THE HEAVY METAL ADSORPTION CAPACITY OF STALK BIOCHAR IN AN AQUEOUS PHASE

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(Received 12th Jul 2019; accepted 12th Feb 2020)

Abstract. Several heavy metal ions including chromium(II), nickel(II), copper(II), zinc(II), cadmium(II), and lead(II) have gained attention due to their common occurrence in recent years. At medium-high temperatures, rice plant stalk (*Oryza sativa* L.) biochar, cassava stalk (*Manihot esculenta Crantz*) biochar and reed stalk (*Phragmites Trin.*) biochar automatically undergo pyrolysis, and the resulting biochar can be used as an adsorbent of heavy metal ions. While maintaining the pH and temperature of the solution and the dosages of biochar, the adsorption capacity of heavy metal ions in biochar under different treatment times (1 h, 6 h, 12 h, 24 h, 48 h, 72 h, and 96 h) were assessed. The physical and chemical characterization of the biochar was also performed. In this article, biochars produced from two common grain crop stalk (rice plant and cassava) and cash crop stalk (reed) were estimated as potential adsorbents for the removal of heavy metal ions from the contaminated solution.
Keywords: *agricultural residues, stalk biochar, heavy metal solution, removal efficiency, potential adsorbent*

Introduction

Biochar products are obtained by the pyrolysis of biomass energy materials under high temperatures (300-900°C) in environments with limited oxygen content (Ahmad et al., 2012), and have been used in agricultural soil improvement. Depending on the porous structure, biochar can be considered anadsorbent and water-retaining admixture material. A large amount of material from agricultural production and industrial processing can be used as biochar raw stock due to its abundance and low cost (Inyang et al., 2016). In the harvest season especially, many agricultural residues are produced, such as rice, wheat, corn and peanut. Processing abundant biomass into biochar by pyrolysis in anaerobic conditions not only greatly reduces the volume, but also improves the value (Abdelhadi et al., 2017). Typical biological carbon has high cation exchange ability (CEC) and alkalinity. With increasing biological soil activity, biochar improves soil properties, ultimately giving potential to increase agricultural yield (Chun et al., 2004). Biochar may also affect the bioavailability of heavy metals in soil and the accumulation of heavy metals in soil-grown plants. However, previous studies have not shed much light on the

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

effects of biocarbon on heavy metals in soil (Chen et al., 2011). Unlike most biodegradable organic and inorganic pollutants, heavy metals cannot be biodegraded and accumulated through the food chain (Inyang et al., 2016). In recent years, more attention has been paid to biological carbon, because of its role in ecological restoration, such as carbon sequestration, soil fertility improvement and soil restoration. Recent literature provides evidence that it has the ability to hold organic and inorganic pollutants in soil (Inyang et al., 2016). Therefore, biochar is considered to be a new type of remediation agent that can help to repair heavy metal soil pollution (Liu and Zhang, 2009).

Water is an important part of human ecological environments. Human health is harmed by the contamination of drinking water, agricultural products, and aquatic products with heavy metals. Owing to the characterization of heavy metal pollutants as being non-degradable, cumulative, and potentially harmful, heavy metal pollution of water has attracted more attention. In light of research results for the application of biochar, multi-aperture, specific surface area, cationic exchange ability, high stability, and other characteristics were considered. Biochar use as an adsorbent material for metal contaminated water treatment has important application prospects (Meng et al., 2014). Researchers found that biochars produced by anaerobic digestion had higher adsorption capacity to heavy metals (Inyang et al., 2011, 2012). Cellulosic biomass waste from agricultural and forestry production are usually used as the raw materials for biochar processing (Keiluweit and Kleber, 2009).

In China, reed is a common cash crop that is often used as the raw material for paper production. Owing to the ability of adsorption and enrichment of heavy metals, reed could be used for wastewater treatment and as a landscape plant in constructed wetlands (Hou et al., 2016). Cassava and rice are common food crops and the residues account for a large proportion of agricultural waste in tropical areas (Deng et al., 2014; Huang et al., 2018). Biochar production from these three stalk materials has been reported (Huang et al., 2017; Edhirej et al., 2017; Li et al., 2018). Therefore, this paper mainly compared the different adsorption capacities of heavy metals by biochars using rice plant stalk, cassava stalk, and reed stalk as raw materials for biochar. The aims of this study were: (1) to examine the physical and chemical characteristics of biochars, (2) to examine the surface and pore characterization of biochars, and (3) to examine their adsorption capacity of common heavy metals.

