are pyrolysed in a muffle furnace under nitrogen protected atmosphere at 350 °C to obtain the Biochar. The process is illustrated in figure 1.

The dried biomass is transferred to the pyrolyser, which is an air tight chamber, fitted with a condenser assembly, to remove the volatiles that may form during pyrolysis. The pyrolysis done is a batch process under nitrogen protected atmosphere and heated to 350 °C at the rate of 10 °C per minute and continued until the charring is complete. The pyrolyser is kept isothermal for 30 minutes after attaining 350 °C. The produced biochars are hereafter abbreviated as CPB (for Biochar produced from coir pith sludge) and BFB (for Biochar produced from Bit Fibre Sludge).

Primarily the elemental analysis- Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) of the biochar were determined using the Elementar Vario-EL-III analyzer. The percentage of Oxygen was determined by subtracting the sum of all other elements from 100 %. The structural

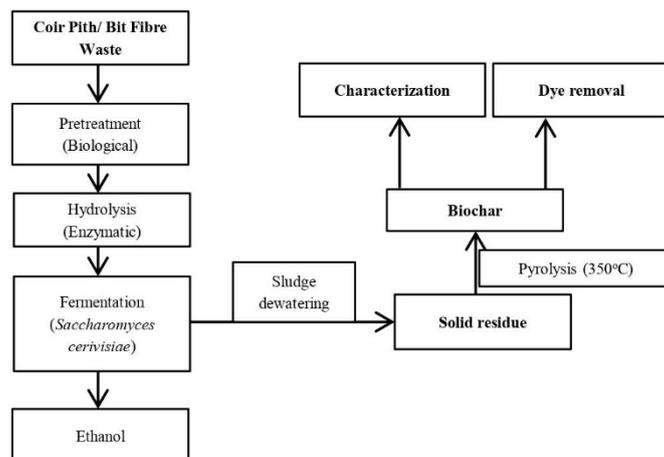


Fig. 1. Schematic of the Methodology

changes of biomass induced by pyrolysis were performed by Fourier Transformation Infrared (FTIR) analysis. FTIR spectrum of the raw samples and biochar were taken with a resolution of  $4\text{ cm}^{-1}$  and 32 scans per sample. The absorbance spectra were recorded at wave numbers from  $500 - 4000\text{ cm}^{-1}$ . The X-Ray diffraction pattern of the biochar were studied using Rigaku X – Ray diffractometer. The radiation used was of Cu $\alpha$  radiation at a wavelength of  $1.5406\text{ \AA}$ . The samples were scanned at a scan rate of  $1^\circ$  per minute with scan angle ( $2\theta$ ) from  $3^\circ$  to  $80^\circ$  and the sampling rate was  $0.02^\circ$  ( $2\theta$ ). The surface modification induced by pyrolysis is obtained by scanning electron microscope FESEM make, Carl Zeiss model, sigma with Gemini column at a resolution of  $1.5\text{nm}$ . The surface functional groups on the biochar has been determined by Boehm Titration method given by Schönherr et al., (2018).

Adsorption experiments were conducted to estimate the adsorption capacity of coir waste biochar on malachite green. The experiments were optimized with respect to adsorbent dosage and pH keeping the temperature constant. The effect of biochar dosage on the adsorption rate was studied by adding different weights of biochar to selected volume of dye solution with a fixed concentration. 0.2, 0.4, 0.6, 0.8 and 1 grams of biochar were added to 100 ml of dye solutions containing 100 mg/l malachite green. The solutions containing biochar was transferred to shaking incubator preset at  $30\text{ }^\circ\text{C}$  and 150 rpm. Aliquots of the dye solution were removed at specific time intervals, centrifuged at 5000 rpm for 5 minutes and the concentration of the dye in each aliquots were determined using a UV-Visible spectrophotometer at 624 nm. The aliquots were withdrawn at specific intervals of 2, 4, 6, 8, 10, 12 and 24 hours. The effect of pH on the adsorption efficiency was determined by adjusting the pH of the dye solution to 4 and 12 using 1 M HCL or 1 M NaOH.

