# Comparison of Adsorption of Biochar from Agricultural Wastes on Methylene Blue and Pb<sup>2+</sup>

Yinhu Qiao,<sup>a</sup> Chunxia He,<sup>b</sup> Chunyan Zhang,<sup>a,\*</sup> Chunxia Jiang,<sup>a</sup> Kechuan Yi,<sup>a</sup> and Feiyue Li<sup>a</sup>

Biochar was prepared from agricultural plant waste, including corn straw (MS), sunflower straw (SS), wheat straw (WS), orange peel (OS), sunflower seed shell (SSS), and chestnut shell (CS) at low temperature in a partially oxygen-limited environment. These biochars were used to adsorb heavy metals and organic pollutants. The results showed that biochar having suitable surface area and microporous area could be obtained from the raw materials at 300 °C under partial oxygen limitation. The total porosity of biochar prepared from corn straw (MS) was 92.8%, and the removal of Pb<sup>2+</sup> was 78.6 mg/g. The obtained biochar had good adsorption properties for methylene blue and Pb<sup>2+</sup> water of different concentrations, and the adsorption performance of biochar prepared from crop straw was better than that of biochar prepared from plant peel. Thus, it was feasible to prepare biochar and to adsorb harmful substances in water through this process. This study promotes the recycling of agricultural wastes and simplifies the preparation of carbon adsorbents.

Keywords: Agricultural wastes; Biochar; Adsorption; Methylene blue; Pb<sup>2+</sup>; Comparison

Contact information: a: School of Mechanical Engineering, Anhui Science and Technology University, Fengyang 233100, China; b: College of Engineering Nanjing Agriculture University, Nanjing 210031, China; \*Corresponding author: xiangyutianji@163.com

# INTRODUCTION

Large amounts of agricultural wastes derived from plant sources (such as maize straws, sunflower straws, wheat straws, orange peel, chestnut shell, *etc.*) are generated because of the use of chemical fertilizers and the expansion of planting scale. (Liu *et al.* 2016). Meanwhile, serious increases in water, soil, and other environmental pollution from heavy metals and organic matter have been noted (Tekin *et al.* 2016). Therefore, the efficient removal of heavy metal ion and organic pollutants from aqueous solutions with plant agricultural wastes has become a significant issue from economical and health perspectives.

Biochar derived from barley straws has been prepared by thermal pyrolysis, and its adsorption behavior on salicylic acid has been previously studied (Ahmed and Hameed 2018). The results showed that barley straw biochar could be a suitable adsorbent to eliminate salicylic acid from wastewater. Lonappan *et al.* (2016) prepared three kinds of biochar microparticles from pine wood, pig manure, and cardboard to adsorb methylene blue. The experimental results showed that the adsorption capacity varied based on the source material and the method of production of the biochar. The adsorption of the atrazine of biochars produced from soybeans (SBB), corn stalks (CSB), rice stalks (RSB), poultry manure (PMB), cattle manure (CMB), and pig manure (PgMB) were investigated. The study indicated that the adsorption capacity decreased in the order SBB > RSB > CMB >

CSB > PMB > PgMB. This order was associated with the total pore volume and pH of the biochar (Liu et al. 2015). The study evaluated the adsorption of Pb and Cu by waste plant materials (the gingko leaf, peanut shell, and Metasequoia leaf, and their biochars), and the results showed that feedstocks and the carbonization had a more important effect on adsorption (Lee et al. 2019). Plant-based agricultural waste has better adsorption than animal manure, but the pretreatment method has a significant effect on the adsorption of biochar. Compared to physical pretreatment, activated carbon that has undergone chemical pretreatment has better adsorption. However, the activation process is complex and introduces acidic or alkaline salts, which can be regarded as pollutants. Thus, biochar and activated carbon that has undergone physical pretreatment are promising sorbents due to their environmental friendliness (Tan et al. 2016; Boakye et al. 2019). Additionally, in pyrolysis the biomass is thermally decomposed in such a way that it is not exposed to the oxygen-containing atmosphere. It is complicated and expensive to achieve oxygen-limited environment pyrolysis commonly used at home and abroad for vacuuming or introducing an inert gas currently (Tripathi et al. 2015, 2016). In particular, the pH is one of the most important environmental factors influencing the dissociation of surface functional groups and the solution chemistry of metals (Sardella et al. 2015). The capacity of biochar to take up heavy metals from contaminated soil and water is influenced by the pyrolysis temperature. On the one hand, the relatively high ash content and pH of biochar have been found to facilitate heavy metal ion precipitation and the formation of langite on the surface of biochar at the higher pyrolysis temperature (Wei et al. 2019). On the other hand, the content of oxygen-containing functional groups in the biochar samples decreased, while that of aromatic structures and alkaline mineral components increased, with a rise in pyrolysis temperature. There have been many studies on the basic properties of specific surface area and functional groups of biochar and the adsorption performance and mechanism of biochar at high temperature. However, there have been few reports of the adsorption performance and adsorption mechanism of biochar (near alkaline and lower specific surface area) prepared at lower temperature.