Materials and methods

Biochar preparation and characterization

The biochars that were texted were made of rice plant stalk, cassava stalk, and reed stalk material. The raw materials used in this study were collected in Fuping County, China. The sorption ability of the biochar was enhanced by pulverization prior to pyrolysis (Tong et al., 2011). In order to do this, the stalk were initially cut to 25 mm pieces with an electronic chipper and then these were cut in a 5 mm cross-cutting mill. The material was dried at 60°C for constant weight before pyrolysis (Sevilla and Fuertes, 2009). Studies have shown that when the carbonization temperature reaches 500°C, the carbon yield biomass is essentially stable (Bridgwater, 2007). Thus, all biochar from this study was produced at a temperature of 550°C for 4 h. Only the small particles that passed through a 0.5 mm sieve were used in the experiments described below.

Ash content was determined by combusting the biochar at 750°C for 6 h in open crucibles on a dry weight basis (105°C for 18 h under argon). A CHN elemental analyzer

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
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(Flash EA 1112, Thermo Finnigan) was used to determine the carbon (C), hydrogen (H), and nitrogen (N) contents of all biochars. Oxygen content was calculated according to *Eq. 1*. Elemental composition was measured in duplicate, and in this paper, the averaged data was used for analysis. Biochar SEM images were obtained by FEI Q45 scanning electron microscop (FEI, USA). The pH of the biochar was measured in a 1:10 ratio of biochar suspension in deionized water. To determine the concentrations of heavy metals in the biochar, each of the 0.1 g of biochar samples was dissolved in 3 mL of HNO_3 (65%), 9 mL of HCl (37%), and digested for 1 h. The digestion solution was poured into 50 mL flask and diluted with deionised water to reach the tick mark (Pundytė et al., 2011; Baltrėnaitė et al., 2016). The concentrations of heavy metals in the solution were determined by ICP-MS (Agilent 7700e, USA).

Metal adsorption experiments

All chemical reagents were of analytical grade. Heavy metal solution (10 mg/L) of Cd, Cr, Pb, Cu, Zn, Ni was prepared. The mixed solutions made to have a pH 7.0±0.1 which was adjusted by the addition of nitric acid or sodium hydroxide solutions. For adsorption efficiency investigation, 50 ml centrifuge tubes were filled with a heavy metal solution into which 0.01 M $CaCl_2$ and 0.2 g/L NaN_3 were added to maintain a constant ionic strength and to inhibit microbial activities. 0.5 g of biochar per sample were added to the test solutions. Other scholars who studied the equilibrium adsorption time in similar biochars found the time to be around 24 h (Deng et al., 2014; Huang et al., 2018). In order to compare the adsorption effects of the three kinds of biochar, the experimental adsorption time was set to 1 h, 6 h, 12 h, 24 h, 48 h, 72 h, and 96 h. Heavy metals mixed without biochar and biochar with the addition of double distilled water were used as blank controls. All tubes were agitated in the dark at 180 rpm at 25°C. After the adsorption completed, samples were centrifuged for 10 min at 5000 rpm, and the supernatant was then filtered through a 0.45 μm membrane. The removed amount was determined by measuring concentration differences of heavy metals before and after the adsorption experiment (Hou et al., 2016).

Evaluation method

Oxygen content of biochar was calculated according to *Eq. 1*.

$$O = 100 - (C + H + N + \text{ash}) \qquad \text{(Eq.1)}$$

where O is the oxygen content of the biochar; *C*, *H* and *N* are the carbon, hydrogen, and nitrogen contents of the biochar, respectively; *ash* is the ash content of the biochar.

Data processing

The adsorption capacity of biochar (q_t) was calculated by *Eq. 2*:

$$q_t = \frac{(C_{i0} - C_{if}) \times V_0}{m} \qquad \text{(Eq.2)}$$

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where C_{i0} and C_{if} are the initial and final concentrations of the tested solution (mg·L^{-1}), respectively; V_0 is the volume of the tested solution volume (ml); m_j (g) is the weight of the biochar; j refers to the different biochars.

Data analysis

ANOVA test was performed at 95% level using SPSS 22 (IBM SPSS Statistics, Version 22) which tested for the significance of the differences between treatments.

Results and Discussion

Characterization of the biochars

The physicochemical properties of the three different biochars are shown in *Table 1*. We found that all the biochars were alkaline (pH > 10). This observed higher pH of the three biochars is an indication that they may have potential to ameliorate and neutralize soil acidity, which can be an important component in the mobility of heavy metals. The ash content of rice plant stalk (40.00%) was higher than that of cassava stalk (9.85%) and reed stalk (15.75%). The ash content of the three biochars is consistent with the productivity trend, rice plant stalk (43.19%), cassava stalk (23.13%) and reed stalk (24.27%), respectively. Ash is made up of solid inorganic substances, which are the residual mineral elements that remain after burning the stalk material, such as sodium, potassium, calcium, magnesium, phosphorus, and iron. The ash content shows the selective absorption and accumulation of minerals by different plants. Higher ash content indicates that rice plant can absorb more mineral elements, which creates favorable conditions for biochar to absorb heavy metals. The productivity of the three biochars are 43.19%, 23.13% and 24.27%, respectively. The productivity of biochars is consistent with the ash content.

