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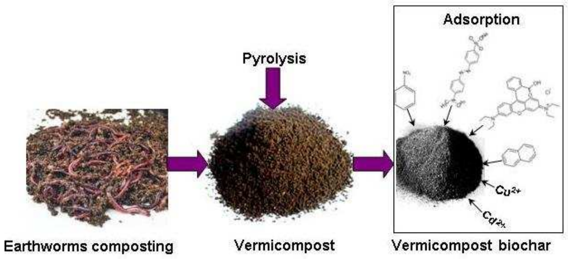
A table of contents



Biochar derived from vermicompost can be employed as an excellent adsorbent for removing contaminants from aqueous solution.

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Physicochemical properties of biochar derived from vermicompost as affected by pyrolysis temperature and potential environmental amendment as an adsorbent

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Abstract: Biochars, produced from vermicompost and subject to pyrolysis at temperatures between 400–700 ℃, were investigated for their physicochemical properties, and for their potential application as an environmental absorbent. Results indicated that the biochar yield was relatively high throughout this temperature range, but it decreased from 78.1% to 70.6% as the pyrolysis temperature increased to 700 ℃. The mineral nutrients and heavy metals in the biochars were also condensed as the pyrolysis temperature increased. Additionally, the pyrolysis temperature also positively affected the formation of total basic functional groups (TBFGs) and pore development. Overall, the biochars generated from vermicompost were characterized by alkalinity, high stability, high buffering ability and high apparent density. When the biochars were employed as an adsorbent for removing heavy metal ions, dyes and organic contaminants, biochar generated at higher temperature possessed better adsorption abilities to these contaminants, and the maximum adsorption capacity of the biochar at 700 ℃ was 36.4 $mg\ g^{-1}$, 29.5 $mg\ g^{-1}$, 12.4 $mg\ g^{-1}$, 12.3 $mg\ g^{-1}$, 17.8 $mg\ g^{-1}$, and 8.2 $mg\ g^{-1}$ for Cu^{2+}, Cd^{2+}, methyl orange, rhodamine B naphthalene, and nitrobenzene, respectively.

Key words: Vermicompost; Biochar; Pyrolysis temperature; Adsorption.

Introduction

As an important by-product of earthworm growth derived from degradation and decomposition of biomass waste, vermicompost possesses a large amount of physical properties, such as being homogeneous, porous, and inodorous. Additionally, it contains rich nutrients for soil, such as N, P, K, Mn, Fe, and organic fractions such as humic acids, fatty acids and enzymes. These have gained interests due to their beneficial environmental applications, including their use in culture crops, and their ability to inhibit soil borne diseases, and to remove organic and inorganic contaminants [1]. Earthworms are currently being industrially bred on a world-wide scale in preparation for the large amounts of sludge, manure, organic waste, and vermicompost that will be produced largely [2]. Vermicompost may potentially contain heavy metals, pathogens, parasites, antibiotics and organic contaminants, which may result in some potential risks to human health once vermicompost is directly applied in the environment [3, 4]. It is, therefore, important to develop a relatively safe way to use vermicompost.

Thermochemical conversion of agricultural organic wastes by pyrolysis under a free oxygen environment, at relatively lower temperatures (300-700 ℃) to obtain a carbon-rich production (biochar), has been identified as a potential way to utilize these wastes [5]. Carbonization in the temperature range of 300-700℃ can be greatly beneficial to deactivate pathogens and parasites in th vermicompost, and the contained antibiotics and organic contaminants can also be degraded. The thermochemical conversion of pyrolysis for biochar production, therefore, can be regarded as a safe way for vermicompost utilization. In addition, biochar can b employed as a carbon-sink and carbon sequestration material due to its resistance to degradation, and because it contains a stable carbon matrix which exhibits extremely important ecological benefits [5, 6]. Biochar can also be considered as a soil ameliorant due to its porous structure, basicity and high mineral concentrations, all of which are responsible for improving water retention, acidic soil neutralization and nutrient accommodation [7, 8]. Furthermore, biochar also plays a positive role in environmental amendment due to its high surface area and abundant functional groups [9, 10]. Developing environmentally beneficial purposes for vermicompost by carbonization can, therefore, significantly increase its profitability and extend the range of its practical applications.

The physicochemical properties of the produced biochar, however, generally depend on the feedstock precursor and carbonization conditions [11]. Traditional feedstocks for biochar production principally included agricultural residues (e.g. rice shell, corn straw, nutshells), forestry wastes (e.g. sawdust), organic wastes (e.g. kitchen waste), animal manures (e.g. poultry, dairy, swine manure) and sludges (e.g. anaerobic digestion slurry and wastewater sludge) [12-16]. Animal manures have lower organic matter contents (lignocellulose) and higher mineral contents, which causes significant differences compared to lignocellulosic wastes [17]. The surface area, pH, elemental composition and surface functional groups of the lignocellulosic waste are significantly different, even when pyrolyzed under similar conditions [18]. The operating conditions of pyrolysis, such as the temperature, the heating rate and holding time have also been identified to seriously affect the biochar properties. The yields and quantities of biochar derived from safflower seeds were investigated at different pyrolysis temperatures (400, 450, 500, 550 and 600 ℃) and at different heating rates (10, 30, 50 ℃ min^{-1}), and the pyrolysis temperature were directly related to biochar yield and properties [19]. Additionally, biochar produced from poultry manure showed some distinguished different chemical compositions when different pyrolysis temperatures, but not different holding times were used [20]. The pyrolysis temperature is, therefore, widely accepted as a key factor controlling the yield and physicochemical properties of biochar.