The kinetic data of the adsorption were analyzed using the pseudo-first and second-order models. The pseudo first order kinetics for adsorption is explained by the equation

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

and second order kinetics is expressed by the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

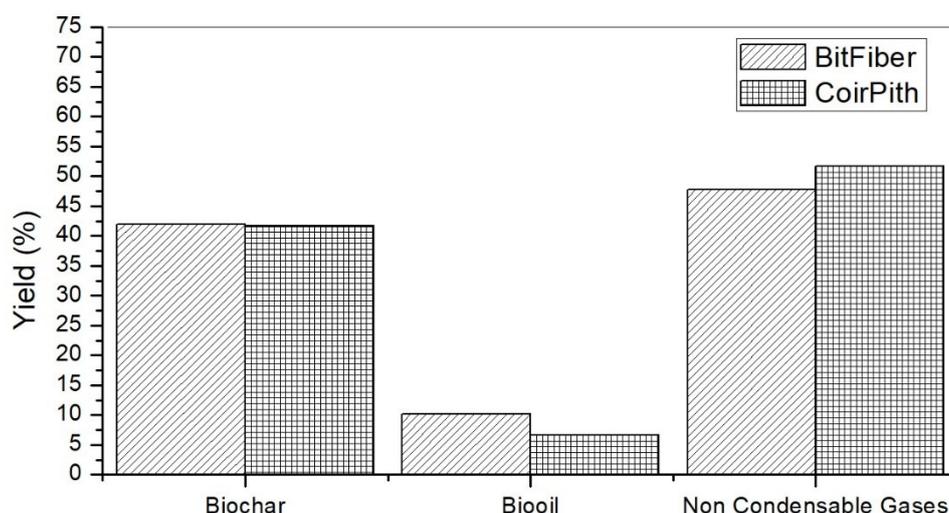


Fig. 2. Yield of various pyrolysis products of CP & BF

where  $q_t$  is the amount of dye adsorbed (mg/g) per unit mass of adsorbent at time  $t$ ,  $q_e$  is the amount of dye adsorbed (mg/g) per unit mass at equilibrium,  $k_1$  is the pseudo-first-order rate constant, and  $k_2$  is a pseudo-second-order rate constant. Adsorption isotherm studies were done based on langmuir and freundlich isotherm models. The Langmuir model of adsorption explains the existence of monolayer coverage of adsorbate on the outer surface of the adsorbent and is based on a structurally homogeneous and energetically equivalent sorption sites.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$$

The Freundlich isotherm assumes a heterogeneous surface of the adsorbent and the amount of adsorbed material is the summation of adsorption on all sites, which is not restricted to the formation of a monolayer. The Freundlich isotherm equation is as follows

$$\log q_e = \log K_F + 1/n \log C_e$$

## RESULTS AND DISCUSSION

The pyrolysis of the substrate yields three major products biooil, biochar and non-condensable gases. The yield of the different components of pyrolysis is shown in figure 2.

The elemental composition, pH and elemental ratios of biochars are presented in table 1A & 1B. The results show that both BFB and CPB have high percentage of carbon with CPB having higher percentage of oxygen. Elemental analysis and their ratios are very important parameters in determining the character of biochar. CPB has comparatively higher O/C, H/C and (O+N)/C ratios indicating higher polarity. According to Rutherford et al., (2012), biomass consists of labile and recalcitrant oxygen, of which the former oxygen is easily lost during initial heating whereas the latter is retained in the biochar. The H /C and O /C ratios are indicators of dehydration and decarboxylation reactions (Jindo et al., 2014). The H/C and O/C ratios are less in BFB compared to CPB indicating increased dehydration and decarboxylation reactions during pyrolysis of BF.

**Table 1a.** Yield, pH, Elemental composition of biochars produced at 350 °C

Sample	Yield	pH	C	H	N	S	O
BFB	42.00	10.26	85.73	1.00	0.38	ND*	12.89
CPB	41.66	10.14	68.02	1.11	0.85	ND	30.02

\*Not Detected

**Table 1b.** Elemental ratios of biochars produced at 350 °C

Sample	O/C	H/C	O/H	C/H	C/O	(O+N)/C
BFB	0.15	0.012	12.89	85.73	6.65	0.15
CPB	0.44	0.016	27.04	61.27	2.27	0.45