Table 1. *Physicochemical characteristics of the three different biochars*

Physicochemical characteristics	Biochar		
	Reed stalk	***Cassava stalk***	***Rice stalk***
pH	10.55	10.24	10.94
Conductivity (μS·cm^{-1})	677	1313	911
TC (%)	65.82±14.62	59.12±10.81	39.23±5.28
Ash content (%)	15.75±0.36	9.85±0.42	40.00±2.08
Productivity (%)	28.53±2.57	31.05±1.69	41.71±0.61
C (%)	61.93±0.98	64.30±0.32	41.05±0.44
H (%)	1.65±0.07	1.61±0.05	1.12±0.02
N (%)	0.73±0.09	1.53±0.11	1.36±0.09
S (%)	0.69±0.27	0.50±0.17	0.35±0.02
O (%)	19.94±0.97	22.71±0.41	16.47±0.49
C/N	85.07±10.13	42.13±2.87	30.15±1.96
H/C	0.027±0.001	0.025±0.001	0.027±0.000
O/C	0.32±0.02	0.35±0.01	0.40±0.02
(N+O)/C	0.33±0.02	0.38±0.01	0.43±0.02

Chemical composition of the three biochars is shown in *Table 1*. Rice stalk biochar contained lower concentrations of C, H, O, and S than cassava stalk and reed stalk biochar. This might be related to the different cellulose content of each feedstock.

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Previous study found that the C content was higher in hardwood than stover (Park et al., 2016). The lignin content in the raw material biomass directly affects the total carbon content of the biochar. While the N content of reed stalk was the least (0.73%), it was probably related to the accumulation of N in plants. In addition, the higher content of hydrogen and oxygen for cassava stalk and reed stalk revealed that more activated sites were available and stable carbon-oxygen complexes existed on the surface of cassava stalk and reed stalk as opposed to rice plant stalk (Guerrero et al., 2005; Tong et al., 2011). The degree of carbonization can be described by the molar H/C ratio, where H is primarily associated with plant organic matter (Tong et al., 2011). Compared to activated carbon (AC) with H/C ratios of 0.12 and 0.256 (Chen et al., 2011; Xu and Zhao, 2013), the observed H/C ratios of 0.027, 0.025, and 0.027 for rice stalk biochar, cassava stalk biochar and reed stalk biochar, respectively, indicate that these biochars are strongly carbonized and are consistent with high amounts of aromatization.

These low H/C ratios suggest that the biochars contain low amount of organic plant residues. The molar oxygen to carbon (O/C) ratio of biochar has been used as a surrogate for surface hydrophilicity since it is indicative of polar-group content, most likely derived from carbohydrates. Based on this assumption, rice plant stalk (0.4) is likely to be more hydrophilic than cassava stalk biochar (0.35) and reed stalk biochar (0.32), as it has a higher O/C ratio. (N+O)/C ratios of rice stalk biochar, cassava stalk biochar and reed stalk biochar were 0.43, 0.38 and 0.33, respectively. The lower O/C and (N+O)/C ratios indicated an increase in aromaticity and a reduction in polarity. Hydrophobic carbon can provide more sorption domains for HOCs (Teixidó et al., 2011; Yang et al., 2011). Different plant types affect the reduction of mass (Keiluweit and Kleber, 2009). The reduction in biomass weight of cassava stalk and reed stalk are more than that of rice stalk. The weight of dry rice stalk biomass, cassava stalk, and reed stalk decreased 2.32, 4.32, and 4.12 times during the production of biochar, respectively.

For rice stalk biochar, ash content and TC had a significant effect at 95% level ($p < 0.05$), C and (N+O)/C had a significant effect at 95% level ($p < 0.05$). For cassava stalk biochar, ash content led to a significant increase in N and C/N. N and C/N had a significant effect at 95% level ($p < 0.001$) and O/C and (N+O)/C had a significant effect at 95% level ($p < 0.05$). For reed stalk biochar, C and O had a significant effect at 95% level ($p < 0.001$), and C and (N+O)/C had a significant effect at 95% level ($p < 0.05$). C and O/C had a significant effect at 95% level ($p < 0.001$), and O and (N+O)/C had a significant effect at 95% level ($p < 0.05$). The O and O/C of the three biochars were all significantly correlated at 95% level ($p < 0.05$).