This work aimed to prepare biochar derived from plant-based agricultural wastes under a partially-limited oxygen environment at a lower temperature and to examine their adsorption of heavy ions and organic pollutants. In this study, maize straw (MS), sunflower straw (SS), wheat straw (WS), orange shell (OS), sunflower seed shell (SSS), and chestnut shell (CS) were employed as the raw materials for biochar production. The biochar produced in a partially-limited oxygen environment at a lower temperature demonstrated good adsorption of methylene blue and Pb<sup>2+</sup> from water with different concentrations of methylene blue and Pb<sup>2+</sup>. The adsorption performance of the biochar derived from crop straws was better than biochar that was produced from plant peel.

#### EXPERIMENTAL

#### Materials and Equipment

Sunflower straw (SS), maize straw (MS), and wheat straw (WS), which are byproducts of agricultural crops, were harvested from Yuling, China, dried at 80 °C for 72 h in a blast oven (DHC-9053A, DAOHAN Industrial Co., Ltd., Shanghai, China), and crushed to 1 mm to 2 mm by a powder machine. Orange shell (OS), sunflower-straw husk (SH), and chestnut shell (CS), which are domestic garbage, were collected in home kitchen, dried at 80 °C for 72 h in a blast oven (DHC-9053A, DAOHAN Industrial Co., Ltd., Shanghai, China), and crushed to 1 mm to 2 mm by a powder machine. The dry solids were sealed in a vacuum bag for carbonization.

About 25 g of raw materials from SS, MS, WS, OS, SH, and CS were sealed in a crucible ( $\varphi 90 \times 45$ ) and pyrolyzed in a box-type resistance furnace (SX-25-10, Shanghai Boluo Laboratory Equipment Co., Ltd., Shanghai, China) at 300 °C (10 °C/min<sup>-1</sup>) for 45 min. The products resulting from SS, MS, WS, OS, SH, and CS were named BSS, BMS, BWS, BOS, BSH, and BCS, respectively; the yield for all samples was more than 30%. After cooling, the BSS, BMS, BWS, BOS, BSH, and BCS were sealed in vacuum bags.

#### Methods

The six types of carbon were characterized by several techniques. The proximate analysis of the samples was conducted by thermogravimetry (TG) (STA449F3, NETZSCH, Selbe, Germany), as described in previous studies (Rashidi *et al.* 2012; Chowdhury *et al.* 2016). In the TG analysis, 5 mg to 10 mg of each powder sample was sealed into a ceramic crucible ( $\Phi 8 \times 5$ ) and heated under a 5 mL/min N<sub>2</sub> flow at 1300 °C with a heating rate of 10 °C/min. The phase identification of the samples was analyzed by X-ray diffraction (XRD) (X'Pert PRO, Almelo, Holland) (Chand *et al.* 2008). The morphology of the samples was characterized by scanning electron microscopy (SEM) (Zeiss EVO18, Oberkochen, Germany) (Chand *et al.* 2009). An elemental analyzer (VarioEL III, Germany) was used for C & N determination (Hawash *et al.* 2017).

Surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR) analysis (Nicolet iS-10, Thermo Fisher Scientific). The samples were dried and crushed with KBr. The samples mixed with KBr were pressed to form transparent sheets. Spectra were measured in the range between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. The basic properties (apparent density, total porosity analysis, *etc.*) of three biochars were measured by a high precision density tester (LH–120YE, Xiamen Qunlong Instrument Co., Ltd, Xiamen, China). Distilled water was added to the density meter sink up to the mark. Five g to 10 g of the biochar was put into a weighing pan and the weight was recorded. Then the material was immersed in water for about 3 s. Then the samples were taken out, wiped dry, and placed into the weighing pan again. Finally, the result was read from the instrument.