**Table 2.** Surface functional groups of biochar (Boehm titration results)

Sample	Total Acidic groups (mmol/g)	Acidic Groups			Total Basic Groups
		n carboxyl	n lactones	n phenols	
BFB	0.50	0.20	0.20	0.10	0.90
CPB	0.50	0.15	0.05	0.30	0.70

These ratios are reduced due to volatilization of easily degradable carbon compounds from the raw substrate. The CPB has a lower C/O ratio indicating a structural arrangement of aromatic rings which forms a stable crystal graphite like structures. The pH of both the biochars are highly basic in nature. The boehm titration results also indicate more basic surface functional groups on the surface of biochar (Table 2). The increased pH and basic surface functional groups may also aid in enhanced removal of acidic dyes from effluent.

The surface functional groups present on the raw substrate and the changes induced by the pyrolysis on the formation of char has been studied using the Fourier Transform Infrared Spectroscopy. The FTIR spectrum of raw substrates and biochars produced are shown in Figure 3.

The major absorption peak present in both CP and BF at 3343  $\text{cm}^{-1}$  is attributed to the vibrational stretching of hydrogen bonded OH group present in phenolic groups including the adsorbed water. This peaks are absent in the FTIR spectra of biochar indicating the complete dehydration and loss of hydroxyl groups during the process of pyrolysis. A small absorbance peak at 2919  $\text{cm}^{-1}$  present in the BF, indicates the presence of  $-\text{CH}_2$  in biopolymers, has shifted to 2978  $\text{cm}^{-1}$  in BFB and reduced in size indicating partial loss of volatile carbon components. A characteristic peak at 2100  $\text{cm}^{-1}$  is prominent in both the substrates which became much more prominent in BFB and CPB, which corresponds to the Si-H vibration. It is an indication of presence of silica in raw substrates and biochar, which is also confirmed by the XRD spectrum. Prominent peaks present in both the raw substrates at 1240  $\text{cm}^{-1}$  (aromatic C-O and phenolic C-O associated with ligneous guaiacyl units) has almost completely disappeared, indicating the destruction of original lignin structure. The most prominent peak at 1035  $\text{cm}^{-1}$  corresponds to the C-O stretching associated with the oxygenated functional groups of cellulose, hemicellulose and methoxy groups of lignin. The loss of this peak in biochar indicates the loss of volatile oxygen form the raw substrates and also the decomposition of major lignocellulosic components present in CP and BF. The emergence of peaks at 750  $\text{cm}^{-1}$ , 809  $\text{cm}^{-1}$  and 870  $\text{cm}^{-1}$  indicates enhancement in the degree of carbonisation, consistent with the decrease of H/C ratio. The absorbance peak at 1511  $\text{cm}^{-1}$  present in raw substrates also confirms the C=C ring stretching vibration of lignin,

