Development of biochar from crofton weed & relationship between biochar properties and its applicability as a heavy metal removal activity

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Abstract - Biochar is a pyrogenic black carbon produced from thermal degradation of carbon-rich biomass (<700°C) in an oxygen-limited environment, and usually has a porous structure, a surface rich in oxygenated functional groups, strong adsorption capacity, and a certain degree of surface area and stability. Biochar has multiple uses, including agricultural applications for soil remediation and pollution control in water and soil. Biochar has several significant socioeconomic and environmental benefits such as carbon sequestration, pollutant removal, and soil improvement. Pyrolysis temperature affects biochar properties, which in turn determines its application potential. The collected Crofton weed (except for the roots) was washed, air-dried at room temperature, and crushed for passage through a 10-mesh sieve. Here, we examined the properties of Crofton weed biochar (C-BC) produced at different pyrolysis temperatures of 300°C, 400°C, 500°C, and 600°C. We measured the yield, ash content, pH, iodine sorption value (ISV), and elemental composition of C-BC. We also characterized C-BC using scanning electron microscopy (SEM), as well as its ability to remove $Pb^{2+}$and Cd^{2+}contaminantsfrom an aqueous solution. C- BC yield decreased with increasing pyrolysis temperature, whereas ash content and pH increased. ISV first increased at 300–400°C and decreased at 500–600°C. For C-BC produced at pyrolysis temperatures 300–600°C (C-BC300 to C-BC600, respectively), H, N, and O content decreased, but C, Ca, Mg, P, and K content increased with increasing temperature. All C-BCs had a certain number of pore structures. Increasing pyrolysis temperatures decreased the amount of -OH, -COOH, aliphatic C-H, and polar C-O on the C-BC surface. The percentage of $Pb^{2+}$and Cd^{2+}removed increased with increasing pyrolysis temperatures. Overall, for C-BC, a low pyrolysis temperature was beneficial for producing a more porous biochar and increased content of water-soluble calcium, magnesium, nitrogen, and phosphorus, whereas high pyrolysis temperatures yield biochar that had high alkalinity, aromaticity, and stability, as well as heavy metal removal activity

Keywords: Pyrolysis, Eupatoriumadeno-phorum Spreng, Iodine Sorption Value

(ISV), Surface Morphology, b^{2+} and Cd^{2+}contaminants.

Introduction

Biochar is a pyrogenic black carbon produced from thermal degradation of carbon-rich biomass (<700°C) in an oxygen-limited environment, and usually has a porous structure, a surface rich in oxygenated functional groups, strong adsorption capacity, and a certain degree of surface area and stability (In yang et al., 2016). Biochar has multiple uses, including agricultural applications, particularly for soil remediation, and pollution control in water and soil (Alwabel et al., 2013; Ahmad et al., 2014). Application of biochar It has several significant socioeconomic and environmental benefits such as carbon sequestration, pollutant removal, and soil improvement. Methods for development and utilization of biochar have been a focus of biochar research. Inexpensive and readily available waste biomasses from agriculture, livestock, and industry (e.g., crop residues, livestock manure, wood pellets, sewage sludge) are the main materials used to prepare biochar. The source materials affect the composition and properties of the resulting biochars, which can have varying yield, pH, ash content, surface morphology, and adsorption properties, which in turn determine their application potential (Chan and Xu, 2009). Therefore, studies on the properties of biochar are important for maximizing its effective use. Pyrolysis temperature is one of the most important factors that affect biochar properties (Yuan et al., 2015). Several recent studies have assessed the properties of biochar materials prepared from different feedstocks using different pyrolysis temperatures and provided data that support the development of methods to optimize production of biochars having desirable properties (Cao and Harris, 2010; Alwabel et al., 2013; Meng et al., 2013; Wang et al., 2015b; Yuan et al., 2015; In yang et al., 2016).