Currently, there are limited investigations into the characteristics of biochar directly derived from vermicompost. This paper aims to increase our understanding by investigating the physiochemical properties of biochars derived from vermicompost produced by pyrolysis temperatures ranging from 400 to 700 ℃. The potential applications of biochar derived from vermicompost as an environmental amendment are preliminarily evaluated for removing some typical contaminants, including heavy metal ions of Cu^{2+} and Cd^{2+}, dyes of methyl orange (MO) and rhodamine B (RB), and organic pollutants of naphthalene (NAPH) and nitrobenzene (NB).

Material and methods

Vermicompost and the preparation of biochar

Vermicompost was collected from a local earthworm breeding plant in Chengdu, Sichuan province of China, where the earthworms lived on dairy manure. The obtained vermicompost was thoroughly mixed, air-dried, and ground to less than 0.45 mm. The ground vermicompost was dried again at 105 ℃ for 6 h prior to pyrolysis. The samples were pyrolyzed at 400, 500, 600, and 700℃ using a tube furnace (OTL 1200, Nanjing NanDa Instrument Co. Ltd.) with N$_2$ of 0.1m^3 h^{-1} as the protective gas. The heating rate of 10℃ min^{-1}, and holding time of 2 h were maintained to produce the desired biochar. The obtained biochars were denoted as VCBC-400, VCBC-500, VCBC-600, and VCBC-700, in which VCBC was the abbreviation of vermicompost biochar, and the number (400, 500 etc.) represented the carbonization temperature. After pyrolysis, the VCBC yield was calculated using the weight ratio of produced biochar to the original vermicompost (dry basis) for pyrolysis.

Characterization of vermicompost biochar

Proximate analysis (i.e. ash, moisture and combustible) of VCBCs were carried out according to the referred methods [18]. Ultimate analysis included the determination of C, H, N, and S, which were measured by a CHNS analyzer (EA112, Thermo Finnigan, USA), and the O content was estimated by the following equation: O (%) = 100% - (C + H + N + S + ash) %.

Additionally, vermicompost and VCBCs were digested according to USEPA 6010 method (concentrated HNO$_3$ +30% H$_2$O$_2$) to analyze the mineral and nutrient contents, including Ca, Mg, Fe, Mn, Zn, Pb, Cr, Ni, Cu, and Cd by an atomic absorption spectrometer (FAAS-M6, Thermo, USA). The contents of K and Na were determined using a flame photometer. The P (including total P and soluble P) was measured using a spectrophotometer.

Thermogravimetry (TG) was carried out using a thermo gravimetric analyzer (SDT Q600，TA instrument, USA) for clarify their thermo stability and pyrolysis behaviours. During the analysis, the samples of vermicompost and VCBCs were heated from 20 to 750 ℃ at a rate of 10 ℃·min^{-1}, in which the employed temperature covered the temperature range for the biochar preparation, and the heating rate was same with biochar preparation.

Surface area (SA) was measured using N_2 sorption isotherms at 77 K (NOVA-2000E, Quantachrome Instruments, USA) according to the Brunauer-Emmett-Teller (BET) method. The micro surface area (MSA) and micropore volume (MPV) of the VCBCs were determined by t-plot method. The total pore volume (TPV) and average pore diameter (APD) were also calculated.

XRD analysis was conducted on a diffractometer equipped with stepping motor and graphite crystal monochromator (I-2, Nicolet, Madison, WI, USA). The data was recorded over the 2θ range from 5 to 50 ° using Cu-Kα radiation with a scan speed of 1° per minute.

Fourier Transformation Infrared spectrometer (FT-IR) (Nicolet 6700，Thermo Fisher Scientific, USA) was employed to collect spectra in the range of 400-4000 cm^{-1} at 4 cm^{-1} resolution and 64 scans of vermicompost and VCBCs.

pH and electrical conductivity (EC) of vermicompost and VCBCs were respectively measured by a pH meter (PHS-3C, Shanghai Leici Instruments Co., Ltd, China) and a conductivity meter (DDS 12DW, BANTE Instrument Co., Ltd, China) using a ratio of 1:20 (m/v) for biochar-to-deionized water. The point of zero charge (pH_{pzc}) was measured according to the methods in reference [10]. Total surface acidic and basic functional groups were determined by Boehm method.

Buffering properties of VCBCs were titrated by adding 0.1M HNO_3, and then plotted with the volume of added acid and the response of solution pH.

Adsorption

The adsorption performances of VCBCs were primarily evaluated by using a batch sorption experiment. Based on the investigations prior to this work, adsorption to Cu^{2+}, Cd^{2+}, MO, RB, NAPH and NB by VMBC was different, in which the adsorption to Cu^{2+} and Cd^{2+} was better than that of MO and RB, and followed by Naphthalene and Nitrobenzene. In order to investigate the effects of pyrolytic temperature on their removal, the initial concentrations of Cu^{2+}, Cd^{2+}, MO, RB, NAPH and NB were selected as 50, 50, 40, 40, 20 and 20 mg L^{-1}, respectively. Their corresponding chemical compounds were directly dissolved in the de-ionized water except that 10 mL ethanol was used as a co-solvent to facilitate dissolution of Naphthalene and Nitrobenzene. The initial pH of these solutions was determined as 5.38 (Cu^{2+}), 6.0 (Cd^{2+}), 6.12 (MO), 4.02 (RB), 6.52 (NAPH), and 5.47 (NB), respectively. The altering concentrations of Cu^{2+} (20-120 mg L^{-1}), Cd^{2+} (20-200 mg L^{-1}), MO (5-60 mg L^{-1}) , RB (5-80 mg L^{-1}), NAPH (1-20 mg L^{-1}) and NB(1-20 mg L^{-1}) were employed to evaluate the maximum adsorption capacity. 0.1 g biochar was employed for the batch adsorption, which was performed in 150 ml flasks with a working volume of 50 ml. The flasks were shaken at 120 rpm at 25 ± 0.5℃. The adsorption time was controlled as 24 h due to the adsorption for Cu^{2+}, Cd^{2+}, NAPH and NB can be equilibrated in 12 h, and it was ~4 h for MO and RB. After a batch adsorption, 5 mL samples were withdrawn and filtered using 0.22 μm nylon filter membrane. The residual concentrations of Cu^{2+} and Cd^{2+} were determined using an atomic absorption spectrometer (FAAS-M6, Thermo, USA), and the concentrations of MO, RB, NAPH, and NB were detected using a UV/vis spectrophotometer (WFZ UV-2102C, Unico Instruments Co., Ltd, China) at wavelengths of 470, 554, 218 and 268 nm, respectively. The adsorption experiments were conducted in triplicate, and the reported results were the averaged values.