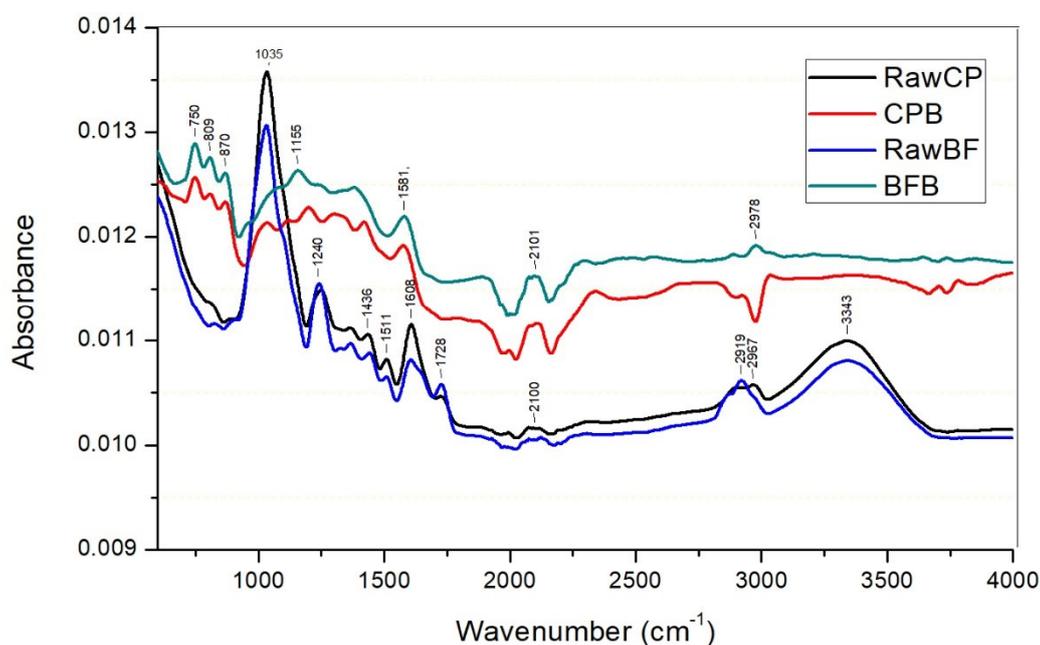


Fig. 3. FTIR spectrum of raw substrates and biochars

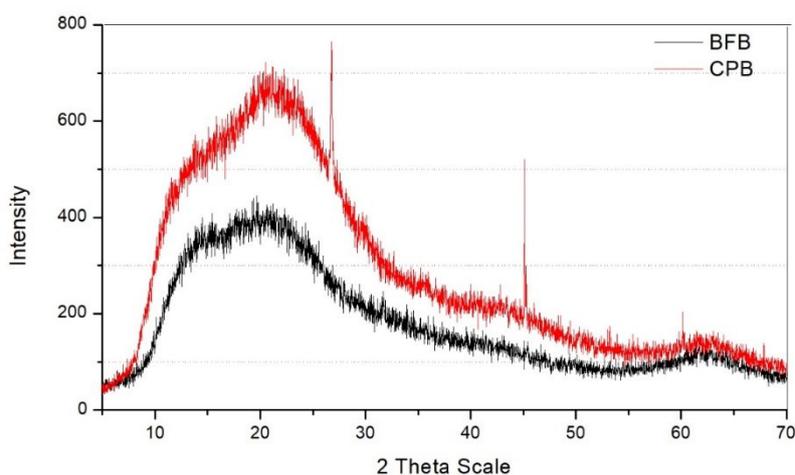
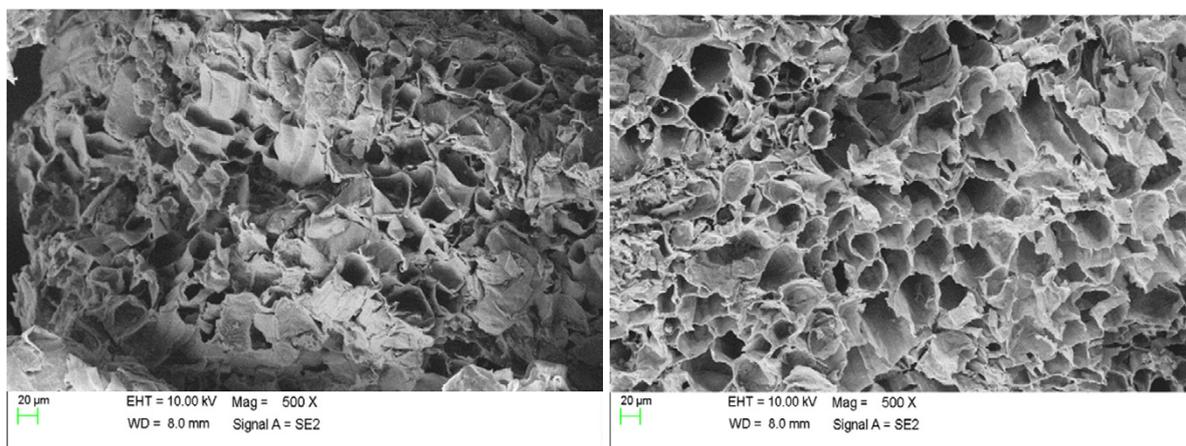