Eupatorium adenophorum -Spreng (commonly known as Crofton weed) is a perennial herb or semi shrubby plant that grows between 0.8 and 2.5 m tall. Crofton weed is native to Central America, but is an invasive plant in America, New Zealand, China, India and many other countries (Liu et al., 2006; Li and Feng, 2009; Wang et al., 2017). Several methods have been developed to control crofton weed, including those that involve chemical control, biological control, and manual control. However, these methods have not produced notable results (Guo et al., 2009). Compared with these control methods, resource utilization of Crofton weed has been explored in recent years (Guo et al., 2009; Sahoo et al., 2011; Zheng et al., 2014). As an invasive plant, Crofton weed is easily obtained at low cost. Based on these properties, crofton weed would be a suitable feedstock for preparation of biochar, but there are few reports describing the properties of Crofton weed biochar (C-BC). The aim of this study was to explore the effect of pyrolysis temperature on the properties of C-BC. Here, C-BC was prepared at different temperatures (300°C, 400°C, 500°C, and 600°C) under oxygen-limited conditions, and the yield, ash content, pH, iodine sorption value (ISV), elemental composition, surface morphology, mineral phase, and surface functional group of the resulting C-BC were characterized and analyzed. The ability of C-BC to remove Pb^{2+} and Cd^{2+} from aqueous solution was also determined in a batch experiment. Results from this study can guide the preparation and utilization of C-BC to maximize its potential applications.

Material and Methods

Preparation of C-BC - Sample collected randomly from Jantanwala, Ghanghora, Dehradun (N $30^0$23’ 18.9” E 078^0 01’40.2”), which was later shade dried for a week. The dried leaf and stem part was first segregated manually from the aerial part and then crumbled and ground to pass through a 10-mesh sieve. The filtered sample was then passed to quartz-covered crucibles which were then pyrolyzed in a Muffle furnace (Muffle Furnace manufacturing unit name) at pyrolyzing temperatures 300^0C, 400^0C, 500^0C, and 600^0C with the heating rate of 10^0C per min for 4 hr. residence time. The charred product was then placed in a desiccator, once the crucibles attain room temperature, removed and weighed immediately, thereafter the charred samples of different temperatures are further crushed to pass through a 60-mesh sieve and were termed as C-BC300, C-BC400, C-BC500, and C-BC600 respectively.

Yield - Yield of C-BC was studied by weighing the samples and C-BC yield % was calculated using the following Equation (1)

Yield (%) = (m_a/ m_b) x 100%……… (1)

Where m_a and m_b represent the weight of C-BC and Crofton weed, respectively.

Ash content of the C-BC - The ash content was detected by heating C-BC at 1000°C for 2 h and was calculated using Equation (2)

Ash Content (%) = (N_a /N_b) x 100,..........(2)

Where, N_a and N_b refer to the weight of C-BC after and before heating, respectively.

pH of the C-BCs - The pH of C-BC was measured with a pH meter (Eutech Instrument) in a mixture of 1.00g C-BC and 20mL demonized water following a 1hr intermittent equilibrium.

Iodine Sorption Value (ISV mg/g) of the C-BCs - The ISV of C-BC was determined according to Chinese National Standards (GB/T12496.8-2015). In brief, a C-BC sample (0.5g) was mixed with 50mL 0.1M I2-KI solution in a 250mL conical flask, which was placed in an oscillator (240 rpm/min) for 15 min. The solution was then filtered, and 10mL of the filtrate was titrated with 0.1M Na2S2O3. A starch solution (5 g/L) was used as an indicator in the titration process. The consumption volume of Na2S2O3 was used to calculate the ISV of C-BC.

Elemental analysis of the C-BCs – Element analysis of C-BC (carbon [C], hydrogen [H], and nitrogen [N]) was performed using an elemental analyzer (Vario EL III; Elementar Corp., Hanau, Germany). The oxygen (O) content was calculated by subtracting the C, H, N, and ash content from the total quantity (Mimmo et al., 2014). For Ca, Mg, K, and P, 0.10 g C-BC was digested with HNO3 using a microwave digestion method, and the concentrations in C-BC were detected and calculated using a ICP-OES (iCAP 6000 series; Thermo Fisher Scientific, Inc., Waltham, MA).

Surface morphology of the C-BCs - The surface morphology of C-BC was analyzed by scanning electron microscopy (SEM) with a field-emission electron microscope and an operating voltage of EHT 15kV (Zeiss EVO 40- EP).

