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Physicochemical properties of biochar produced from aerobically composted swine manure and its potential use as an environmental amendment

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HIGHLIGHTS

- High quality biochar can be produced from composted swine manure by pyrolysis.
- Composting and pyrolysis processes increased mineral nutrient contents in biochars.
- The highest maximum adsorption capacity for Cu(II) was obtained from TB2-400.
- TB2-400 can be beneficially used as an environmental amendment.

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ABSTRACT

Biochars derived from the pyrolysis, at 400 and 700 °C, respectively, of fresh (T0), 21d (T1) and 84d (T2) aerobically composted swine manure, were characterized and investigated for their potential use as environmental amendments. The biochar yield significantly increased following composting, but decreased with increased temperature. The ash content, surface area (SA), pH, electrical conductivity (EC), mineral nutrients, total heavy metals (except Cd) and available As, Cu, Mn and Zn concentrations of biochar produced at 700 °C were higher than in biochar produced at 400 °C, whereas the volatile matter, higher heating value (HHV) and elemental composition were decreased. The maximum Cu(II) adsorption capacity was 20.11 mg g^{-1} by biochar produced from T2 at 400 °C. The pyrolysis of 84d aerobically composted swine manure to produce biochar at 400 °C could be used as a soil amendment, or as an adsorbent for the removal heavy metal ions from wastewater.

1. Introduction

The intensification of swine production has led to increased manure as a by-product, of which the majority is applied to a small number of local agricultural fields as an organic fertilizer. However, a national standard has been produced for the livestock and poultry industry because the discharged manure has led to environmental problems, such as odors resulting from the emission of toxic gases, pollution of waterways due to leaching and run-off of nutrients and heavy metals (Zhu, 2006; Ashjaei et al., 2009). Traditionally, composting processes have been used to eliminate or reduce the risk of spreading of pathogens, parasites and weed seeds with manure to land, which leads to a stabilized product which can be used to improve and maintain soil quality and fertility (Tiquia and Tam, 1998; Larney and Hao, 2007). However, the amelioration effects on soils caused by direct incorporation of manure and/or composted manure can be short due to their decomposition by soil microorganisms. Similarly, most manure is currently exported from farms because there is not enough space for manure storage and soils in areas of intensive swine production often contain nutrients in excess of crop needs. Therefore, the development of environmentally beneficial uses for manure and/or composted manure can significantly increase the profitability of swine manure management.

Pyrolysis, the most familiar thermochemical conversion process, is a method of carbonizing organic material in dried biomass with an oxygen-free atmosphere at relatively low temperatures (<700 °C) to produce energy-rich and valuable end products such as bio-oil, gaseous hydrocarbons, and solid (biochar). The conversion of animal manure to biochar is of potential economic benefits due to agriculture waste reduction, biomass energy production and carbon credits derived from carbon sequestration (Cantrell et al., 2008). Biochar can reduce nutrient leaching in soils (Laird et al., 2010), improve soil fertility and increase the pH of acid soils (Chan et al., 2008). It can also effectively adsorb metal- and organic

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contaminants from wastewater (Cao et al., 2009; Chen et al., 2011; Zhang et al., 2013). However, the yield and physicochemical characteristics of biochars depend on the properties of the feedstock and operating conditions (e.g., particle size, temperature, heating rate, and residence time) used to produce it (He et al., 2000; Lehmann, 2007; Zhang et al., 2009; Cantrell et al., 2012). Some research has been conducted on the physicochemical characteristics of biochar production from anaerobically digested biomass such as sugarcane bagasse (Inyang et al., 2010), sugar beet tailings (Yao et al., 2011), and pig manure (Troy et al., 2013). However, there is limited literature on the characteristics of biochar directly derived from aerobically composted swine manure.

The objectives of this work were to investigate the physicochemical properties of biochars derived from fresh and aerobically composted swine manures at two pyrolytic temperatures and their prospective use as environmental amendments.

2. Methods

2.1. Swine manure

The manures were obtained from an intensive swine production area, located in Hangzhou, Zhejiang Province, China. The raw manure samples were collected from a pit from a farrow-to-finish production system, with a capacity for 40000 animals. Swine manure consists of straw and/or sawdust for bedding, swine urine, faeces, and waste feed. In order to reduce the water content of swine manure, some low moisture carbon rich materials such as sawdust are used as bulking agents. The ratio of sawdust to swine manure was 1:4 (w/w, fresh weight) to produce the compost. Fresh (T0), 21d (T1) and 84d (T2) composted swine manures were obtained from a composting mixture at the initial composting phase, the thermophilic phase, and the maturing phase, respectively. All samples were air-dried, ground to pass through a 2 mm sieve and stored in labeled plastic bottles prior to biochar preparation. The physicochemical properties of the experimental materials are shown in Table 1.

Table 1
Physicochemical properties of fresh (T0), 21d (T1) and 84d (T2) composted swine manures.