Surface characterization

Scanning electron microscope images (*Fig. 1*) indicated that three biochar samples consisted of small 1–20 μm diameter pores. The pores of cassava stalk biochar were larger than that of rice stalk biochar. And the pores of reed stalk biochar were the smallest. SEM imaging showed that heat-treated stalk retained its original stalk pores structure.

The strong sorption ability of biochars may be attributed to their surface properties, which is inherited from the feedstock materials. Obvious microporous structures were observed after carbonization of the three substances. The average pore size of the rice biochar was the smallest (1.0 μm–4.2 μm) followed by reed stalk biochar (3.5 μm-4.4 μm), and cassava stalk biochar (7.0 μm–20.0 μm). Within the same field of vision, the pore arrangement of cassava stalk biochar was more compact and the reed stalk biochar had the least number of pores.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

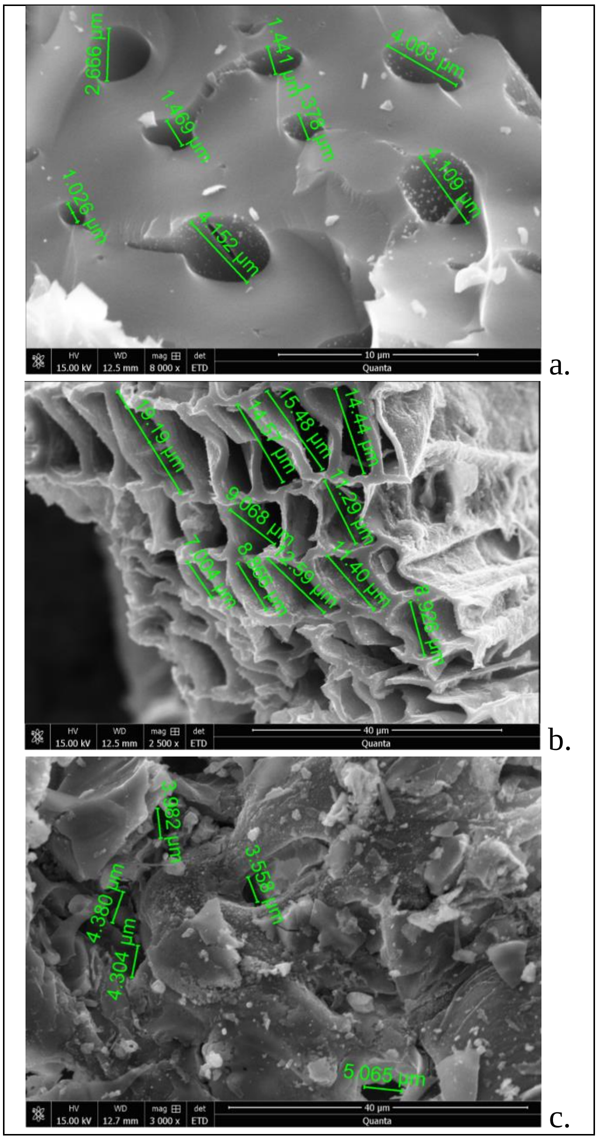

Figure 1. *Scanning electron microscope images of biochar (a. reed stalk biochar, b. Cassava stalk biochar, c. rice stalk biochar)*

Capacity of heavy metal adsorption for three biochars

The capacity of adsorpion of heavy metals q_t (*Eq. 2.*) by three types of biochar is shown in *Fig. 2*. The temperature, pH, dosage of biochar were kept the same. Within the entire experimental adsorption time range, the amount of heavy metal adsorption of the three biochars all showed an increasing trend with the increase in adsorption time. During the entire adsorption process, cassava stalk biochar had the largest cumulative adsorption of heavy metals. When the adsorption time was at 1 h, the reed stalk biochar had a stronger adsorption capacity for various heavy metals than the rice stalk biochar. At other adsorption times, the cumulative adsorption of various heavy metals by rice stalk biochar was higher than that of reed stalk biochar. There are some differences in the adsorption capacity of the three biochars for each of the different heavy metals. For example, cassava stalk biochar had stronger adsorption capacity for Cr, Cu, and Pb than the other two biochars. Their adsorption amounts accounted for 49.17%, 70.56%, and 65.27% of the

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

total adsorption of the three heavy metals, respectively. Rice stalk biochar showed good adsorption capacity for Zn, and its adsorption amount accounted for 51.67% of the total adsorption. The final adsorption amount of rice stalk biochar for Ni and Cd was higher than that of cassava stalk biochar. However, the contribution of cassava stalk and rice stalk biochar to the adsorption of Ni and Cd was not much different. For example, rice stalk biochar adsorption contribution rates of Ni and Cd were 36.66% and 36.69%, respectively, and cassava stalk biochar adsorption contribution rates of Ni and Cd were 34.81% and 35.64%, respectively.