Results and discussion

TG analysis of vermicompost and VCBCs

As shown in Fig.1, the TG curves between the vermicompost and the VCBCs were distinctively different, and the weight loss of vermicompost varied significantly with increasing pyrolysis temperature. The VCBCs, however, only changed slightly. When the temperature was under 220℃, the weight loss of all samples could be attributed to water volatilization. However, above 220℃ there were three distinct weight loss stages: 220-315℃, 315-390℃ and over 400℃. As previously identified [20, 21], it can be inferred that weight loss between 220-315℃ was mainly related to hemicellulose degradation; and between 315-390℃weight loss may mainly be linked to cellulose degradation. Additionally, weight losses that occurred between 400-750℃ may be pertinent to lignin degradation (higher than 400℃) and minerals and biogenic salts degradation (600-750℃). Overall, the vermicompost contained a large amount of organic matter (hemicellulose, cellulose and lignin), and, therefore, lost a significant amount of weight. The weight losses of VCBC-400, VCBC-500, VCBC-600, and VCBC-700 were 10.25%, 6.76%, 4.83%, and 4.57%, respectively, which indicated that the remaining organic matter in the VCBCs were predominantly removed during pyrolysis. Additionally, the degradation of mineral matters (for example $CaCO_3$-CaO) potentially also occurred in the pyrolysis process which partially caused the weight loss [18, 22].

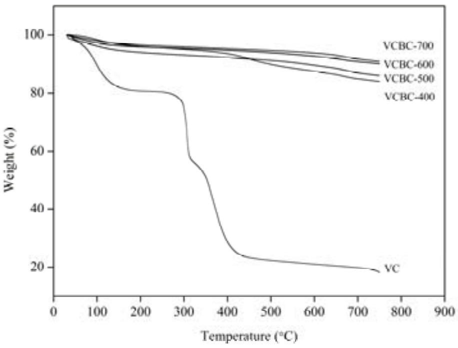

Fig. 1 The TG results of vermicompost (VC) and VCBCs

Biochar yield of VCBCs, proximate analysis and apparent density

As exhibited in Table 1, it was not surprising that the yield of VCBCs decreased from 78.1% to 70.6% with the increase of pyrolysis temperature from 400 to 700 ℃. In contrast to the vermicompost, the yield-reduction of VCBCs with elevating temperatures can be explained by the volatilization of organic compounds from the vermicompost [22]. As reported by Harris (2010), moisture can be evaporated at 220 ℃, and hemicellulose and cellulose can be decomposed at 220-315℃ and 315-400℃. When the pyrolysis temperature is higher than 400℃, the lignin begins to decompose [21]. In this investigation, vermicompost pyrolysis was studied between 400-700℃, and the labile compositions such as moisture, hemicellulose and cellulose were completely converted and volatilized, whilst lignin only just began to decompose. The latter mainly contributed to the observed yield-reduction with elevating pyrolysis temperatures from 400 to 700℃. In addition, almost all of the organic compositions of lignocellulose were degraded at temperatures higher than 500℃, which was mainly responsible to the slight decrease in yield when the pyrolysis was performed in the range of 500-700℃.

Table 1 Proximate analysis, ultimate analysis and mineral compositions of vermicompost and VCBCs.

	Vermicompost	VCBC-400	VCBC-500	VCBC-600	VCBC-700
Yield (%)	/	78.11	72.44	71.94	70.56
Proximate analysis					
Ash (%)	44.69±0.13	70.82±0.13	75.01±0.86	77.47±0.01	78.98±0.06
Moisture (%)	11.32±0.12	2.51±0.04	3.10±0.47	1.91±0.12	1.74±0.10
Combustible (%)[a]	43.99	23.98	20.18	17.50	15.48
Ultimate analysis					
C (%)	17.14	17.78	15.57	15.01	14.92
H (%)	3.07	1.67	1.21	0.88	0.72
N (%)	1.57	1.41	1.15	0.90	0.67
S (%)	0.91	0.57	0.51	0.58	0.57
O (%)	32.62	7.75	6.55	5.17	4.42
C/N	10.92	12.61	13.54	16.68	22.27
Minerals					