The surface area and pore sizes in the pyrolyzed biochar were determined by the multipoint N<sub>2</sub> adsorption-desorption method at -196.15 °C using a surface area and pore size analyzer (JW-BK132F, Beijing Micro High-Bo Ltd., Beijing, China) (Li et al. 2013). The adsorption of  $Pb^{2+}$  in the pyrolyzed biochar was measured by an atomic absorption spectrometer (SOLAAR M6, Thermo Fisher Scientific, Waltham, MA, USA) (Li et al. 2014). Isothermal adsorption and the effect of initial pH on the adsorption of  $Pb^{2+}$  on biochar were included in the adsorption experiments. For isothermal adsorption,  $Pb^{2+}$  stock solution (1000 mg·L<sup>-1</sup>), using 0.01 mol·L<sup>-1</sup> NaNO<sub>3</sub> as background electrolyte, was prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> in deionized water. The pH of the Pb<sup>2+</sup> solutions was adjusted to  $5.0 \pm 0.2$  by adding 0.1 mol·L<sup>-1</sup> HNO<sub>3</sub> and NaOH solutions. The sorption equilibrium was attained by shaking 0.1 g of biochar in 20 mL of working solution, with Pb<sup>2+</sup> concentrations of 10 mg·L<sup>-1</sup>, 20 mg·L<sup>-1</sup>, 40 mg·L<sup>-1</sup>, 60 mg·L<sup>-1</sup>, 80 mg·L<sup>-1</sup>, 100 mg·L<sup>-1</sup>, and 120 mg·L<sup>-1</sup>, respectively, at 180 rpm in a shaker at  $25 \pm 1$  °C. The concentrations of Pb<sup>2+</sup> were measured after the adsorption. Then, the solution was filtered through a 0.45 µm syringe filter and diluted with 1% HNO<sub>3</sub>. To determine the effect of the initial pH value of the solution on the adsorption of  $Pb^{2+}$  by biochar,  $Pb^{2+}$  stock solutions (400 mg·L<sup>-1</sup>) were prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> in deionized water. The pH of the Pb<sup>2+</sup> solutions was adjusted to 2.5, 3.5, 4.5, and 5.5 by adding 0.1 mol·L<sup>-1</sup> HNO<sub>3</sub> and NaOH solutions. The sorption equilibrium was attained by shaking 0.1 g of biochar in 20 mL of Pb<sup>2+</sup> solutions with pH 2.5, 3.5, 4.5, and 5.5 respectively at 180 rpm in a shaker at  $25 \pm 1^{\circ}$ C for 24 h. Concentrations of Pb<sup>2+</sup> were measured after the adsorption, the solution was filtered through a 0.45µm syringe filter, and diluted with 1% HNO<sub>3</sub> (Wang and Liu 2017; Zama *et al.* 2017).

#### **RESULTS AND DISCUSSION**

#### TG Analysis

TG curves were utilized to analyze the mass loss of raw materials with changes in temperature. The TG curves are shown in Figs. 1(a), (b), (c), (d), (e), and (f). The process was divided into three stages. The initial stage of the TG graph shows the moisture and volatile substance of the six types of carbons in SS, MS, WS, OS, SH, and CS. The moisture content reflects the water retained by physical bonds only, and intrinsic and extrinsic moisture are the two basic kinds of moisture available. The extrinsic moisture is affected by the weather conditions, and the intrinsic moisture is the moisture content of the material itself (Cox et al. 2002). The second stage of the curves included the loss of the volatile substances and organics. The biomass composition (i.e., lignin, cellulose, and hemicelluloses) were reduced in this stage. While hemicelluloses and cellulose start to degrade at 220 °C and 300 °C, respectively, lignin degrades more gradually in a wider temperature range (Pazó et al. 2010). Mahanim et al. (2011) reported that the temperature ranges for the degradation of hemicellulose, cellulose, and lignin are 250 °C to 320 °C, 320 °C to 380 °C, and room temperature to 900 °C, respectively. The third stage of the curves represented a slow decline to a stable char residual composition. The fixed carbon was calculated from the flat mass region of TG curve after equilibrium temperature was reached.

The analysis is consistent with the theory of pyrolysis kinetics. Pyrolysis kinetics is one of the main research theories of pyrolysis mechanism. Equations 1 and 2 are Class I pyrolysis kinetics equations and Class II pyrolysis kinetics equations, respectively,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E}{RT}\right)$$
(1)

$$\frac{d\alpha}{dT} \left[ \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) + \frac{\beta \cdot t \cdot A \cdot E}{\beta RT^2} \exp\left(-\frac{E}{RT}\right) \right] f(\alpha) = \left\{ \frac{A}{\beta} \left[ 1 + \frac{E}{RT} \cdot \frac{(T - T_0)}{T} \right] \exp\left(-\frac{E}{RT}\right) \right\} f(\alpha)$$

$$= \left\{ \frac{A}{\beta} \left[ 1 + \frac{E}{RT} \cdot \left(1 - \frac{T_0}{T}\right) \right] \exp\left(-\frac{E}{RT}\right) \right\} f(\alpha)$$
(2)

where A is the apparent pre-factor, E is the apparent activation energy, R is the universal gas constant,  $T_0$  is the starting point temperature where the DSC curve deviates from the baseline (K),  $\beta$  is the constant heating rate (K·min<sup>-1</sup>), k is the reaction rate constant, t is time,  $\alpha$  is the fraction of the substance that has reacted at time t, and  $f(\alpha)$  is the dynamic mechanism function of differential form. Obviously, pyrolysis process and raw material types were the two important influence factors on biochar yield and performance based on kinetic modeling analysis and related pyrolysis theory. Literature studies have shown that

the yield of biochar was higher because of higher lignin content in raw materials, larger feedstock size, slower heating rates, lower pyrolysis temperatures (below 400 °C), and longer holding times. And it had a significant effect on other properties of biochar (Intani *et al.* 2016; Gonzaga *et al.* 2018; Lam *et al.* 2018).