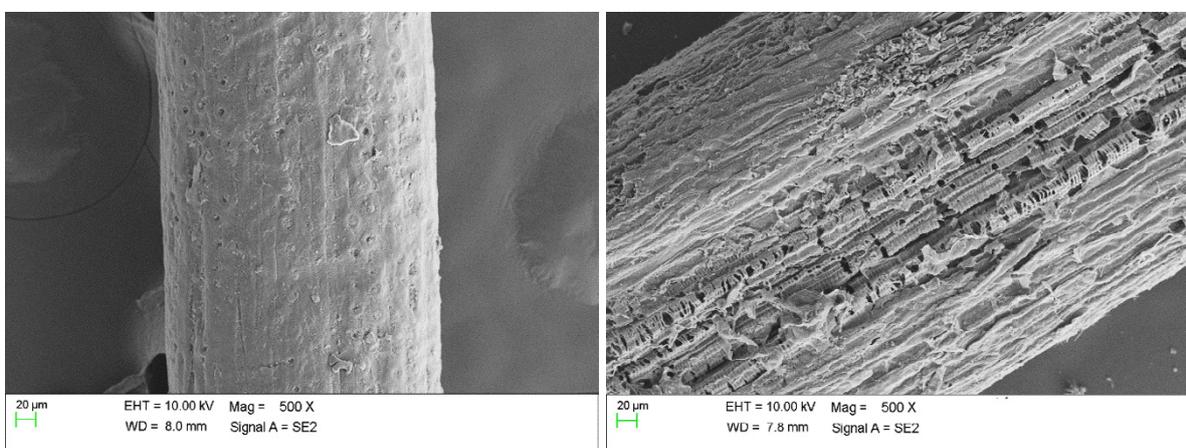
Fig. 4. XRD spectrum of biochars produced at 350 °C

which is absent in the biochar. Another peak at  $1436\text{ cm}^{-1}$  in the raw substrates is attributed to the Phenolic O-H bending, which is also absent in the biochar which also confirms the loss of volatile hydroxyl groups. An absorbance peak at  $1608\text{ cm}^{-1}$  (C=O stretching of aromatic rings) which is more prominent in CP has reduced in its strength and shifted to  $1581\text{ cm}^{-1}$ . This result is consistent with the XRD Spectra, pH and elemental composition of bio-char. The observed spectra showed that bio-char produced consisted of several surface functional groups, which may have contributed positively to its adsorption efficiency. The assignment of FTIR peaks were done based on the data published by Abdel-Fattah et al., (2015); Claoston et al., (2014); Piyushi Nautiyal et al., (2016); Purakayastha et al., (2015); Tsai et al., (2012); Zhang et al., (2011); and Zolfi Bavariani et al., (2019).

The Powder X-Ray Diffraction (PXRD) patterns for the BFB and CPB are shown in Figure 4. The peaks at  $2\theta = 20^\circ\text{--}30^\circ$  refer to the stacking structure of aromatic layers with broadening