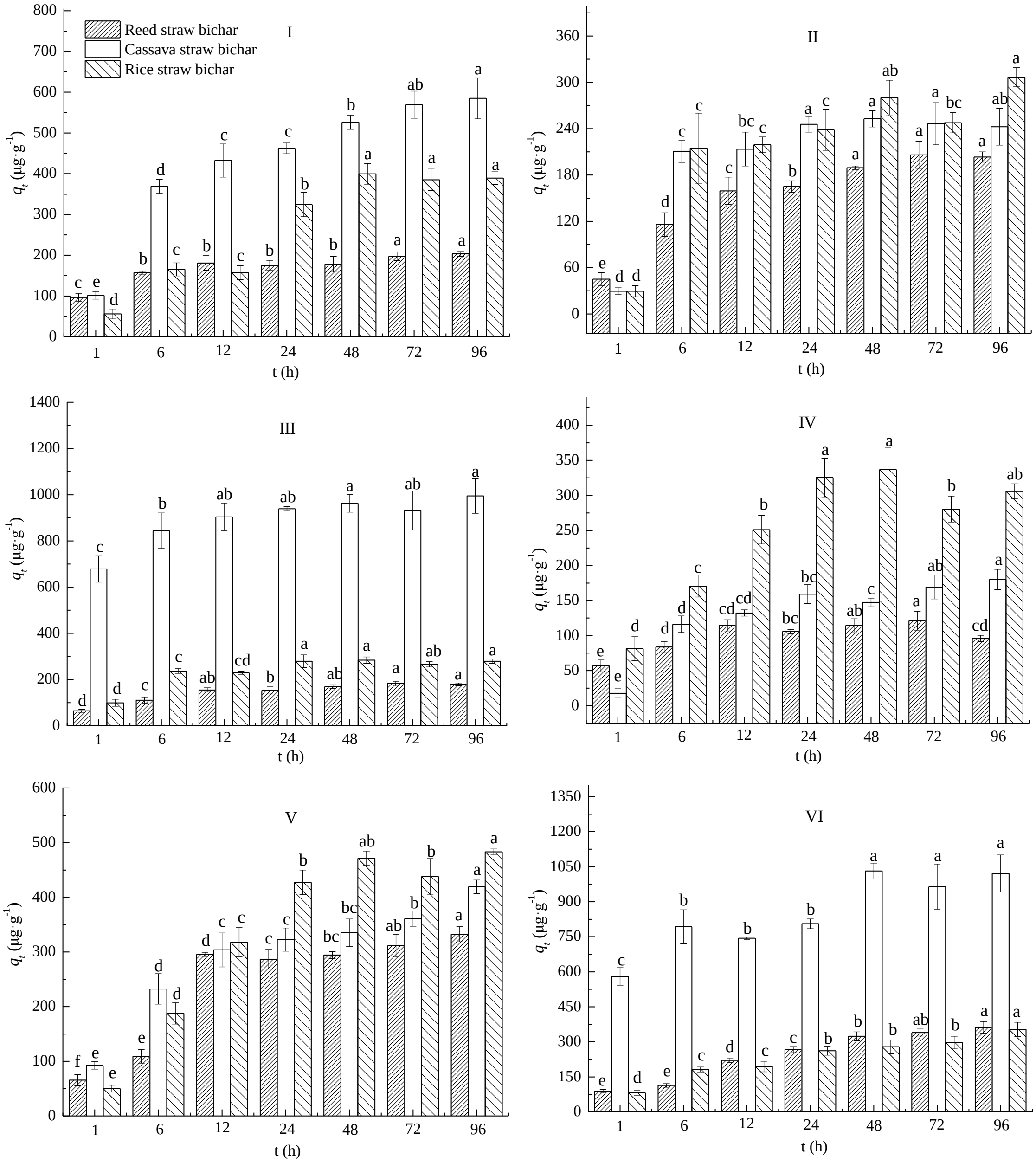

Figure 2. *Effect of biochar concentration on heavy metal adsorption efficiency for three different biochars. I, II, III, IV, V, and VI represent Cr, Ni, Cu, Zn, Cd, and Pb, respectively. Bars indicate standard errors. Lowercase letters indicate significant differences in heavy metal adsorption capacity of the same biochar at different adsorption times ($p < 0.05$)*

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DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

As the contact time increased, available adsorption sites became occupied, followed by an increase in adsorption capacity of heavy metals and a decrease in adsorption efficiency. Research has shown that biochars with higher O content and more acidic surface sites have higher CECs (Harvey et al., 2011). High carbonization temperatures (> 400℃) also promote the formation of graphene structures in biochars, which favor electrostatic attraction sorption mechanisms (Keiluweit and Kleber, 2009). High temperature pyrolysis can remove aliphatic groups and form surface functional groups that have strong adsorption ability, increasing the adsorption and fixation strength of biochar for heavy metal ions.