**Fig. 1.** Proximate analysis of the biochars from (a) sunflower straw (SS), (b) maize straw (MS), (c) wheat straw (WS), (d) sunflower husk (SH), (e) chestnut shell (CS), and (f) orange shell (OS)

This was consistent with the results of the composition analysis and industrial analysis in Table 1. As shown in the table, the six types of biomass feedstocks were all composed of three main building blocks: cellulose, hemicellulose, and lignin, but the content were significantly different (Marion *et al.* 2011). The same pyrolysis process can

be used for the same composition, but different compositional contents lead to certain differences in pyrolysis products (biochar). In addition, industrial analysis showed that volatile matter content was very high, and the sunflower seed husk (SH) was up to 78.0%. Theoretically, biomass with higher volatile fraction may result in less production of biochar with increasing temperature (Vaibhav *et al.* 2017). The yield of biochar under different temperature was calculated using Eq. 3,

$$Q = \frac{m_2}{m_1} \times 100 \,\% \tag{3}$$

where  $m_1$  and  $m_2$  are the mass (g) of SS, MS, WS, OS, SH, and CS before and after carbonization, respectively, and Q is the biochar yield of SS, MS, WS, OS, SH, and CS (%).

Especially, the capacity of biochar to take up heavy metals from contaminated soil and water is influenced by the pyrolysis temperature. Generally, the relatively high ash content and pH of biochar facilitated heavy metal ion precipitation and the formation of langite on the surface of biochar at the higher pyrolysis temperature (Wei *et al.* 2019). Moreover, the pH is one of the most important environmental factors influencing the dissociation of surface functional groups and the solution chemistry of metals (Sardella *et al.* 2015).

	Con	nponent Analysis	(%)	Industrial Analysis (%)			
Туре	Cellulose	Hemicellulose	Lignin	Moisture	Ash	Volatile	
						matter	
SS	33.0	18.0	23.0	14.17	14.93	66.33	
MS	41.7	27.2	20.3	7.53	5.80	71.45	
WS	45.2	28.6	25.0	3.3	3.23	74.53	
SH	50.14	22.33	26.37	9.34	1.16	77.99	
CS	16.29	29.19	52.61	11.58	1.91	71.03	
OS	3.72	77.9	16.38	-	2	-	

Table 1. Composition Analysis and Industrial Analysis of Raw Materials

# X-Ray Diffraction Analysis

A comparison of XRD patterns between the biochars and raw materials from SS, MS, WS, OS, SH, and CS is shown in Fig. 2. The XRD patterns of SS, MS, WS, OS, SH, and CS before pyrolysis exhibited two more significant peaks at around  $2\theta = 16^{\circ}$  and  $22^{\circ}$ , which mainly were related to the crystalline structure of cellulose in the raw materials (Keiluweit *et al.* 2010). For the six biochars (BMS, BSS, BWS, BOS, BSH, and BCS) prepared at 300°C, the peak near at  $2\theta = 16^{\circ}$  disappeared, and the peak around  $22^{\circ}$  showed a broadening tendency, which indicated degradation of cellulose components (Liou *et al.* 2009).

The XRD patterns of BMS, BSS, BWS, BOS, BSH, and BCS exhibited a significant peak near  $2\theta = 28.3$ °, which was mainly a signal peak of CaCO<sub>3</sub>, which indicated that the six biochars had high ash contents. In addition, there was a significant peak near  $2\theta = 40.5$ °, which was the signal peak of potassium salt (Kim *et al.* 2012). In other words, the six feedstocks of MS, WS, SS, OS, SH, and CS might have undergone a similar transformation process in pyrolysis.



Fig. 2. The comparison of XRD patterns between the biochars and raw materials

#### **Surface Morphologies**

The SEM images of the samples in Fig. 3 show the differences in surface morphology. The biochar surfaces contained pores. There were more pores or cracks in the BMS, which had a larger surface area because of its high porosity. Therefore, the raw materials were the main reason for the differences in surface areas and micropore areas of the biochars. The results were consistent with the porosity analysis in Table 2. In addition, the biochars surfaces contained more cracks and pores compared to feedstocks. Meanwhile, there were relatively higher C&N content in biochars than feedstocks, as showed in Table 3. The above results also reveals that feedstocks had been changed largely in the pyrolysis process concluding element content and micro structure. This is consistent with the literature results, which the highest carbon content as well as the highest fixed carbon content was exhibited by lignin (Akubo *et al.* 2018).