Removal of Pb^{2+} and Cd^{2+} from aqueous solution - Pb^{2+} and Cd^{2+}solutions (50 mg/L) were prepared with Pb(NO3)2 and Cd(NO3)2 4H2O. The initial pH of the solution was adjusted to 5.0 by adding 0.1 M HNO3 or NaOH solutions. A C-BC sample (0.10 g) was added to 50 mL Pb^{2+} 50 mg/L) or Cd^{2+} (50 mg/L) solution, and the mixture was shaken for 24 h at 120 rpm/min at room temperature before filtration through a 0.45-micrometer filter membrane. The final pH of the filtrate was measured with a pH meter, and ICP-OES was used to determine the final concentration of Pb^{2+} and Cd^{2+}. In this experiment, the percentage of Pb^{2+} and Cd^{2+} removed was used to evaluate the removal activity of C-BC. The percentage of Pb^{2+} and Cd^{2+} removed was calculated using the following Equation (3)

Percentage removed (%) = [(C0 – C1) / Co] x 100,……. (3)

where C0 represents the original concentration of Pb^{2+}or Cd^{2+} (i.e., 50 mg/L), and C1 refers to the remaining concentration of Pb^{2+} or Cd^{2+}.

Data processing each experiment was repeated three times, and the average value of the three replicates was taken as the experimental result. Excel 2007, Minitab 11, and Origin 8 were used for data management and processing.

Results and Discussion

General properties of C-BC - The yield of C-BC decreased with increasing pyrolysis temperature (Table 1), and this decreasing trend was consistent with other reports concerning biochar produced from herbaceous biomass (Peng et al., 2011; Ronsse et al., 2013; Wang et al., 2015b). The decrease in C-BC yield was related to the further pyrolysis of raw materials upon increases in the pyrolysis temperature (Onay, 2007; Angin, 2013). An obvious decrease ($p<0.05$) occurred as the pyrolysis temperature increased from 300°C to 400°C, which could be due to the decomposition of hemicellulose and cellulose (Cao and Harris, 2010). The yield of C-BC at different pyrolysis temperatures ranged from 28.69% to 54.69%, and was approximately the same as that seen for other biochars, such as rice straw (Peng et al., 2011), canola straw, corn straw, soybean straw, peanut straw (Yuan et al., 2011), and pig manure (Zhao et al., 2013). The ash content of C-BC ranged from 9.7% to 14.87% (Table 1), and increased with increasing pyrolysis temperature, which was also consistent with previous studies (Yuan et al., 2011; Wang et al., 2015b). The increase in ash content was due to increases in the amount of minerals and com- bustion of residual organic matter at high temperature (Cao and Harris, 2010). Upon increasing the pyrolysis temperature from 300°C to 400°C, the ash content increased by 3.80% ($p < 0.05$) after the decomposition of hemicellulose and cellulose in this temperature range (Table 1).

Table - 1 Yield (%), Ash Content, pH and ISV (mg/g) of the C-BC300, C-BC400, C-BC500 and C-BC600

S.No.	Pyrolysis Temperature	Part of the *Eupatorium adenophorum*	Yield (%)	Ash Content (Aerial Part)	Intermittence pH (Aerial part)	ISV (mg/g)

1.	300^{0}C	Stem part Leaf part Aerial Part	54.69 43.25 49.75	9.74	7.238	234.75 228.73 230.73
2.	400^{0}C	Stem part Leaf part Aerial Part	37.73 34.10 30.40	14.36	8.721	301.87 264.54 292.84
3.	500^{0}C	Stem part Leaf part Aerial Part	34.73 30.45 29.73	14.51	10.187	245.35 240.46 242.53
4.	600^{0}C	Stem part Leaf part Aerial Part	31.78 27.34 28.69	14.87	10.324	220.61 215.15 218.73

The pH of C-BC ranged from 7.238 to 10.324, with only C- BC300 falling outside the alkaline range (pH=7.238; Table 1). Generally, the pH of C-BC increased with increasing pyrolysis temperature. A previous study indicated that biochar pH is significantly and positively correlated with ash content (Wang et al., 2015b). Indeed, the high ash content seen for C- BC prepared at high pyrolysis temperatures was associated with a higher pH, and a significant change in pH occurred between C-BC300 and C-BC400 ($p < 0.05$). Furthermore, organic nitrogen present in amine functional groups was transformed into pyridine-like compounds, and the amount of acidic surface functional groups decreased (De Filippis et al., 2013; Chen et al., 2014), both of which contributed to the increased alkalinity of C-BC with increasing pyrolysis temperature. The surface functional group changes of C-BC are discussed in additional detail in the Fourier transform infrared section.