The correlation analysis of the adsorption test data shows that when the adsorption time does not exceed 6 h, the amount of Cr, Zn, and Cu adsorbed by the biochar of reed stems and the amount of Ni, Cu, Zn, and Pb adsorbed by the biochar of cassava stalks was significantly related to the adsorption time ($p < 0.05$). When the adsorption time did not exceed 12 h, the amounts of Cr and Cd adsorbed by cassava stalk biochar and Zn and Cd by rice stalk biochar were significantly related to the adsorption time ($p < 0.05$). When the adsorption time was at 24 h, the amount of Cd adsorbed by reed stalk biochar increased significantly with the increase in the adsorption time ($p < 0.05$). When the adsorption time was less than 48 h, the adsorption amount of Ni and Pb by reed stem biochar was positively correlated with the adsorption time ($p < 0.05$).

In addition, there are some other notable adsorption phenomena. Within 6-48 h, the adsorption amount and adsorption time of Cr by reed stem biochar was not significant ($p > 0.05$), and the adsorption amount of Zn within this adsorption time range was not significant ($p > 0.05$). The adsorption amount of Cr at 72 h and 96 h was significantly correlated with adsorption amount at 48 h ($p < 0.05$), but there was no correlation between the adsorption amount at 72 h and 96 h ($p > 0.05$). The result shows that the adsorption amount of Cr by reed stalk biochar falls within 6 h of adsorption time, and the adsorption amount increases rapidly with adsorption time. The adsorption amount from 6-48 h does not increase or increases very slowly with the adsorption time. Once a certain adsorption amount was reached, the adsorption amount stabilized itself from the time points of 72-96 h.

The adsorption of Ni (II) and Zn (IV) by cassava stalk biochar was not significant at 6 h and 12 h ($p > 0.05$). The adsorption amount of these two heavy metals did not increase during this adsorption time. Ni (II) adsorption increased at 12 h and 24 h ($p < 0.05$), but stabilized at 24-96 h. The adsorption amount of Zn (IV) increased from 12 h to 48 h ($p < 0.05$) and the adsorption amount was stable after 48 h. The adsorption amount of Cu (III) gradually stabilized after 12 h. The adsorption amount of Pb (VI) stabilized from 6 h to 24 h, increased from 24 h to 48 h, and then stabilized again.

Based on the above analysis, cassava stalk biochar and rice stalk biochar can achieve high adsorption efficiency for six heavy metals in a relatively short time (that is, an adsorption time less than 12 h). The adsorption of the heavy metal Cd (V) by reed stalk biochar reached its highest level within 24 h of adsorption time, but its final adsorption amount was lower than that of cassava stalk biochar and rice stalk biochar. The reed stalk biochar adsorbed heavy metals Ni (II) and Pb (VI) only after 48 h, and the final adsorption of Ni (II) was lower than that of rice stalk and cassava stalk biochar. The final Pb (VI) adsorption amount by reed stalk biochar was basically the same as that of rice stalk, indicating that compared with cassava stalk biochar and rice stalk biochar, reed stalk biochar has poor adsorption capacity and poor adsorption strength for these six heavy metals. For reed stalk biochar, it may take longer to adsorb the same amount of heavy metals as the other two biochar types in this study.

Higher quantities of biochar minerals are produced at higher temperature ranges (350-600℃). Most of the biochar minerals produced at high temperatures are insoluble and are slowly released during the adsorption process, forming precipitate with heavy metals (Inyang et al., 2011). Higher specific surface area and pore volume can physically adsorb heavy metal ions on the surface of biochar and in its pores. The surface of biochar is often negatively charged and can attract positively charged metal ions (Patra et al., 2017).

The three biochar raw materials used in this study were primary stalk residues from agricultural and forestry production. In China, a large amount of agricultural and forestry production residues provide feasibility for biochar production. Biocharing technology not only efficiently treats biomass waste, but also produces by-products such as biochar and bio-oil which both have a higher utilization value.