**Fig. 5a & b.** SEM image of CP and CPB (20 μm, 500 X)

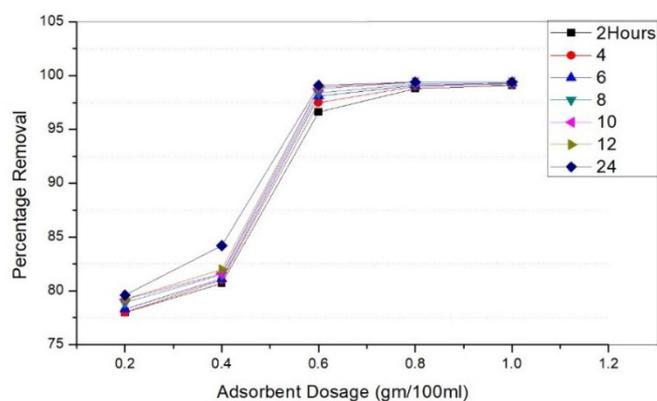


**Fig. 5c & d.** SEM image of BF and BFB (20 μm, 500 X)

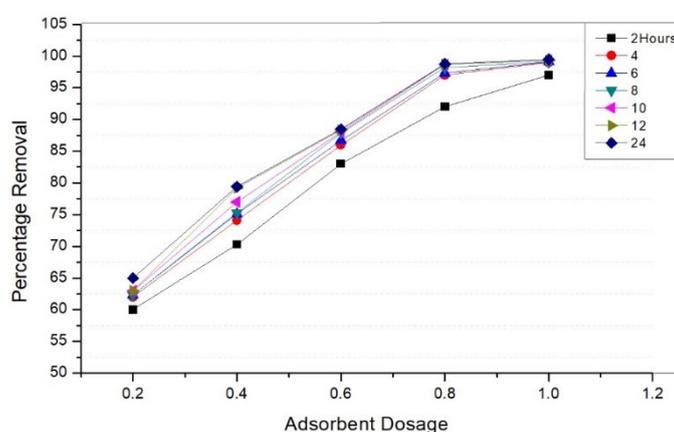
due to the small dimensions of crystallites perpendicular to aromatic layers (Takagi *et al.* 2004). Sharp, nonlabeled peaks in bio-char indicate miscellaneous inorganic components. The presence of higher content of SiO<sub>2</sub>, CaO, and MgO are the major components responsible for these miscellaneous peaks. A sharp and strong peak at  $2\theta = 26.6^\circ$  in the graph of CPB is originated from crystalline SiO<sub>2</sub> (quartz). Thus the surface of both the biochars are heterogeneous as indicated by the X-ray diffraction peaks (Liu *et al.*, 2012).

Figure 5 a-d shows the surface morphology of the raw substrates and biochar. It is clear from the figures the morphological and microstructural changes induced by pyrolysis on the substrates. Compared to Figure 5a (CP), Figure 5b has more pore opening and the pores are oriented in almost same direction. This increased pores also increase the surface area of biochar which aids in increased adsorption of the dye onto the surface. Figure 5c shows that the surface of coir fibers are more even when compared to figure 5d (BFB). The cavities and ridges produced as a result of pyrolysis on BF increase the surface area and may act as holding sites for the dye molecules.

The amount of dye adsorbed by CPB and BFB was studied as a function of adsorbent doses (0.2 to 1 g/100 mL) at 100 mg L<sup>-1</sup> dye concentration for 24 hours. The percentage removal of dye from solution by adsorption using BFB and CPB is shown in figure 6 A and 6 B respectively. The effect of change in pH with respect to adsorption was also studied. 78% dye removal efficiency could be achieved by using 0.2 g BFB within 2 hours whereas CPB was less efficient (60 %) in



**Fig. 6a.** Malachite green removal efficiency of BFB at adsorbent dosages of 0.2 to 1.2 gm/100 ml (contact time 2 to 24 hours)



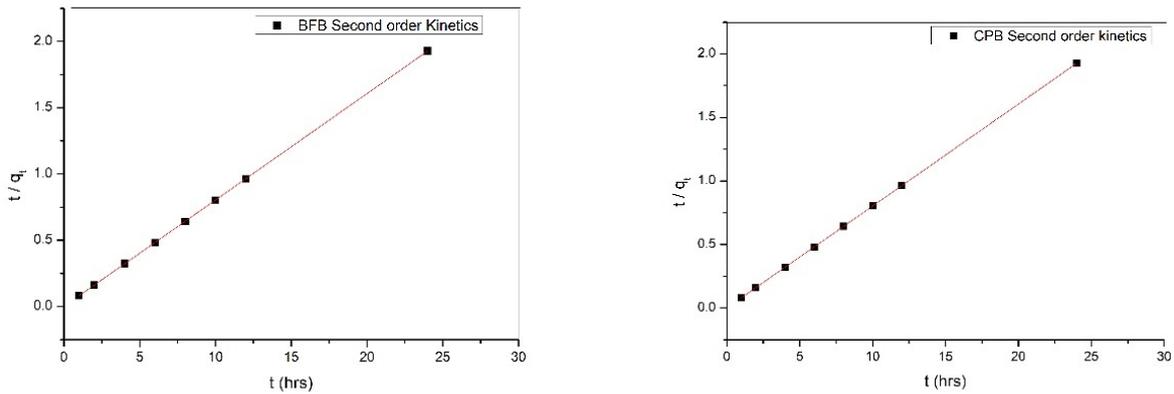
**Fig. 6b.** Malachite green removal efficiency of CPB at adsorbent dosages 0.2 to 1.2 gm/100 ml (contact time 2 to 24 hours)