Biochar	Yield (%)	Bulk Specific Gravity (g/cm <sup>3</sup> )	Apparent Density (g/cm <sup>3</sup> )	Apparent Porosity (%)	Water Absorption Percentage (%)	Total Porosity (%)
BMS	47.76	0.2181	0.259	15.62	71.43	92.78
BSS	48.97	0.2210	0.230	22.80	17.02	92.63
BWS	40	0.2322	0.245	12.79	20.59	92.20
BOS	43.32	-	0.469	12.16	29.51	93.37
BSH	35.83	-	0.333	2.94	9.09	99.95
BCS	48.55	-	0.631	6.30	15.63	86.35

**Table 2.** Basic Properties of Six Biochars

**Table 3.** Elemental Analysis of Six Feedstocks and Biochars

Туре	MS	BMS	SS	BSS	WS	BWS	OS	BOS	CS	BCS	SH	BSH
C/%	53.29	58.20	46.55	57.92	46.50	53.83	56.78	63.79	54.73	62.22	52.31	60.30
N/%	1.30	1.39	0.230	0.70	0.81	0.96	1.32	1.93	0.54	0.68	0.87	1.05



**Fig. 3.** Surface morphologies of feedstocks of (a1) maize straw (MS), (b1) sunflower straw (SS), (c1) wheat straw (WS),(d1) orange shell (OS), (e1) chestnut shell (CS),, and (f1) sunflower seed husk (SH) and the biochars from (a2) maize straw (BMS), (b2) sunflower straw (BSS), (c2) wheat straw (BWS), (d2) orange shell (BOS), (e2) chestnut shell (BCS), and (f2) sunflower seed husk (BSH)

#### Fourier Transform Infrared Spectroscopy

To determine the changes in the functional groups, the FTIR spectra of SS, MS, WS, OS, SH, and CS before and after pyrolysis are shown in Fig. 4. The main absorption peaks of samples appeared in the wavenumber region between 500 cm<sup>-1</sup> and 2000 cm<sup>-1</sup>. Generally, the C=O stretching vibration in the carboxyl group appeared at 1706 cm<sup>-1</sup>. The characteristic peak intervals of the benzene ring or aromatic occurred between 1450 cm<sup>-1</sup> to 1610 cm<sup>-1</sup>. The absorption peaks that are representatives of C=O stretching vibrations, C=C stretching, and the -OH out-of-plane bending vibration of phenols, ethers, and alcohols appeared between 1102 cm<sup>-1</sup> to 1252 cm<sup>-1</sup>. The absorption peaks of the aromatic compound C-H was at 793 cm<sup>-1</sup>. Compared to the raw materials, the absorption peaks of

biochars were noticeably reduced from 1102 cm<sup>-1</sup> to 1252 cm<sup>-1</sup>. This result indicated that the samples with different feedstocks before and after pyrolysis had hydroxyl, aromatic, and some oxygen-containing functional groups, but the absorption intensity was somewhat different. The reduction of the absorption peaks from 1102 cm<sup>-1</sup> to 1252 cm<sup>-1</sup> after pyrolysis was mainly because the -OH functional groups of phenols, ethers, and alcohols of raw materials disappeared due to the increasing temperature. These results were similar to those obtained for other biochars (Sardella *et al.* 2015).



Fig. 4. FTIR spectra of the biochars from sunflower straw, maize straw, and wheat straw

#### Surface Area and Pore Size Analysis

The specific surface area and total pore volume of the BMS, BSS, BWS, BOS, BSH, and BCS are shown in Table 4. The specific surface area and total pore volume of the six biochars were all lower. BSS had the highest values of specific surface area and total pore volume at  $5.62 \text{ m}^2/\text{g}$  and  $0.00908 \text{ m}^3 \cdot \text{g}^{-1}$ , respectively. Compared to active carbon of better absorbent, the specific surface area and total pore volume of the six biochars were much lower. Generally, the specific surface area and total pore volume are the main indicators that are used to measure the adsorption performance of materials. However, these results showed that the specific surface area and total pore volume had little influence on adsorption performance of the three samples (Yang *et al.* 2015).

**Table 4.** Specific Surface Area, Total Pore Volume, and Average Pore Size of

 Six Biochars

Туре	BMS	BSS	BWS	BOS	BSH	BCS
Specific surface area/m <sup>2</sup> ·g <sup>-1</sup>	4.15224	5.61552	2.48631	2.56621	2.58611	2.28421
Total pore volume/m <sup>3</sup> ·g <sup>-1</sup>	0.03222	0.03008	0.02024	0.02234	0.02514	0.01774

#### Adsorption Performance for Pb<sup>2+</sup>

Figure 5a presents the effect of contact time on  $Pb^{2+}$  adsorption by BMS, BSS, BWS, BOS, BSH, and BCS. The adsorption of  $Pb^{2+}$  by all six biochars reached equilibrium by around 8 h. The intraparticle diffusion model was used to fit the adsorption results. The results showed that BMS and BSS had better fitting effects for  $Pb^{2+}$  adsorption, with  $R^2$  values of 0.93236 and 0.92118, respectively.

The pH is one of the most important environmental factors influencing the dissociation of surface functional groups and the solution chemistry of metals (Sardella *et al.* 2015). Figure 5b presents the effect of pH on the removal of Pb<sup>2+</sup> by BMS, BSS, BWS, BOS, BSH, and BCS. The amount adsorbed increased sharply with increasing pH, for and the equilibrium quantities of Pb<sup>2+</sup> were reached at pH 5.0. The values were similar for all adsorbents studied in this work and were comparable to those found in previous studies (Li *et al.* 2014, 2015).