The ISV of C-BC (Table 1) increased from 230.75 (C- BC300 Aerial Part) to 292.84mg/g (C-BC400 Aerial Part), before gradually decreasing to 218.73 mg/g (C-BC600). The ISV of C-BC400 (299.54 mg/g) was significantly higher than that of the other C-BCs ($p < 0.05$), whereas the ISVs of C-BC300, C-BC500, and C-BC600 were all approximately the same ($p > 0.05$). Mianowski et al. (2007) showed a positive correlation between ISV and surface area. Thus, our results indicate that the C-BC surface area increased first, and then decreased with increasing pyrolysis temperature. This is consistent with studies performed by Tsai et al. (2012), Angın (2013), and Lu et al. (2013), who also showed decreased surface area for biochar produced at pyrolysis temperatures >500°C. The general consistency of C-BC properties with those of other biomass-biochars suggests that crofton weed is suitable for conversion into biochar. The C-BC prepared using pyrolysis temperatures >400°C is alkaline, and thus could be used to reduce soil acidity for agricultural planting. All of the C-BCs in this study had a certain degree of ISV, and thus addition of C-BC to soil could be a practical method to reduce nutrient loss and capture pollutants.

Biochar elemental analysis

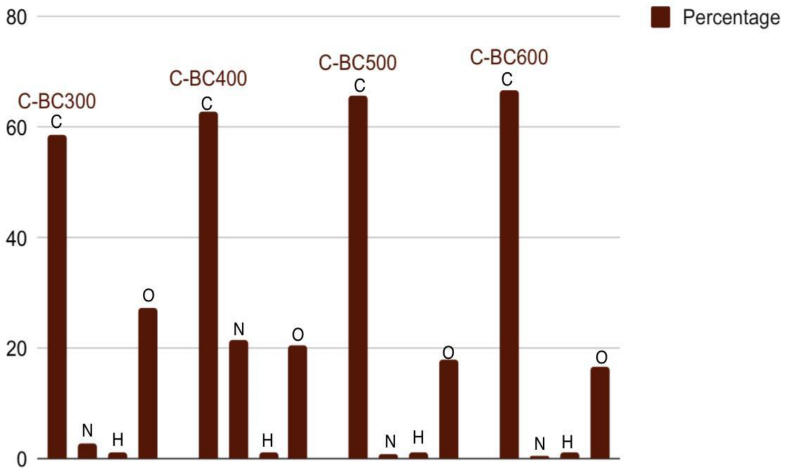
C content of C-BC increased by 26.1% between C- BC300 and C-BC600 (Table 2), likely due to the concentration effect of pyrolysis (Kloss et al., 2012; Sun et al., 2014). Meanwhile, the H, N, and O content decreased with increasing pyrolysis temperature. Specifically, the H, N, and O content decreased from 4.37%, 1.75%, and 25.07% (C-BC300) to 0.85%, 1.25%, and 16.43% (C-BC600), respectively (Table 2). During pyrolysis, the loss of increasing amounts of volatile agents, hemicellulose, and cellulose with increases in pyrolysis temperatures decreases the overall amount of H, O, and N elements (Chen et al., 2014). Here, the atomic ratios of H/C, O/C, and (O+N)/C were, respectively, decreased from 0.52, 0.39 and 0.35(C-BC300) to 0.15, 0.21 and 0.19 (C-BC600).

The ratios of H/C and O/C can be used as carbonization indicators (Wang et al., 2015b). Thus, the low H/C and O/C for C-BC600 indicated that highly carbonized biochar was formed at this pyrolysis temperature. The atomic ratios of H/ C and (O+N)/C can serve as indices for aromaticity and polarity, respectively (Chen et al., 2005; Pujol et al., 2013). The decreasing trends for the atomic ratios H/C and (O+N)/C demonstrated that high-temperature pyrolysis is beneficial to produce C-BC that has enhanced aromaticity and decreased polarity, respectively. In previous studies, Spokas (2010) found that biochar having an O/C ratio between 0.2 and 0.6 was stable and had

a 100–1,000 year half-life. Schimmelpfennig and Glaser (2012) showed that an O/C < 0.4 and an H/ C ratio <0.6 as well as C content >15% are associated with stable biochar. For all C-BCs in this study, the ratios of O/C, H/C, and C content fell within these intervals, suggesting that they have good stability and thus would be suitable for use as materials or additives for soil remediation. Content of Ca, Mg, K, and P ranged from 16,540.54–25,362.16, 4,752.36–5,897.53, 33,864.94–79.879.24, and 4,963.08–5,483.75mg/kg, respectively. Overall, the content of Ca, Mg, K, and P had an increasing trend from C-BC300 to C-BC600 (p< 0.05), which was consistent with previous studies (Cao and Harris, 2010; Hossain et al., 2011; Yuan et al., 2011; Cantrell et al., 2012).