K ($g.kg^{-1}$)	5.18±0.09	7.29±0.49	8.47±0.03	8.84±0.03	6.28±0.20
Na ($g.kg^{-1}$)	1.49±0.01	2.50±0.04	2.53±0.13	2.79±0.01	2.62±0.06
Ca ($g.kg^{-1}$)	8.29±0.03	15.39±0.21	15.82±0.09	15.97±0.18	9.39±0.02
Mg ($g.kg^{-1}$)	0.26±0.01	0.39±0.01	0.44±0.01	0.46±0.02	0.24±0.05
Fe ($g.kg^{-1}$)	10.72±0.18	15.08±0.06	16.42±0.04	16.48±0.06	16.38±0.15
Mn ($g.kg^{-1}$)	0.14±0.00	0.16±0.00	0.17±0.00	0.18±0.00	0.18±0.00
Zn ($g.kg^{-1}$)	0.25±0.00	0.39±0.01	0.44±0.01	0.46±0.02	0.24±0.05
Pb ($g.kg^{-1}$)	0.05±0.00	0.06±0.00	0.07±0.00	0.07±0.00	0.09±0.00
Cr ($g.kg^{-1}$)	0.11±0.00	0.12±0.00	0.14±0.00	0.15±0.00	0.19±0.00
Ni ($g.kg^{-1}$)	0.02±0.00	0.03±0.00	0.03±0.00	0.04±0.00	0.04±0.00
Cu ($g.kg^{-1}$)	0.06±0.00	0.08±0.00	0.10±0.00	0.10±0.01	0.08±0.00
Cd ($g.kg^{-1}$)	0.002±0.00	0.002±0.00	0.002±0.00	0.004±0.00	0.001±0.00
TP ($g.kg^{-1}$) [b]	9.90±0.13	15.29±0.13	15.57±0.00	15.94±0.00	16.22±0.13
Soluble P ($g.kg^{-1}$)	1.23±0.04	0.66±0.01	0.41±0.01	0.40±0.01	0.20±0.03
Other properties					
pH	7.83±0.03	8.87±0.03	8.96±0.07	9.65±0.05	10.86±0.16
pHpzc	/	8.41	8.85	8.71	10.27
EC ($\mu s\ cm^{-1}$)	499.5±10.6	776.3±18.2	444.3±6.8	293.3±5.0	403.3±8.0
AD ($g.cm^{-3}$) [c]	1.05±0.12	1.76±0.01	1.90±0.00	1.95±0.03	1.96±0.03
TAFG[d] ($mmol\ g^{-1}$)	/	0.053±0.04	0.050±0.00	0.050±0.00	0.051±0.00
TBFG[e] ($mmol\ g^{-1}$)	/	0.408±0.00	0.431±0.01	0.441±0.00	0.457±0.01

[a] These values are calculated by difference; [b] TP refers to the total P; [c] AD is the abbreviation of apparent density; [d] TAFG refers to the total acidic functional groups; [e] TBFG refers to the total basic functional groups.

As presented in Table 1, the ash content was 70.8%, 75.0%, 77.5%, and 79.0% in VCBC-400, VCBC-500, VCBC-600, and VCBC-700, respectively. By contrast, due to the relatively higher ash content in the parent material of VCBCs (44.7%), the resulting ash content of VCBCs themselves was also typically higher than that of biochars derived from agricultural wastes [18, 23]. Additionally, the yield of biochar derived from vermicompost was considerably higher (78-70%) than that of pine needles (14-30%) and swine manure (40-30%) produced under similar temperatures [18, 24]. The combustible components (fixed carbon + volatile matters) in vermicompost were determined as 44.0%, which was typically lower than in carbon-like materials. When vermicompost was pyrolyzed with increasing temperatures from 400 to 700℃, this caused an increase in the fixed carbon and a decrease in volatile matter. However, the sum of fixed carbon and volatile matters were in gradual decline, which subsequently resulted in the decease of combustible material.

The apparent density (AD) of vermicompost and VCBCs are shown in Table 1.The value of the vermicompost was 1.050, which is close to water. Thus, it may suspend in an aqueous solution once the vermicompost is employed as an adsorbent, which is not favorable for recovery. The AD values of VCBCs were considerably higher and ranged from 1.763 to 1.960g cm^{-3}, which is much higher than water. This makes VCBCs, therefore, a potentially beneficial adsorbent.

Ultimate analysis, EC, pH, and surface functional groups of VCBCs

The results from the ultimate analysis of vermicompost and VCBCs are shown in Table 1. According to the ultimate analysis, the empirical formula of vermicompost derived from ultimate analysis could be expressed as $C_{1.000}H_{0.179}O_{1.903}N_{0.092}S_{0.053}$. Compared with vermicompost, all elements including C, H, O, N and S in VCBCs decreased as the pyrolysis temperature increased from 400 to 700℃ (except for the C content in VCBC-400). A previous study of rice straw biochar and swine manure biochar generated at 700℃ showed that these biochars had C contents of 91.6% and 33.7%, respectively [25]. By contrast, the C content of VCBC-700 was 14.92%. The C content in the generated biochar was positively related to that of their raw materials, with the C content of their raw materials being sorted as the double-digested biomass (represented by vermicompost) < the single-digested biomass (represented by swine manure) < the undigested biomass (represented by rice straw). Moreover, as pyrolysis temperature increased, the C content in biochar derived from undigested biomass generally increased. However, biochar derived from the digested feedstocks (manure and sludge) decreased [21, 26], as is shown by the relatively low biochar productions of vermicompost, and this finding requires further investigation. The decrease of H, O, N and S content in the VCBCs with the increased pyrolytic temperature was mainly attributed to the decomposition and degradation of lignocellulose to volatile organic components [15].