	Unit	T0	T1	T2
pH		7.46 (0.12)[a]	7.75 (0.02)	7.81 (0.03)
EC	mS cm^{-1}	3.04 (0.57)	2.84 (0.12)	3.71 (0.06)
Proximate analysis				
Moisture	%	12.54(0.05)	13.68 (0.04)	14.35 (0.15)
Volatile matter	%	58.18 (0.35)	45.52 (0.48)	33.46 (0.20)
Ash	%	27.56 (0.29)	38.98 (0.39)	49.19 (0.06)
Fixed carbon	%	3.40 (0.05)	3.76 (0.09)	2.71 (0.26)
HHV	MJ kg^{-1}	14.08 (0.02)	11.74 (0.04)	11.40 (0.07)
Ultimate analysis				
C	%	34.79 (0.03)	29.89 (0.05)	28.18 (0.07)
N	%	2.51 (0.03)	1.82 (0.01)	1.67 (0.03)
H	%	4.83 (0.05)	4.04 (0.07)	3.74 (0.03)
O	%	30.32 (0.31)	25.26 (0.37)	17.22 (0.07)
P	g kg^{-1}	11.52 (0.45)	14.69 (0.22)	19.36 (1.00)
Soluble P	g kg^{-1}	2.28 (0.02)	2.36 (0.01)	2.74 (0.02)
Ca	g kg^{-1}	33.32 (0.45)	40.60 (0.64)	50.38 (0.07)
K	g kg^{-1}	13.20 (0.46)	17.10 (0.30)	20.69 (0.02)
Mg	g kg^{-1}	6.08 (0.03)	7.59 (0.01)	9.87 (0.02)
Na	g kg^{-1}	1.87 (0.04)	3.05 (0.02)	3.43 (0.04)
As	mg kg^{-1}	48.17 (0.82)	52.12 (0.20)	59.31 (0.80)
Cd	mg kg^{-1}	0.35 (0.02)	0.35 (0.03)	0.40 (0.01)
Cu	mg kg^{-1}	536.37 (3.32)	638.87 (30.86)	862.38 (8.11)
Mn	mg kg^{-1}	354.40 (1.69)	447.44 (10.11)	562.05 (17.76)
Ni	mg kg^{-1}	2.01 (0.01)	2.76 (0.17)	3.10 (0.03)
Pb	mg kg^{-1}	0.95 (0.03)	1.72 (0.01)	2.09 (0.04)
Zn	mg kg^{-1}	793.42 (8.65)	927.57 (9.56)	1258.81 (26.58)

[a] Standard deviation in parenthesis.

2.2. Biochar preparation

The ground T0, T1 and T2 were placed in ceramic crucibles, each covered with a fitting lid, and pyrolyzed under oxygen-limited conditions in a muffle furnace. The pyrolysis temperature was raised to the selected value of 400 or 700 °C at a rate of approximately 25 °C min^{-1} and held constant for 2 h (Chun et al., 2004). The resulting biochars are hereafter referred to as T0-400, T1-400, and T2-400 for 400 °C pyrolysis temperature and T0-700, T1-700, and T2-700 for 700 °C pyrolysis temperature. Biochar samples were sieved <0.145 mm and stored in amber glass bottles for further analysis. All the pyrolytic processes were performed in triplicate per manure at 400 or 700 °C.

2.3. Biochar characterization

The yield of biochar was calculated from the mass of the composted swine manure and the weight of the produced biochar after completion of the pyrolysis. Moisture was determined as the weight loss after heating the biochar in an open crucible to 105 °C and holding at this temperature until biochar weight stabilized. Volatile matter was determined as the weight loss after heating the biochar in a covered crucible to 950 °C and holding for 7 min. The ash content of the biochar was measured by the residual weight after heating the biochar at 750 °C for 6 h in a muffle furnace. After the determination of moisture, volatile matter, and ash, fixed carbon was calculated by difference. The higher heating value (HHV) was calculated from the ultimate analysis and ash contents using the equation of Channiwala and Parikh (2002):

$$\text{HHV}\ (\text{MJ kg}^{-1}) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A} \quad (1)$$

where, C, H, S, O, N and A represents carbon, hydrogen, sulfur, oxygen, nitrogen and ash contents of material, respectively, expressed in mass percentages on dry basis. The content of S was negligible in this study.

Pore characteristics of the biochars were measured by N_2 gas adsorption–desorption at 77 K using a TriStar II 3020 surface area analyzer. The samples were pretreated by degassing at 300 °C under nitrogen flow for 4 h. The surface area (SA) was determined by a multipoint Brunauer–Emmett–Teller (BET) analysis of the adsorption data points with relative pressures (p/p_0) between 0.05 and 0.3. The total pore volume (V_{total}) was estimated from a single N_2 adsorbed point at a N_2 relative pressure of 0.97. The t-plot method was used to estimate the microporous surface area (S_{micro}) and microporous volume (V_{micro}) of the samples. The average pore size (D_{ap}) was calculated from the measured values of SA and V_{total} (Tsai et al., 2012).

The pH and electrical conductivities (EC) of the biochars were measured with a Mettler-Toledo SevenMulti dual pH/conductivity meter using a ratio of biochar/distilled water of 1:10 (w/v). Elements (C, H, N) were analyzed on a Thermo Finnigan EA1112 CHN elemental analyzer, and oxygen (O) was calculated by subtracting C, N, H and the ash contents from the total mass of the sample. Atomic ratios of elements were calculated to estimate the aromaticity (H/C) and polarity (O/C and (O+N)/C) of each biochar (Uchimiya et al., 2010).

Total and water soluble phosphorus concentrations were determined by the ammonium molybdate–ascorbic acid method of Murphy and Riley (1962) on a Shimadzu UV-2550 spectrophotometer. For mineral nutrients (Ca, K, Mg, and Na) and heavy metals