Table-2 Elemental composition of C-BCs and Atomic Ratios

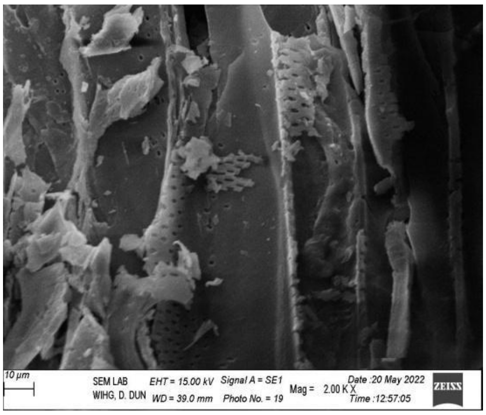
Biochar	C%	H%	N%	O%	H/C	O/C	(O+N)/C
C-BC300	53.07	4.321	1.75	25.07	0.52	0.39	0.35
C-BC400	63.25	3.16	1.32	20.60	0.29	0.27	0.25
C-BC500	75.28	1.01	1.39	17.97	0.17	0.24	0.20
C-BC600	79.17	0.85	1.25	16.43	0.15	0.21	0.19



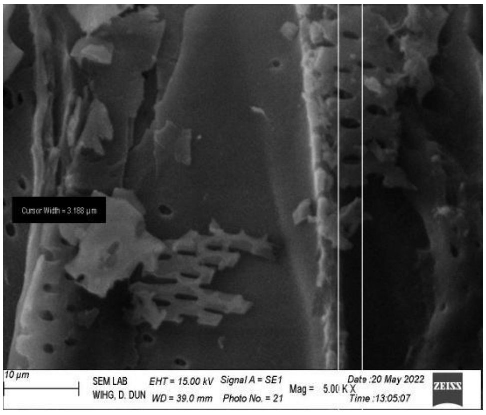
C, H, N, and O data of different C-BC respectively.

Surface morphology

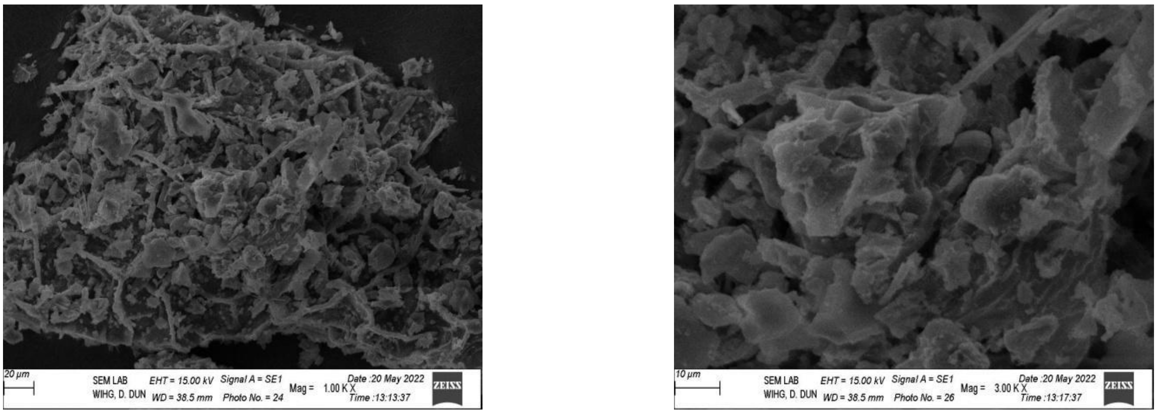
Morphologies of the four C-BCs are shown in Fig. 2. C-BC300 and C-BC400 retained the relatively complete tubular cell structure of Crofton weed, whereas this structure was gradually destroyed in C-BC500 and C-BC600 with the degree of destruction increasing with increasing temperatures as reported by Fan L et al. 2019. All C-BCs had a certain number of pore structures (Fig. (A), (B), (C), and (D)) formed from the large amounts of pyrolysis gas released from the C-BC surface during pyrolysis. However, excessive pyrolysis gas released through the surface of C-BC could lead to the expansion and coalescence of pores (Angın, 2013), which might result in the collapse of pore structures. Although the expansion and coalescence of pore structures are not visible in Fig. (C) and in Fig. (D), the decreased ISVs for C-BC500 and C-BC600 (Table 1) support this possibility to some extent.



(A)



(B)



(B) (D)

Figure - (A), (B), (C), and (D) represent the surface morphology of the C-BC400 and C-BC600 respectively.