Atomic ratio can be generally considered as a predictor of biochar stability, and it is therefore important in reflecting the properties of biochar. A lower O/C value consequently represents a higher polarity indicating a more hydrophobic biochar. A lower H/C value indicates a lower polarity suggesting a more stable biochar. The O/C and H/C ratio of VCBCs decreased with increasing pyrolysis temperature, and they were significantly lower than those of vermicompost (Data not shown). Furthermore, the atomic ratio of O/C and H/C of vermicompost and VCBCs were presented by a Van Krevelen diagram, showed in Fig. 2. The values of O/C and H/C for VCBC-400, VCBC-500, VCBC-600 and VCBC-700 were 0.44, 0.42, 0.34, 0.29 and 0.09, 0.08, 0.06, 0.05, respectively. It is generally regarded that a threshold value of H/C<0.6 indicates the highly condensed aromatic ring systems in the biochar, which can be characterized by being slow to degrade in the environment [27]. Based on this information, VCBCs were characterized by high stability, and can be favorable for agricultural application.

Additionally, the N and C/N ratio are important fertility indicators for agronomic application. Although the increased pyrolytic temperatures led to removing N containing structures, including amino acid, amines and amino sugar, into N heterocyclic aromatic structures to form recalcitrant heterocyclic N, the low C/N value ranging from 10.9 to 22.3 suggests that VCBCs could potentially act as a slow-releasing fertilizer [14, 22]. Compared to the biochars derived from various lignocellulosic residues, they exhibited relatively high C/N (approximately 80), which was typical higher than that of VCBCs (20). Theoretically, it could be valuable to employ the VCBCs for soil application as a potential N source [28].

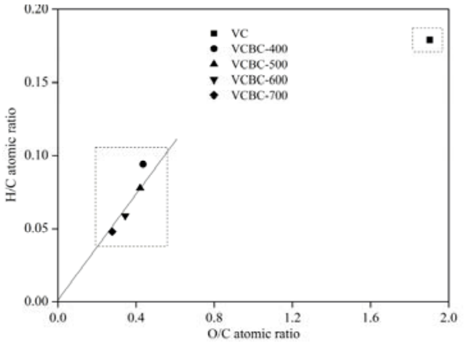

Fig. 2 Van Krevelen diagram of biochar at different temperatures

The electrical conductivity (EC) is usually used to evaluate the amount of salinity. As indicated in Table 1, the EC of the vermicompost was 499.5 μs cm^{-1}. Overall, the EC of VCBCs gradually decreased from 776.3 μs cm^{-1} to 293.3 μs cm^{-1} with increasing the pyrolytic temperature from 400 to 600℃,except for a slight increase at 700℃. It can be inferred that formation of insoluble salts or minerals caused the decrease of total dissolved salts as the pyrolysis temperature was increased in the range of 400 to 600℃. The higher temperature and the oxygen-free conditions may partially cause the degradation of insoluble salts or minerals (e.g. (Ca, Mg)$_3$(PO$_4$)$_2$) resulting in the increase of EC.

The pH$_{pzc}$, which refers to the pH value when the surface charge of biochar is zero, can be significantly influenced by the functional groups. As seen in Table 1, the pH$_{pzc}$ of VCBCs increased from 8.41 to 10.27 with the increase of the pyrolysis temperature, indicating that basic functional groups were gradually increasing. When the pH of the solution was lower than the pHpzc of biochar, it suggests that the biochar surface had net positive charges. On the contrary, when the pH was higher than pH_{pzc}, the biochar surface had net negative charges, and the groups or ions of the opposite charge could, therefore, be adsorbed by electrostatic adherence.

The vermicompost was alkaline (pH approximately 7.83) which could be attributed to the high composition of alkali and alkaline earth metals (see Table 1). The pH of VCBCs increased from 8.87 to 10.86 as the pyrolysis temperature increased from 400 to 700℃. These results imply that minerals were largely separated from the organic matrix and basic functional groups were formed during the pyrolysis process. Compared to lignocellulose-based biochars (with pH being acidic or natural), VCBCs appeared to be alkaline, which could potentially be used for soil amendment to reduce soil acidity.

Based on the basic character of VCBCs, their acid neutralizing ability was also investigated. The relationships between the volume of titration acid and solution pH for VCBCs were plotted in Fig. 3, with deionized water used as a blank for comparison. Overall, the total volume of added acid for VCBCs, used to adjust the pH of the solution to 3, was 3-5 times more than that of blank. These results indicated that pyrolysis can enhance the buffering capacity of vermicompost, which mainly attributes to the presence of numerous surface basic groups (see Table 1) [19].

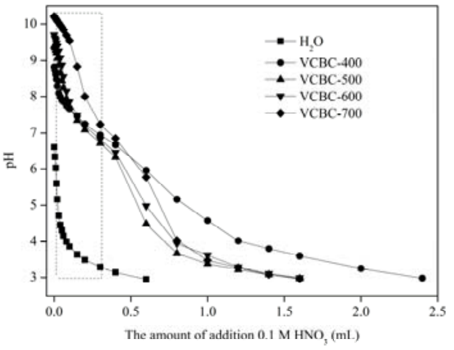

Fig. 3 Titration curves of H_2O (deionized water) and VCBCs derived from different temperatures

Generally, acidic functional groups are related to the exchange or adsorption of cations, while basic functional groups are associated to anions. As indicated in Table 1, total acidic functional groups (TAFGs) of VCBCs are in the range of 0.050-0.053 mmol g^{-1} and are decreasing with increasing pyrolytic temperature, whereas total basic functional groups (TBFGs) of VCBCs increased from 0.408 to 0.457 mmol g^{-1} with increasing pyrolysis temperature. Overall, the values of TBFGs of VCBCs were 8 times higher than the corresponding TAFGs, which were responsible for the high pH and pH_{pzc} of the generated VCBCs.