Isothermal adsorption assays for  $Pb^{2+}$  were developed by adjusting the initial pH of the suspension to over 5.5 (Bogusz *et al.* 2015). Figure 5b shows the curves obtained for  $Pb^{2+}$  adsorption assays using BMS, BSS, BWS, BOS, BSH, and BCS. In all cases, the maximum removal amount was achieved when the initial concentration of  $Pb^{2+}$  was 80 mg/L, as shown in Fig. 5a. Figure 5a shows that BMS had a better performance in  $Pb^{2+}$  adsorption than the other two biochars. In this case, BSS and BWS showed an improved performance in  $Pb^{2+}$  adsorption, reaching 94.83% and 80.98% of metal removal, respectively. Compared to the study by Tekin *et al.* (2016), the six biochars had much lower specific surface areas and total pore volumes, but the adsorption of  $Pb^{2+}$  was as good as the cited study. It was apparent that the porous structure had some influence on metal retention. The difference in adsorption performance of the biochars were mainly caused by surface chemical groups of biochars (Sardella *et al.* 2015).



Fig. 5. The effect of biochars from (a) contact time on  $Pb^{2+}$  adsorption, and (b) pH influence on  $Pb^{2+}$  adsorption

#### **Adsorption Performance for Methylene Blue**

Figure 6 shows six biochars adsorption solutions of BSS, BMS, BWS, BOS, BSH, and BCS and methylene blue standard solution (SS), 5 g/L CuSO<sub>4</sub> solution absorbance, and adsorption percentage comparison analysis. Straw biochar had a better adsorption performance for methylene blue than for chaff and nutshell biochar. The order of adsorption of the methylene blue standard solution from high to low was: BMS > BSS > BWS > BSH >

BOS > BCS. Among them, the absorbance of BMS to methylene blue solution was 0.3356. It had the highest adsorption of 94.60%, followed by BSS, with an absorbance of 0.6885, and an adsorption percentage of 85.90%. BCS has the worst adsorption effect, and its adsorption percentage was only 10.25%.



**Fig. 6.** The effect of biochars adsorption on methylene blue from (a) absorbance, and (b) adsorption percentage

# CONCLUSIONS

- 1. Under the selected conditions of biochar preparation under limited-oxygen conditions, the surface area and micropore area of biochars were mainly determined by the raw materials.
- 2. A biochar with the highest total porosity of 92.8% and the maximum removal of Pb<sup>2+</sup> adsorption of 98.3% (78.6 mg/g) was produced from MS at a temperature of 300 °C under partially limited oxygen conditions.
- 3. The low-temperature pyrolysis and the partially limited oxygen condition process that was used to carbonize SS, MS, WS, OS, SH, and CS was feasible and beneficial to the recycling of agricultural wastes, which simplified the preparation of carbon adsorbents.
- 4. The six biochars with lower specific surface areas and total pore volume had better adsorption to Pb<sup>2+</sup>. It is apparent that the porous structure had some less influence on metal retention. The difference in adsorption performance of biochars were mainly caused by surface chemical groups of biochars.

#### ACKNOWLEDGMENTS

The authors thank the following for their support of this work: the Key Project Supported by Foundation University of Science and Technology of Anhui (No. JXWD201602 and ZRC2016492), the Project Supported by Anhui Science and Technology Department (No.KJ2018A0536, 1704a0902058, KJ2017ZD44, KJ2015A195, 1708085QD85, gxyqZD2016213and 1704e1002238), the Key Construction Disciplines Project Supported by University of Science and Technology of Anhui (No. AKZDXK2015C03), and the Project Supported by the National Natural Science Foundation of China (No. 21607002, 2017YFD0200808).