removing the dye within 2 hours. But on increasing the contact time and the adsorbent dose (0.8 g BFB) 99% removal could be achieved within 4 Hours. Using the same amount of biochar and analyzing the dye concentration after 24 hours residence time, it was observed to achieve a removal efficiency of 99.4 %. There was no considerable changes induced on adsorption on further increase of contact time and adsorbent dosage using BFB. Comparatively CPB could achieve removal efficiency of 99 % within 4 hours only when the adsorbent dosage was increased to 1 g/ 100 ml of the dye solution. Another important observation was that CPB could remove dye from solution upto 99.5% when the contact time was increased to 24 hours using 1 g/100 ml, at normal pH. Even though a maximum of 99.5 % dye was removed using CPB, the adsorption was comparatively better using BFB. BFB could achieve a removal efficiency of 99.4 % using 0.8g biochar within a time period of 12 hours whereas CPB needs more adsorbent dosage and increased contact time for an equivalent dye removal efficiency. Thus a minimum of 0.8 g/100 ml was sufficient for better removal of MG from solution using BFB or CPB.

The effect of change in pH brought up a considerable increase in adsorption and dye removal efficiency in both the biochars. Two different pH were selected and adsorbent dosage was taken to be minimum of 0.8 g/100 ml or above. Using BFB, at pH 4 removal efficiency of 99.4% was achieved using 0.8 g after 2 hours, which increased to 99.6 % after 10 hours and did not vary further on increasing the residence time or adsorbent dosage. On using CPB, at pH 4, the maximum removal efficiency achieved was 99.7 % using 0.8 g biochar after 4 hours and no

**Table 3.** Kinetic studies of BFB and CPB

Biochar	q <sub>e</sub> exp	Pseudo first order kinetics			Pseudo second order kinetics		
		q <sub>e</sub> cal	K <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub> cal	K <sub>2</sub>	R <sup>2</sup>
BFB	12.450	2.19	0.152	0.8551	12.459	6.0202	0.9999
CPB	12.462	3.63	0.144	0.8100	12.463	13.88	0.9998



**Fig. 7.** Second order kinetics of MG adsorption onto Biochar; 7a- BFB, 7b- CPB (Contact time 2 to 24 hours, initial concentration 100 mg/l, volume 100ml)

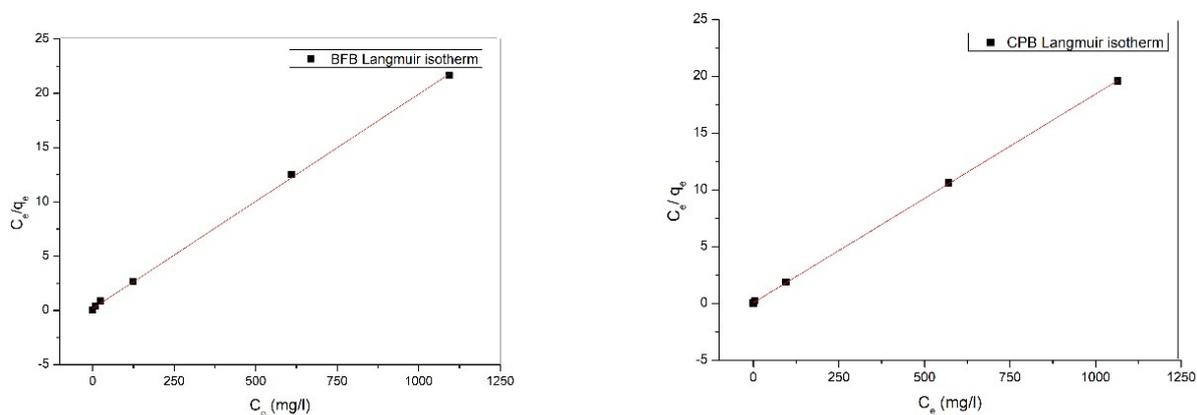
**Table 4.** Adsorption isotherm of BFB and CPB

Biochar	Langmuir isotherm				Freundlich isotherm		
	Q max (mg g <sup>-1</sup> )	K <sub>L</sub> (L mg <sup>-1</sup> )	a <sub>L</sub> (L mg <sup>-1</sup> )	R <sup>2</sup>	K <sub>F</sub> (mg g <sup>-1</sup> )	1/n	R <sup>2</sup>
BFB	50.61	6.4432	0.1273	0.9993	13.1656	0.2144	0.9493
CPB	54.41	17.2473	0.3170	0.9999	15.9613	0.2051	0.8563

further increase in adsorption efficiency was observed. The data for adsorption of MG onto biochar surface at pH 12 is not represented as the increment of adsorption at pH higher than 9.0 would probably be due to the alkaline fading of MG for that MG turns into a carbinol base at a basic pH (Leng *et al.* 2015). Thus both the biochars are equally efficient in removing Malachite Green from solutions and could be used as an ecofriendly, cost effective technique for removal of dyeing effluents in coir industry.