Mineral nutrients and heavy metals

The contents of the minerals in vermicompost and VCBCs are presented in Table 1. Vermicompost contained abundant minerals, including the macronutrients K, Ca and Mg, and the micronutrients of Zn, Fe, Cu and Mn, which directly resulted in relatively higher content of these minerals in VCBCs. For example, the contents of K, Na, Ca and Fe in vermicompost were 5.2, 1.5, 8.3, 10.7 g kg^{-1} respectively. Overall, the mineral contents were decreased with increasing pyrolysis temperature. The mineral content showed a slight reduction at the upper most temperature (700℃) due to volatilization by the pyrolytic gas. Heavy metals which were measured are presented in Table 1. The results revealed that the pyrolysis process could enhance heavy metal content, but that all of the recorded levels are lower than the permitted legal limits as identified by WHO [29]. Due to the fact that heavy metals can be gradually accumulated by soils, and that their chemical forms may vary with the environment, the application of VCBCs to soils should, therefore, be carefully investigated and controlled.

The level of soluble P, as a percentage of the total P in the vermicompost was 12.4% (see Table 1). As the temperature increased during pyrolysis, the levels of soluble P in the VCBCs decreased whilst the amount of the total P increased. Correspondingly, the soluble P accounted for 4.3%, 2.7%, 2.5%, and 1.2% of the total P in VCBC-400, VCBC-500, VCBC-600, VCBC-700, respectively. These results indicates that P leaching from the VCBCs should be relatively low and the biochars might be potentially suitable as slow release P fertilizers for soil application [15].The potential risk of P pollution was also identified to be relatively low when VCBCs were employed as an adsorbent in aqueous solution.

Pore property and pore size distribute of VCBCs

The pyrolysis temperature significantly affected the pore characteristics of the VCBCs (see Table 2). Surface area (SA) gradually increased from 17.63 to 82.40 m^2g^{-1} as the pyrolysis temperature was increased from 400 to 600℃. Above 600 ℃, it slightly decreased to 80.85 m^2g^{-1}. These results indicated that the pores gradually developed with increasing pyrolytic temperature, which was mainly due to the decomposition and condensation of organic matters (e.g. lignin). A slight decrease of SA was observed as the temperature increased from 600 - 700℃, which was related to a collapse of the porous structures. In comparison, the SA of swine manure biochar produced at 700℃ was shown to be 59 m^2g^{-1} [18], that of sybean stover of 420.3 m^2g^{-1} and that of peanut shells of 448.2 m^2g^{-1} [30]. The SA of VCBCs in this study were similar to the manure-based biochars and typically lower than the carbon-like material biochars.

Table 2 Pore characteristics of VCBCs.

	VCBC-400	VCBC-500	VCBC-600	VCBC-700
SA ($m^2\,g^{-1}$) [a]	17.63	56.63	82.40	80.85
MSA ($m^2\,g^{-1}$) [b]	3.38	26.56	32.98	31.72
TPV ($ml\ g^{-1}$) [c]	0.040	0.075	0.115	0.111
MPV ($ml\ g^{-1}$) [d]	0.001	0.011	0.014	0.013
APD (nm) [e]	9.15	5.28	5.58	5.49

[a] SA refers to the BET surface area; [b] MSA is micropore surface area; [c] TPV is total pore volume; [d] MPV is micropore volume; [e] APD is average pore diameter

As showed in Table 2, VCBCs had a large micropore surface area (MSA) which would be favorable for improving their adsorption performance. Furthermore, VCBCs also had an abundance of mesopore and macropore surfaces which indicated they could potentially offer habitats for bacteria fungi and protozoa [31]. In addition, the total pore volume (TPV) and the micropore volume (MPV) of VCBCs also increased from 0.04 to 0.111 ml g^{-1} (TPV), and from 0.001 to 0.014 ml g^{-1} (MPV) with increasing pyrolysis temperature. The average pore diameter (APD) was used to evaluate the porous properties of the VCBCs. Overall, APD decreased to approximately 5 nm as the pyrolysis temperature increased, due to the destruction and condensation of the pore structure.

The pore size distribution of VCBCs, ranging from 1 to 18 nm, was obtained using the BJH (Barrett-Joyner-Halenda) method. It can be seen that there are two sharp peaks at about 1 and 4 nm (see Fig. 4), which indicated that micropores and mesopores significantly contributed to the biochar's porous structure and surface area. The micropores and mesopores are also primarily related to the potential adsorption performance of VCBCs. As presented in Fig. 4, the maximum micropore was related toVCBC-600, which responded to micropore area and micropore volume (see Table 2). Micropores can be transformed into mesopores and macropores at higher pyrolysis temperatures, which maybe the reason why VCBC-700 had slightly lower micropores than VCBC-600. Furthermore, the mesopores rapidly developed with the increase of pyrolysis temperature, which was also attributed to the melted micropores and collapsed macropores in the biochar matrix.