Studies have shown that adding a certain amount of biochar to heavy metal contaminated soils usually has the effect of improving pH in acidic soils, increasing soil nutrient content and its effectiveness. Biochar can increase the pH of acidic soil by increasing the alkaline saturation of the soil, reducing aluminum levels, thereby reducing the transportable forms of heavy metal ions (Zhao et al., 2015). Adding biochar can increase soil available P, available K, organic matter, total N, total P, and total K to different degrees. First, biochar contains mineral nutrients such as N, P, K, etc., which can be directly applied to soils in order to increase soil nutrient content (Yuan et al., 2011). Second, biochar can also significantly increase the available content of major cations such as K, Mg, and Ca in the soil, provide essential nutrients for plant growth, and improve soil nutrient effectiveness (Lehmann et al., 2003). Third, the strong adsorption and structural characteristics of biochar have a retention effect on water-soluble nutrients in the soil, effectively reducing soil nutrient leaching-loss, slowly and continuously releasing nutrients, and enhancing effective soil nutrient content (Angst and Sohi, 2012). In summary, the application of stalk-based biochar in the restoration of contaminated land is very significant. Not only is the biomass waste used efficiently, but it can also achieve carbon sequestration, improve soil structure and soil fertility.

Conclusions

Excellent removal of heavy metals from soil results from the advantageous physical and chemical characteristics of biochar. Due to the fact that heavy metal removal mechanisms vary with respect to different biochars and metal contaminants, the interest in understanding adsorption processes and the removal efficiency of various pollutants by different types of biochar has increased in recent years. For certain heavy metals, the suitable biochar repairer is different. For Cu, Pb, and Cr, cassava stalk biochar should be chosen as the adsorbent. For Zn, rice stalk biochar is more suitable for treatment, because of the stability of the heavy metal adsorption efficiency. For Ni and Cd, cassava stalk biochar and rice stalk biochar are more suitable as adsorbents than reed biochar.

The soil system is more complex than just a mixed solution of heavy metals. In this experiment, we initially obtained the heavy metal ion adsorption effect for different types of biochar under different adsorption time conditions. The types of biochar with specific adsorption capacity for different heavy metals were summarized. The simulation and calculation of heavy metal chemical conversion processes, heavy metal ion infiltration,

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

and diffusion processes in the soil solution will be carried out in the future. The application of biochar for the remediation of contaminated land will soon become an effective treatment rapidly used across the world.

Acknowledgements. Financial support were provided by the Fund Project of Shaanxi Key Laboratory of Land Consolidation (2019-JC04, 2018-JC16, and 2019-JC05), and the Research Project of Shaanxi Provincial Land Engineering Construction Group in China (DJNY2019-18).

REFERENCES

[1] Abdelhadi, S. O., Dosoretz, C. G., Rytwo, G., Gerchman, Y., Azaizeh, H. (2017): Production of biochar from olive mill solid waste for heavy metal removal. – Bioresource Technology 244: 759-767.

[2] Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J. K., Yang, J. E., Ok, Y. S. (2012): Effects of pyrolysis temperature on soybean stover and peanut shell-derived biochar properties and TCE adsorption in water. – Bioresource technology 118: 536-544.

[3] Angst, T. E., Sohi, S. P. (2013): Establishing release dynamics for plant nutrients from biochar. – Gcb Bioenergy 5(2): 221-226.

[4] Baltrėnaitė, E., Baltrėnas, P., Lietuvninkas, A. (2016): Contamination Features of Ecosystem Components in a Forested Surrounding Environment. – The Sustainable Role of the Tree in Environmental Protection Technologies. Springer International Publishing: Cham. 29-80.

[5] Bridgwater, T. (2007): Biomass pyrolysis. – Biomass and Bioenergy 31(4): 7-18.

[6] Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., Hay, A. G. (2011): Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. – Bioresource technology 102(19): 8877-8884.

[7] Chun, Y., Sheng, G., Chiou, C. T., Xing, B. S. (2004): Compositions and Sorptive Properties of Crop Residue-Derived Chars. – Environmental Science & Technology 38(17): 4649-4655.

[8] Deng, H., Yu, H., Chen, M., Ge, C. (2014): Sorption of atrazine in tropical soil by biochar prepared from cassava waste. – BioResources 9(4): 6627-6643.

[9] Edhirej, A., Sapuan, S. M., Jawaid, M., Zahari, N. I. (2017): Cassava: Its polymer, fiber, composite, and application. – Polymer Composites 38(3): 555-570.

[10] Guerrero, M., Ruiz, M. P., Alzueta, M. U., Bilbao, R., Millera, A. (2005): Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity. – Journal of Analytical and Applied Pyrolysis 74(1-2): 307-314.

[11] Harvey, O. R., Herbert, B. E., Rhue, R. D., Kuo, L. J. (2011): Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. – Environmental science & technology 45(13): 5550-5556.

[12] Hou, J., Huang, L., Yang, Z., Zhao, Y., Deng, C., Chen, Y., Li, X. (2016): Adsorption of ammonium on biochar prepared from giant reed. – Environmental Science and Pollution Research 23(19): 19107-19115.