# **REFERENCES CITED**

- Akubo, K., Nahil, M. A., Williams, P. T. (2018). "Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas," *Journal of the Energy Institute*. DOI: 10.1016/j.joei.2018.10.013.
- Ahmed, M. J., and Hameed, B. H. (2018). "Adsorption behavior of salicylic acid on biochar as derived from the thermal pyrolysis of barley straws," *Journal of Cleaner Production* 195, 1162-1169. DOI: 10.1016/j.jclepro.2018.05.257
- Boakye, P., Tran, H. N., Lee, D. S., and Woo, S. H. (2019). "Effect of water washing pretreatment on property and adsorption capacity of macroalgae-derived biochar," *Journal of Environmental Management* 233, 165-174. DOI: 10.1016/j. jenvman.2018.12.031
- Bogusz, A., Oleszczuk, P., and Dobrowolski, R. (2015). "Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water," *Bioresource Technology* 196, 540-549. DOI: 10.1016/j.biortech.2015.08.006
- Chand, R., Watari, T., Inoue, K., Torikai, T., and Yada, M. (2008). "Evaluation of wheat straw and barley straw carbon for Cr (VI) adsorption," *Separation and Purification Technology* 65(3), 331-336. DOI: 10.1016/j.seppur.2008.11.002
- Chand, R., Watari, T., Inoue, K., Kawakita, H., Luitel, H. N., Parajuli, D., Torikai, T., and Yada, M. (2009). "Selective adsorption of precious metals from hydrochloric acid solutions using porous carbon prepared from barley straw and rice husk," *Minerals Engineering* 22(15), 1277-1282. DOI: 10.1016/j.mineng.2009.07.007
- Chowdhury, Z. Z., Hamid, S. B., Rahman, M. M., and Rafique, R. F. (2016). "Catalytic activation and application of microspherical carbon derived from hydrothermal carbonization of lignocellulosic biomass: Statistical analysis using Box-Behnken design," *RSC Advances* 6(104), 102680-102694. DOI: 10.1039/c5ra26189a
- Cox, P. M., Betts, R. A., Betts, A., Jones, C. D., Spall, S. A., and Totterdell, I. J. (2002). "Modelling vegetation and the carbon cycle as interactive elements of the climate system," *International Geophysics* 83, 259-279. DOI: 10.1016/S0074-6142(02)80172-3
- Gonzaga, M. I. S., Mackowiak, C., Almeida, A. Q., Junior, J. I. C., Andrade, K. R. (2018). "Positive and negative effects of biochar from coconut husks, orange bagasse and pine wood chips on maize (*Zea mays* L.) growth and nutrition," *Catena* 162, 414-420. DOI: 10.1016/j.catena.2017.10.018

- Hawash, S.I., Farah, J. Y., El-Diwani, G. (2017). "Pyrolysis of agriculture wastes for biooil and char production," *Journal of Analytical and Applied Pyrolysis* 124, 369-372. DOI: 10.1016/j.jaap.2016.12.021
- Intani, K., Latif, S., Kabir, A. K. M. R., Müller, M. (2016). "Effect of self-purging pyrolysis on yield of biochar from maize cobs,husks and leaves," *Bioresource Technology* 218, 541-551. DOI: 10.1016/j.biortech.2016.06.114
- Keiluweit, M., Nico, P. S., Johnson, M. G., and Kleber, M. (2010). "Dynamic molecular structure of plant biomass-derived black carbon (biochar)," *Environmental Science & Technology* 44(4), 1247-1253. DOI: 10.1021/es9031419
- Kim, K. H., Kim, J. Y., Cho, T. S., and Choi, J. W. (2012). "Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (*Pinus rigida*)," *Bioresource Technology* 118, 158-162. DOI: 10.1016/j.biortech.2012.04.094
- Lam, S. S., Liew, R. K., Cheng, C. K., Rasit, N., Ooi, C. K., Ma, N. L., Ng, J. H., Lam, W. H., Chong, C. T., Chase, H. A. (2018). "Pyrolysis production of fruit peel biochar for potential use in treatment of palm oil mill effluent," *Journal of Environmental Management* 213, 400-408. DOI: 10.1016/j.jenvman.2018.02.092
- Li, K. Q., Li, Y., Zheng, Z., and Sang, D. Z. (2013). "Preparation, characterization, and adsorption performance of high surface area biomass-based activated carbons," *Environmental Science* 34(1), 328-335. DOI: 10.13227/j.hjkx.2013.01.042
- Li, K. Q., Wang, Y. J., Yang, M. R., Zhu, Z. Q., and Zheng, Z. (2014). "Adsorption kinetics and mechanism of lead(II) on polyamine-functionalized mesoporous activated carbon," *Environmental Science* 35(8), 3198-3205. DOI: 10.13227/j.hjkx.2014.08.051
- Li, R. Y., Chen, D., Li, L. Q., Pan, G. X., Chen, J. Q., and Guo, H. (2015). "Adsorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> in aqueous solution by biochars derived from different crop residues," *Journal of Agro-Environment Science* 34(5), 1001-1008. DOI: 10.11654/jaes.2015.05.025
- Lonappan, L., Rouissi, T., Das, R. K., Brar, S. K., Ramirez, A. A., Verma, M., Surampalli, R. Y., and Valero, J. R. (2016). "Adsorption of methylene blue on biochar microparticles derived from different waste materials," *Waste Management* 49, 537–544. DOI: 10.1016/j.wasman.2016.01.015
- Liou, T. H., and Wu, S. J. (2009). "Characteristics of microporous/mesoporous carbons prepared from rice husk under base and acid-treated conditions," *Journal of Hazardous Materials* 171(1-3), 693-703. DOI: 10.1016/j.jhazmat.2009.06.056
- Liu, Y., Meng, M., Yao, J., Da, Z., Feng, Y., Yan, Y., Li, C. (2016). "Selective separation of phenol from salicylic acid effluent over molecularly imprinted polystyrene nanospheres composite alumina membranes," *Chemical Engineering Journal* 286, 622-631. DOI: 10.1016/j.cej.2015.10.063
- Mahanim, S. M. A., Wan Asma, I., Rafidah, J., Puad, E., and Shaharuddin, H. (2011).
  "Production of activated carbon from industrial bamboo wastes," *Journal of Tropical Forest Science* 23(4), 417-424.
- Marion, C., Anne L. S., Dominique D., Lasnier, J. M., Fre' de' rique, H. P., Francois, C., Cyril, A. (2011). "Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass," *Biomass and Bioenergy* 35, 298-307. DOI: 10.1016/j.biombioe.2010.08.067.