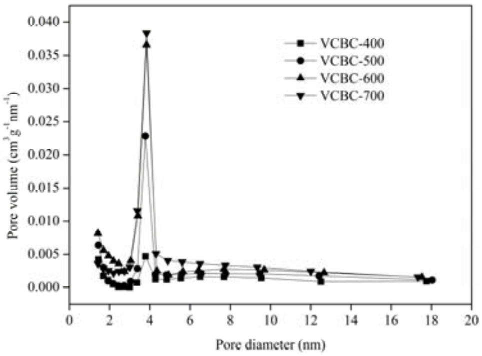

Fig. 4 Pore size distributions of VCBCs produced at different temperatures

XRD and FT-IR analysis of VCBCs

The overarching results in Table 1 indicated that the VCBCs contain abundant minerals, and the XRD study indicated that most of these minerals existed in the form of a crystalline structure. As shown in Fig. 5, the peaks at 21° and 26° were responsible for quartz, and the presence of sylvite was identified at 28° [12, 13]. Whitlockite peaks can also be observed at many angles (see Fig. 5) suggesting that Ca, Mg_3 and $(PO_4)_2$ commonly exist in VCBCs. Calcite crystalline XRD peaks were identified at 39.8°, 43° and 44°, and the existing calcite may relate to the alkalinity of VCBCs, which was consistent with previous studies on dairy manure biochars [22].

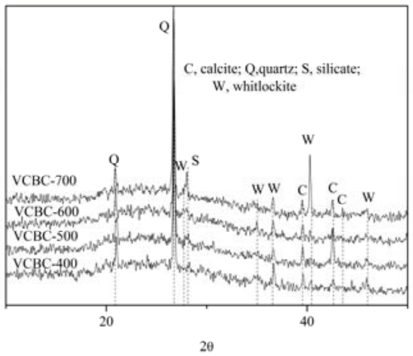

Fig. 5 XRD patterns of vermicompost biochar derived from 400-700℃ (denoted as VCBC-400, VCBC-500, VCBC-600, VCBC-700). C, calcite; Q, quartz; S, sylvite; W, whitlockite

The FT-IR spectra of vermicompost and VCBCs revealed that they were made up of organic and inorganic functional groups (see Fig. 6). The bands between 400 and 800 cm^{-1} are in the fingerprint region, in which the crowed functional group vibrations can be observed, but the difference between vermicompost and VCBCs was not distinguished. The spectra below 600 cm^{-1} were mainly attributed to M-X stretching vibrations (M-metal, X-halogen) in inorganic halogens compounds. The spectra between 600 and 800 cm^{-1} were mainly due to the out-of-plane vibrations of C-H in aromatic and heteroaromatic compounds [14]. The bands between 1000 and 1100 cm^{-1} are the P-O band of phosphate, C-O stretching vibration structures and Si-O-Si in-plane vibration [32]. The peak at 1422 cm^{-1} was assigned to CO_3^{2-} [22]. The C=C stretching in aromatic skeletal vibrations (indicative of lignin) were observed at 1510 and 1644cm^{-1}, which gradually became weak as the temperature increased due to the thermal composition of lignin at high temperatures [33]. While the vibration band at 1616 cm^{-1} was assigned to aromatic C=C, which occurred in VCBCs, it is believed that thermochemical conversion of biomass increased the stability. The bands at 2851 and 2919 cm^{-1} were associated to symmetric or asymmetric $–CH_2$ stretching in biopolymers which can only be observed in vermicompost and VCBC-400, indicating that the carbonization degree was low. The wide broad bands which ranged from 3200 to 3400 cm^{-1} were found in both vermicompost and VCBCs indicating the presence of –OH and –NH stretching. However, the intensities decreased with the increasing of pyrolysis temperature [23, 34].

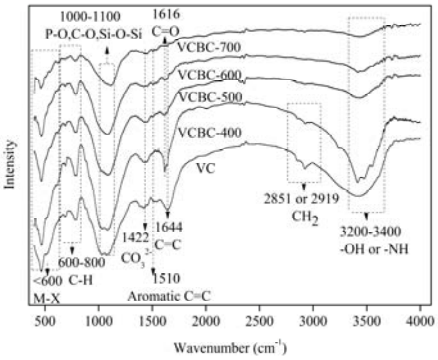

Fig .6 FT-IR spectra of vermicompost and VCBCs

Potential environmental amendment of VCBCs

The VCBCs were applied to adsorb typical contaminants, including Cu^{2+}, Cd^{2+}, MO, RB, NAPH and NB, to examine their potential environmental applications. As presented in Fig. 7, there were no significant differences on Cu^{2+} removal among VCBC-400, VCBC-500 and VCBC-600 (approximately 68%). However, Cu^{2+} removal maximally reached 89% by VCBC-700. Although Cd^{2+} removal by VCBCs exhibited a decreasing trend as the pyrolysis temperature increased from 400 to 600℃, the Cd^{2+} was almost completely removed when VCBC-700 was employed. As shown in previous studies, the release of cations (K, Na, Ca) in the solution play an important role in heavy metal adsorption as a reflection of cation exchange [35]. Besides, the effective removal of Cu, Cd, Zn by dairy manure biochars may also potentially results from precipitation of PO_4^{3-} or CO_3^{2-} [36]. Based on the physicochemical characteristics, the high ash content in VCBCs may be beneficial to ion exchange and precipitation, which may contribute significantly to the removal of heavy metal ions (see Table 1). In addition, an increase pH (8.87-10.86) can be observed with increasing pyrolysis temperature from 400 to 700℃. It can be implied that the formation of speciation of cadmium and copper may partially increased Cu^{2+} and Cd^{2+} removal by VCBCs obtained at higher pyrolysis temperature [37]. Besides, the initial pH of Cu^{2+} and Cd^{2+}solutions was 5.38, and 6.0, respectively, which was lower than the pH_{pzc} of VCBCs, the increased pH can enhance the pH of Cu^{2+} and Cd^{2+}solutions, which can potentially weaken the electrostatic repulsion between Cu^{2+} (Cd^{2+}) and biochar. Therefore, the adsorption to Cu^{2+} and Cd^{2+} can be facilitated more or less by VCBCs obtained at higher pyrolysis temperature [38]. According to FT-IR spectra, VCBCs contain a large amount of surface functional groups, including –NH, -OH, C=C, C=O, Si-O-Si and –PO (see Fig. 6), which may potentially improve their adsorption performance [22, 32, 34].