[13] Huang, D., Liu, L., Zeng, G., Xu, P., Huang, C., Deng, L., Wang, R., Wan, J. (2017): The effects of rice straw biochar on indigenous microbial community and enzymes activity in heavy metal-contaminated sediment. – Chemosphere 174: 545-553.

[14] Huang, P., Ge, C., Feng, D., Yu, H., Luo, J., Li, J., Strong, P. J., Sarmah, A. K., Bolan, N. S., Wang, H. (2018): Effects of metal ions and pH on ofloxacin sorption to cassava residue-derived biochar. – Science of the Total Environment 616: 1384-1391.

[15] Inyang, M. D., Gao, B., Ding, W. C., Pullammanappallil, P., Zimmerman, A. R., Cao, X. D. (2011): Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. – Separation Science and Technology 46(12): 1950-1956.

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DOI: http://dx.doi.org/10.15666/aeer/1802_25692579

[16] Inyang, M. D., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., Cao, X. (2012): Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. – Bioresource Technology 110: 50-56.
[17] Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y. S., Cao, X. (2016): A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. – Critical Reviews in Environmental Science and Technology 46(4): 406-433.
[18] Keiluweit, M., Kleber, M. (2009): Molecular-Level Interactions in Soils and Sediments: The Role of Aromatic π-Systems. – Environmental Science & Technology 43(10): 3421-3429.
[19] Lehmann, J., da Silva, J. P., Steiner, C., Nehls, T., Zech, W., Glaser, B. (2003): Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. – Plant and soil 249(2): 343-357.
[20] Li, Y., Zhang, Y., Wang, G., Li, S., Han, R., Wei, W. (2018): Reed biochar supported hydroxyapatite nanocomposite: Characterization and reactivity for methylene blue removal from aqueous media. – Journal of Molecular Liquids 263: 53-63.
[21] Liu, Z., Zhang, F. S. (2009): Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. – Journal of Hazardous Materials 167(1): 933-939.
[22] Meng, J., Feng, X., Dai, Z., Liu, X., Wu, J., Xu, J. (2014): Adsorption characteristics of Cu(II) from aqueous solution onto biochar derived from swine manure. – Environmental Science and Pollution Research 21(11): 7035-7046.
[23] Park, J. H., Cho, J. S., Ok, Y. S., Kim, S. H., Heo, J. S., Delaune, R. D., Seo, D. C. (2016): Comparison of single and competitive metal adsorption by pepper stem biochar. – Archives of Agronomy & Soil Science 62(5): 617-632.
[24] Patra, J. M., Panda, S. S., Dhal, N. K. (2017): Biochar as a low-cost adsorbent for heavy metal removal: A review. – International Journal of Research in Biosciences 6(1): 1-7.
[25] Pundytė, N., Baltrėnaitė, E., Pereira, P., Paliulis, D. (2011): Anthropogenic effects on heavy metals and macronutrients accumulation in soil and wood of Pinus sylvestris L. – Journal of Environmental Engineering and Landscape Management 19(1): 34-43.
[26] Sevilla, M., Fuertes, A. B. (2009): Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. – Chemistry 15(16): 4195-4203.
[27] Teixidó, M., Pignatello, J. J., Beltrán, J. L., Granados, M., Peccia, J. (2011): Speciation of the ionizable antibiotic sulfamethazine on black carbon (biochar). – Environmental science & technology 45(23): 10020-10027.
[28] Tong, X. J., Li, J. Y., Yuan, J. H., Xu, R. K. (2011): Adsorption of Cu(II) by biochars generated from three crop straws. – Chemical Engineering Journal 172(2): 828-834.
[29] Xu, R. K., Zhao, A. Z. (2013): Effect of biochars on adsorption of Cu(II), Pb(II) and Cd(II) by three variable charge soils from southern China. – Environmental Science and Pollution Research 20(12): 8491-8501.
[30] Yang, Y., Shu, L., Wang, X., Xing, B., Tao, S. (2011): Impact of de-ashing humic acid and humin on organic matter structural properties and sorption mechanisms of phenanthrene. – Environmental science & technology 45(9): 3996-4002.
[31] Yuan, J. H., Xu, R. K., Zhang, H. (2011): The forms of alkalis in the biochar produced from crop residues at different temperatures. – Bioresource technology 102(3): 3488-3497.
[32] Zhao, R., Jiang, D., Coles, N., Wu, J. (2015): Effects of biochar on the acidity of a loamy clay soil under different incubation conditions. – Journal of soils and sediments 15(9): 1919-1926.

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DOI: http://dx.doi.org/10.15666/aeer/1802_25692579