The application of C-BC with suitable pore structures to soils can improve the physical properties of the soil by augmenting porosity, reducing bulk density, and increasing water-holding capacity. Moreover, the pore structure in C-BC can provide a good habitat for microbes, and in turn, increase the number and activity of beneficial microbes to improve the soil microbial environment. Based on our findings, C-BC prepared at low pyrolysis temperature (<400°C) would be suitable to produce biochar that has these properties.

Removal of Pb^{2+} and Cd^{2+} with C-BC

Percentage of Pb^{2+} removed by C-BC treatment of a 50 mg/L aqueous solution increased from 97.79% (C-BC300) to 99.52% (C-BC600) ($p< 0.05$), whereas the percentage of Cd^{2+} removed increased from 85.78% (C-BC300) to 97.56% (C-BC600) ($p< 0.05$) (Table 3). These results were consistent with those reported by Chi et al. (2017), and indicated that C-BC prepared using a high pyrolysis temperature had a better ability to remove $Pb^{2+}$and Cd^{2+}contaminants. However, the increasing trends for the percentage of $Pb^{2+}$and Cd^{2+} removed were not consistent with the trends for ISV (Table 1), implying that the $Pb^{2+}$and Cd^{2+} removal activity was not closely related to the surface area of C-BC. Cao and Harris (2010) reported that the main mechanism for the removal of $Pb^{2+}$with biochar involved an interaction between the phosphate in biochar with $Pb^{2+}$to form stable Pb phosphate minerals. Cui et al. (2016) showed that the formation of Cd-phosphate precipitate, cation exchange, and relevant functional groups together promoted the biochar-mediated removal of Cd^{2+}. Therefore, the increasing $Pb^{2+}$and Cd^{2+} removal activity by biochar could be related to the amounts of P, Ca, Mg, and K, and a certain amount of surface functional groups that are present on biochars produced using different pyrolysis temperatures.

Table - 3 Adsorption capacity of C-BC Biochar from Pb^{2+} and Cd^{2+} Solutions and Final pH of the solution.

Biochar	**Pb^{2+} (%)**	**Final pH**	**Cd^{2+} (%)**	**Final pH**

C-BC300	97.79± 0.18	7.45± 0.07	85.78±0.30	7.39± 0.23
C-BC400	98.36± 0.06	8.92± 0.02	95.31±0.28	7.64±0.18
C-BC500	99.05 ± 0.10	9.56 ±0.47	96.79±0.11	8.61±0.15
C-BC600	99.52± 0.20	9.71±0.06	97.56±0.18	8.95±0.45

Moreover, from C-BC300 to C-BC600, regardless of whether Pb or Cd removal was considered, the final pH tended to increase (Table 3). All of the C-BCs in this study had a final pH >7.0 for Pb^{2+}removal, whereas for Cd^{2+} removal all except C-BC300 raised the final pH >7.0. These results indicated that the pH in the solution can be increased by the presence of C-BC, particularly those C-BCs that were prepared at high pyrolysis temperatures. This significant pH elevation caused by C-BC is, on the one hand, conducive to deprotonation of the biochar surface, which helps capture Pb^{2+}and Cd^{2+} by C-BC (Yap et al., 2016), yet on the other hand, the elevated pH creates conditions for Pb^{2+}and Cd^{2+} precipitation (or surface precipitation) (Wang et al., 2015a). Therefore, the percentage of Pb^{2+} and Cd^{2+} removed by C-BC300 to C-BC600 was increased. In general, C-BC prepared using high pyrolysis temperatures may be more suitable for the removal of Pb^{2+}, ≥and Cd^{2+}.

Conclusions

As mentioned above, The C-BCs prepared at different temperatures exhibited the ability to remove Pb^{2+}and Cd^{2+} from aqueous solution. Increasing pyrolysis temperature was associated with enhanced ability to remove these heavy metals. Thus, C-BC, particularly C-BC prepared at high temperature, may be used as a remediation material to reduce heavy metal pollution in future. Moreover, converting crofton weed to biochar would be a desirable approach to control the spread of this weed. However, to achieve practical application of crofton weed biochar, several issues must be addressed, including (1) efficient methods to collect crofton weed, (2) safe transport of croton weed that avoids spreading the weed to areas that are not yet affected, and (3) determination of ideal amounts of C-BC to different soils to achieve effective remediation.

Conflict of Interest

Authors have no conflict of interest of any kind

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