- Lee, M. E., Park, J. H., and Chung, J. W. (2019). "Comparison of the lead and copper adsorption capacities of plant source materials and their biochars," *Journal of Environmental Management* 236, 118-124. DOI: 10.1016/j.jenvman.2019.01.100
- Liu, N., Charrua, A., Weng, C.-H., Yuan, X., and Ding, F. (2015). "Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: A comparative study," *Bioresource Technology* 198, 55-62. DOI: 10.1016/j.biortech.2015.08.129
- Pazó, J. A., Granada, E., Saavedra, Á., Eguía, P., and Collazo, J. (2010). "Uncertainty determination methodology, sampling maps generation, and trend studies with biomass thermogravimetric analysis," *International Journal of Molecular Sciences* 11(10), 3660-3674. DOI: 10.3390/ijms11103660
- Rashidi, N. A., Yusup, S., Ahmad, M. M., Mohamed, N. M., and Hameed, B. H. (2012). "Activated carbon from the renewable agricultural residues using single step physical activation: A preliminary analysis," *APCBEE Procedia* 3, 84-92. DOI: 10.1016/j.apcbee.2012.06.051
- Sardella, F., Gimenez, M., Navas, C., Morandi, C., Deiana, C., and Sapag, K. (2015). "Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium," *Journal of Environmental Chemical Engineering* 3(1), 253-260. DOI: 10.1016/j.jece.2014.06.026
- Tan, X.-f., Liu, Y.-g., Gu, Y.-l., Xu, Y., Zeng, G.-m., Hu, X.-j., Liu, S.-b., Wang, X., Liu, S.-m., and Li, J. (2016). "Biochar-based nano-composites for the decontamination of wastewater: A review," *Bioresource Technology* 212, 318-333. DOI: 10.1016/j.biortech.2016.04.093
- Tekin, K., Akalin, M. K., Uzun, L., Karagöz, S., Bektaş, S., Denizli, A. (2016). "Adsorption of Pb(II) and Cd(II) ions onto dye-attached sawdust," *CLEAN–Soil, Air, Water* 44(4), 339-344. DOI:10.1002/clen.201500222
- Tripathi, M., Sahu, J. N., Ganesan, P., Dey, T. K. (2015). "Effect of temperature on dielectric properties and penetration depth of oil palm shell (OPS) and OPS char synthesized by microwave pyrolysis of OPS,"*Fuel* 153, 257-266. DOI: 10.1016/j.fuel.2015.02.118.
- Tripathi, M., Sahu, J. N., Ganesan, P. (2016). "Effect of process parameters on production of biocha from biomass waste through pyrolysis: A review," *Renewable and Sustainable Energy Reviews* 55, 467-481. DOI: 10.1016/j.rser.2015.10.122.
- Vaibhav, D., Thallada B. (2017). "A comprehensive review on the pyrolysis of lignocellulosic biomass," *Renewable Energy*, 1-12. DOI: 10.1016/j.renene.2017.04.035
- Wang, Y., and Liu, R. H. (2017). "Comparison of characteristics of twenty-one types of biochar and their ability to remove multi-heavy metals and methylene blue in solution," *Fuel Processing Technology* 160, 55-63. DOI: 10.1016/j.fuproc.2017.02.019
- Wei, J., Tu, C., Yuan, G.D., Liu, Y., Bi, D.X., Xiao, L., Lu, J., Theng, B.K.J., Wang, H.L., Zhang, L.J., Zhang, X.Z. (2019). "Assessing the effect of pyrolysis temperature on the molecular properties and copper sorption capacity of a halophyte biochar," *Environmental Pollution* 251, 56-65. DOI: 10.1016/j.envpol.2019.04.128
- Yang, J. B., Yu, M. Q., and Chen, W. T. (2015). "Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from longan seed: Kinetics, equilibrium, and thermodynamics," *Journal of Industrial and Engineering Chemistry* 21, 414-422. DOI: 10.1016/j.jiec.2014.02.054

Zama, E. F., Zhu, Y.-G., Reid, B. J., and Sun, G.-X. (2017). "The role of biochar properties in influencing the sorption and desorption of Pb(II), Cd(II) and As(III) in aqueous solution," *Journal of Cleaner Production* 148, 127-136. DOI: 10.1016/j.jclepro.2017.01.125

Article submitted: March 18, 2019; Peer review completed: May 25, 2019; Revised version received and accepted: October 21, 2019; Published: October 25, 2019. DOI: 10.15376/biores.14.4.9766-9780