The adsorption kinetics for the present study has been analyzed using pseudo-first-order and pseudo-second-order models. Kinetic parameters for the models and the corresponding correlation coefficients are presented in table 3. On analyzing correlation coefficient R<sup>2</sup>, it is seen that the experimental data fit with the pseudo-second-order model (R<sup>2</sup>=0.999) (figure 7a and b) which is an indication of a chemisorption mechanism, than the pseudo-first order model. In the case of the pseudo-second-order model, R<sup>2</sup> was greater than 0.999 for both the biochars and the q<sub>e,cal</sub> were in good agreement with the q<sub>e,exp</sub> values, indicating the applicability of the kinetic model to the adsorption of MG onto BFB and CPB.

The equilibrium adsorption isotherm was studied using different initial concentrations of 50, 80, 100, 120, 150, 250, 500, 1000 and 1500 mg/l of dye solution using 0.8 gm of the biochars. Equilibrium data were analyzed using langmuir and freundlich isotherms and each isotherm parameters were calculated and presented in table 4. The coefficient values (R<sup>2</sup>) was used in



**Fig. 8.** Langmuir adsorption isotherm of Biochar; 8a- BFB, 8b-CPB ( concentration 50 to 1500 mg/l, mass of adsorbent 0.8 g)

selecting the better isotherm model fit for malachite green adsorption onto the produced biochars. Results show that langmuir isotherm ( $R^2$ - 0.999) as presented in figure 8, fit better for malachite green adsorption than freundlich isotherm model. This indicates a monolayer adsorption of malachite green onto the outer surface of BFB and CPB through uniform adsorption onto the active sites present on the surface.

The maximum adsorption capacity was determined to be 50.61 and 54.41  $\text{mg g}^{-1}$  for BFB and CPB respectively, which is comparable to other adsorbents. Parab et al., (2009) studied the use of coir pith for the removal of crystal violet and rhodamine B which showed an adsorption capacity of 65.53 and 55.54  $\text{mg g}^{-1}$  respectively. Similarly malachite green adsorption on to biochar produced from rice husk showed an adsorption capacity of 32.5 to 61.6  $\text{mg g}^{-1}$ , to which the present results are comparable (Leng *et al.* 2015).

The reusability of biochars was studied using HCl, NaOH and water and a small decrease in adsorption capacity was observed for both the biochars when HCl was used. BFB and CPB showed a reduction in adsorption capacity by 38 % (31.38  $\text{mg/g}$ ) and 36% (34.82  $\text{mg/g}$ ) respectively in HCl after five cycles. The reduction in adsorption capacity was small (29 % for BFB and 26 % for CPB) in NaOH solution. Thus CPB having having higher adsorption and reusability is more economical since it can be easily regenerated and is more ecofriendly as it is produced from a spent waste resource.

## CONCLUSION

BFB and CPB are very high efficient in removing Malachite Green from waste water. A minimum amount of 0.8 g/100 ml of the adsorbent was enough for a removal of 99.7 % dye at pH 4 within 2 hours. The adsorption is governed by pseudo second order kinetics and follows a monolayer adsorption as indicated by langmuir isotherm. Both these biochars are produced from waste resources and is an ecofriendly, cost effective technique for the removal of dyeing effluents released from coir industry. The efficient utilization of sludge produced from the saccharification process of lignocellulosic substrates for protection of water resources from dyeing effluents serves a better way of sustainability. The efficiency of both these biochars in adsorption for the various other dyes used in coir industry need also be studied. Thus this is a feasible technique for the effective protection of water resources from the dyeing effluents released from the coir industry.

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## CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publishing of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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