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RESEARCH ARTICLE

Effect of Process Temperature on Coconut Shell Biochar Production and its Iodine and Methylene Blue Adsorption

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Abstract

Biomass derived biochar materials are in greater need as an effective adsorbent in variety of applications. Coconut shell biochar was produced from slow pyrolysis process at different temperatures (400, 500, 600, 700 and 800ºC) and was characterized for proximate and elemental composition. Biochar with fixed carbon and elemental carbon of 86.38 and 82.14%, respectively was produced achieved at 800ºC. Coconut shell biochar was examined for its adsorption capacity using iodine and methylene blue (MB) adsorption. Maximum iodine adsorption of 550 mg g^{-1} and MB adsorption of 65.6 mg g^{-1} were observed for biochar produced achieved at 700ºC and 800ºC, respectively. Results concluded that biochar produced at 700ºC had more microporous and biochar produced at 800ºC had more mesoporous with higher iodine and methylene blue adsorption.

Keywords: *Biochar, coconut shell, iodine, methylene blue, adsorption*

Introduction

Adsorption is one of the important processes used for both aqueous phase and gaseous phase pollutant removal (Jian *et al*., 2018). Biochar is a stable and non-polluting carbonaceous material that is gaining importance in recent years for its adsorption properties (Lehmann *et al*., 2011; Ahmad *et al*., 2014; Lou *et al.,* 2011). There is an increasing attention towards biochar due to its suitability for different applications starting from soil amendment, water treatment to carbon sequestration (Chan *et al*., 2007; Woolf *et al.,* 2010).

The adsorption capacity of biochar mainly depends on the physical and chemical properties which are influenced by the treatment conditions and the nature of the substrates (Hansen *et al.,* 2015; Meng *et al*., 2013; Mukome *et al*., 2013). Higher carbon content and porous nature of coconut shell, makes it viable for biochar production. Iodine and methylene blue adsorption methods are used for analysing the adsorption capacity of the biochar (Rozada *et al*., 2005; Nunes and Guerreiro, 2011). Iodine predominantly adsorbed by micropores (pore diameter 2–50 nm) and methylene blue in mesopores (pore diameter higher than 100 nm) (El-Hendawy *et al.,* 2001). The aim of this study was to investigate the iodine and MB adsorption ability of coconut shell biochar varying with production process temperature and to examine the suitability of biochar for dye removal from waste water.

Material and Methods

Raw material and its characterization

Coconut shell was collected from local farm holds in Coimbatore. The material was shredded and sieved to the size of 2 to 5 mm before biochar production.

Biochar preparation

Batch type pyrolysis reactor of 1kg capacity was designed and developed for biochar production. Inert atmosphere was maintained by passing nitrogen at a flow rate of 300 ml min^{-1} throughout the process. Heating rate was maintained at 10ºC min^{-1} using electrical heating furnace. Biochar was produced at 400, 500, 600, 700 and 800ºC with 1h residence time. The produced biochar samples were analysed for their characteristics.

Physiochemical characteristics

Proximate composition of raw material was carried out based on ASTM D-5142 procedure and for biochar ASTM D1762-84 method was followed. Elemental composition of raw and biochar samples were determined using Thermo scientific flash 2000, CHNS/O analyser.

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Iodine adsorption

Iodine adsorption indicates the amount of iodine adsorbed (in mg) by 1 g of biochar when the iodine concentration of the filtrate is 0.02 N. It was determined according to ASTM D4607-94 method. Biochar of 1 g was added with 10 ml of 5 % (wt) HCl in a conical flask and the mixture was boiled for 5 s and then cooled. 100 ml of 0.1 N iodine solution was mixed thoroughly and filtered. From the filtrate, 10 ml was taken and titrated against 0.1 N sodium thiosulphate with starch indicator. The concentration of iodine adsorbed by the biochar was calculated using equation 1.

$$\text{Iodine number, mg g}^{-1} = \{(N_1 \times 126.93 \times V_1) - [(V_1 + V_{Hcl})/V_F] \times (N_{Na2S2O3} \times 126.93) \times V_{Na2S2O3}\}/Mc \quad (1)$$

Where N_1 is the iodine solution normality, V_I is the added volume of iodine solution, V_{HCl} is the added volume of 5% HCl, V_F is the filtrate volume used in titration, $N_{Na2S2O3}$ is the sodium thiosulfate solution normality, $V_{Na2S2O3}$ is the consumed volume of sodium thiosulfate solution and Mc is the mass of sample.

Methylene Blue (MB) Adsorption

The MB adsorption is defined as the milligram of methylene blue adsorbed onto 1.0 g of adsorbent which was obtained by following JIS K 1470-1991 method. In this study, 0.1 g of powdered biochar samples were placed in contact with 100 ml of MB solution at different concentrations (10, 25, 50, 100, 250, 500 and 1000 mg l^{-1}), for 24 h at room temperature in a shaker. The solutions were filtered and the supernatant solution concentration was measured using Cary 60 UV-Vis spectrophotometer at 660 nm.

Results and Discussion

Yield and proximate composition

The yield of biochar, indicated as the per cent of initial weight of sample, varied from 25.6 to 35.5 per cent. As the process temperature increased, yield was decreased (Fig. 1). The reduction in yield was due to the evolvement of moisture and volatile matter from the material. Proximate analysis of coconut shell showed the moisture content, volatile matter, ash and fixed carbon content (on dry basis) as 8.5, 76.24, 0.68 and 23.08 %, respectively. The results were on par with the results reported by Daud and Ali (2004). Maximum fixed carbon content of 90.4 percent was obtained at 800ºC with 93 percent volatile reduction. Ash content increased with temperature due to volatile removal. Upto 700ºC the volatile removal was intense and when the temperature increased (>700ºC) the reduction in volatile was found to be stable. This is due to lower degradation rate during secondary decomposition at higher temperatures. Similar trend was reported by Zhao *et al.* (2018) for rapeseed stem biochar production.