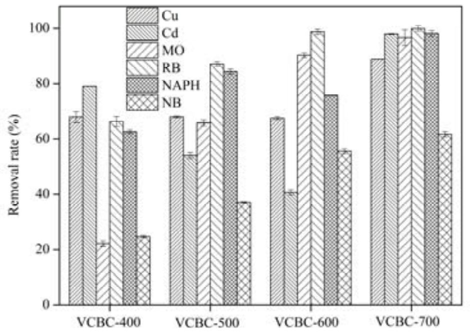

Fig. 7 Sorption of Cu^{2+}, Cd^{2+}, MO, RB, NAPH and NB by VCBCs

Overall, 22-97%, 66-100%, 63-98%, 24-62% of MO, RB, NAPH, and NB can be removed by VCBCs, respectively, and their removal rates increased in conjunction with the increased pyrolytic temperatures. According to Table 2, the improved porous structure may be responsible for removing these organic contaminants by interparticle diffusion and surface adsorption [24, 39]. Moreover, as the cationic dyes, the potentially weakened electrostatic repulsion between MO (RB) and biochar at higher pyrolysis temperatures may also facilitated their adsorption [38]. The initial concentration of MO and RB were 2 times comparing with NAPH and NB (See **Method and Materials**), and the removal rate of MO and RB was similar to that of NAPH, and significantly higher than NB. The differences may be a result of the characteristics of the employed contaminants. Generally, MO and RB are regarded as ionic organic matters, whereas NAPH and NB are regarded as nonionic organic matter. In addition to the pore-related interparticle diffusion and surface adsorption, the promoted adsorption of ionic organic matters may also relate to the complexation with the surface functional groups.

Overall, the VCBC-700 can achieve a relatively high adsorption abilities to these investigated contaminants, and the isothermal adsorption of these contaminants were also investigated using different initial concentrations. The relationships between adsorption capacities and the equilibrium concentration of the corresponding contaminants were plotted in Fig. 8. The data were fitted using 2 classic isothermal adsorption models of Langmuir model and Freundlich model, and the isotherm parameters were listed in Table 3. It can be found that the adsorption data from experiment can fitted better by Freundlich model (R^2>0.93) than that of Langmuir model (R^2>0.88), indicating the multilayer adsorption mainly controlled the removal of these contaminants. When the Langmuir model was employed to estimate the maximum adsorption capacities (Q_{max}), it was 36.4 mg g^{-1}, 29.5 mg g^{-1}, 12.4 mg g^{-1}, 12.3 mg g^{-1}, 17.8 mg g^{-1}, and 8.2 mg g^{-1} for Cu^{2+}, Cd^{2+}, MO, RB, NAPH, and NB, respectively, suggesting that the VCBC can potentially be used as an adsorbent for environmental amendment. Moreover, the especially high apparent density may facilitate the collection after adsorption in aqueous solution compared with traditional lignocellulose-based biochars.

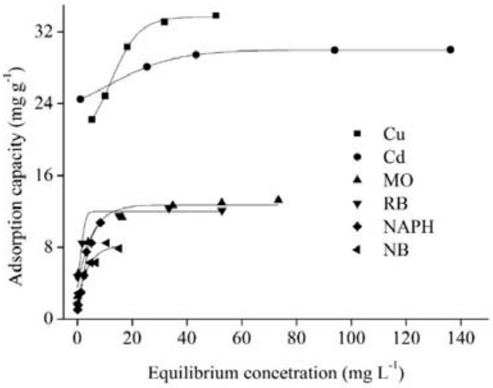

Fig. 8 Relationships between adsorption capacities and equilibrium concentration of the corresponding contaminants

Table 3 Langmuir and Freundlich isotherm parameters

VMBC-700	Langmuir model			Freundlich model		
	Q_{max}	K_l	R^2	K_f	n	R^2
Cu^{2+}	36.4	0.27	0.95	16.5	5.22	0.93
Cd^{2+}	29.5	4.31	0.88	24.5	22.66	0.97
MO	12.4	1.60	0.89	6.2	5.29	0.97
RB	12.3	1.32	0.91	8.3	9.46	0.98
NAPH	17.8	0.18	0.97	3.2	1.70	0.97
NB	8.2	0.93	0.88	3.8	3.37	0.95

Q_m is Langmuir maximum adsorption capacity (mg·g^{-1}); K_l and K_f represent Langmuir bonding term related to interaction energies (L· mg^{-1}) and Freundlich affinity coefficient ($mg^{(1-n)}L^ng^{-1}$); n is the Freundlich linearity constant.

Conclusions

Increased pyrolysis temperature used to carbonize vermicompost decreases VCBC yield. However, carbon content, stability, TBFGs formation and pore development increased when pyrolysis temperatures were higher. In addition, higher pyrolysis temperatures increased concentrations of mineral nutrients and heavy metals, but the heavy metal concentrations were still within permitted limits by WHO. The VCBCs were typically characterized by alkalinity, high ash content, high buffering ability and high apparent density. Moreover, the VCBCs excellently adsorbed Cu^{2+}, Cd^{2+}, MO, RB, NAPH, and NB in aqueous solution. The biochar from vermicompost by carbonization can, therefore, potentially be used as an adsorbent to improve environmental conditions.

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Notes and references

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