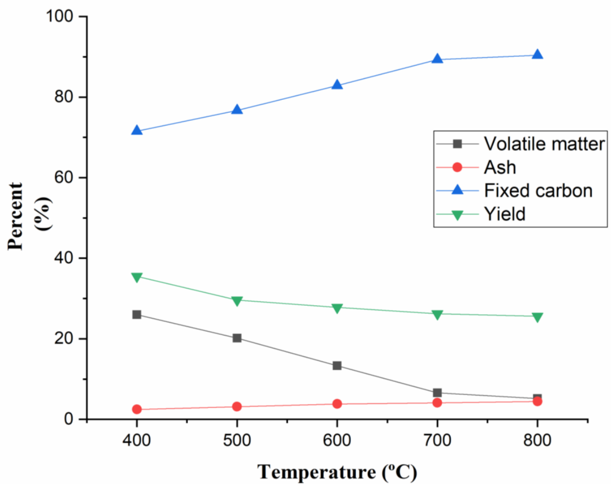

Fig. 1. Effect of temperature on yield, volatile matter, ash and fixed carbon

Elemental Analysis

Elemental composition of biochar samples and H/C and O/C ratios at different process temperatures are presented in Table 1. The raw coconut shell had the elemental composition of 0.47 % nitrogen, 46.90 % carbon, 6.18 % hydrogen, 0.36 % sulphur and 45.88 % oxygen.

It is evident from the results that the carbon content of biochar was increased with increasing in temperature, whereas nitrogen, hydrogen and oxygen per cent were decreased. Carbon content increased from 65.84 to

82.14% while the hydrogen content was reduced from 3.24 to 0.58% from 400 to 800ºC. Decrease in hydrogen was due to initial loss of moisture by dehydration reaction. Similarly H/C and O/C ratios were reduced at constant rate up to 700ºC and further no significant reduction was observed. This was due to evolving of water vapour and low molecular weight gases like CO and CO_2 during the degradation process which led to carbonaceous biochar (Fu *et al*., 2011; Jindo *et al*., 2014). At 800ºC, 12.11 per cent of oxygen was present in the biochar which shows the presence of recalcitrant oxygen bound to the carbon. Sulphur was eliminated at all the process temperatures as the sulphur was oxidized during pyrolysis reaction which was also reported by Ghani *et al*. (2013).

Table 1. Elemental composition of biochar at different process temperatures

Biochar process temperature (ºC)	N (%)	C (%)	H (%)	S (%)	O (%)	H/C ratio	O/C ratio
400	0.42	65.84	3.24	0.00	29.49	0.05	0.45
500	0.39	69.15	3.04	0.00	25.22	0.04	0.36
600	0.31	75.23	1.84	0.00	20.11	0.02	0.27
700	0.21	79.61	0.81	0.00	15.34	0.01	0.19
800	0.22	82.14	0.58	0.00	12.11	0.01	0.15

Iodine and methylene blue adsorption

Effect of biochar process temperature on iodine and methylene blue adsorption was demonstrated in Table 2. The data indicates that, as the temperature increased both iodine and methylene blue adsorption were also increased.

Table 2. Effect of process temperature on iodine and methylene blue adsorption

Process temperature (ºC)	Iodine adsorption (mg g^{-1})	Methylene blue adsorption (mg g^{-1})
400	333.83	18.5
500	477.2	21.4
600	530.25	23.4
700	550.24	45.1
800	485.12	65.6

Iodine adsorption was varied from 333.83 to 550.24 mg g^{-1} and MB from 18.5 to 65.6 mg g^{-1}. Maximum iodine adsorption of 550.24 mg g^{-1} and maximum MB adsorption of 65.6 mg g^{-1} were obtained at 700 and 800ºC, respectively. Upto 700ºC iodine adsorption was increased and further it was reduced. MB adsorption was increased at a constant rate with temperature. At lower pyrolysis temperatures, pore formation was lower due to incomplete removal of volatiles. Therefore biochar produced at lower temperatures, had lower adsorption. As more volatiles were evolved, surface turns to be porous so maximum iodine adsorption achieved at 700ºC. Further increase in temperature leads to more carbon degradation which leads to pore widening, thereby iodine adsorption lowers and MB adsorption was greatly enhanced (Patnukao and Pavasant, 2008). Biochar produced at 700ºC was microporous and after 700ºC it was turned to be mesoporous. These microporous and mesoporous biochars can be utilized for waste water treatment and also for soil carbon sequestration.

Conclusion

The present work showed the influence of temperature on biochar adsorption characteristics. As the temperature increases, pore formation occurred due to volatile removal and adsorption capacity increased. Upto 700ºC, iodine adsorption increased and at higher temperature it was decreased due to widening of micropores. MB adsorption increased as the temperature increases and maximum of 65.6 mg g^{-1} was attained at 800ºC. These results indicated that coconut shell biochar was more microporous at 700ºC process temperature and turned to be mesoporous after 700ºC. The produced biochar had higher iodine and MB adsorption capacity so it can be well suited for pollutant removal from waste water streams and also for carbon sequestration in soils.

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