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Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge

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ABSTRACT

This work investigated the influence of pyrolysis temperature on biochar production and evaluated its properties for agricultural applications. Biochar yield decreased and its pore structure developed with the increase of temperature from 300 to 700 °C. Biochar produced at 300 °C was acidic whereas at higher temperatures it was alkaline. Fewer dissolved salts were contained in the biochars produced at higher temperatures. The rich nutrients, other than nitrogen, were intensified with the temperature rise. The results of (diethylenetriaminepentaacetic acid) DTPA-extraction showed the pyrolysis process abated the bioavailability of trace nutrient elements (Mn, Fe, Zn and Cu). The leaching toxicity of Pb, Zn, Ni, Cd, As, Cu and Cr in the biochars was lower than that in the sewage sludge although the pyrolysis process enriched the heavy metals in the biochars. Hence, the biochar was safer than sewage sludge as a soil amendment.

1. Introduction

Sewage sludge is one type of biomass residue resulting from wastewater treatment plants, and is composed of organic compounds, macro and micronutrients, trace elements, micro organisms and micro pollutants [1,2]. More than 25 million of sewage sludge (moisture content of approximate 80%) has been annually produced in China [3], it is crucial to treat sewage sludge with an economically and environmentally acceptable manner. Agricultural utilization might recover nutrients contained in sewage sludge, incineration can recover energy, and both of them have large treatment capacity [4,5]. However, the subsequent environmental contamination limits their extensive applications. For instance, noxious viruses, pathogens, ova and heavy metals might present hazards for plants and animals, and further jeopardize human health when sewage sludge is direct applied in soils [4]. The releases of dioxin, NO_x, SO_2, and heavy metals during sewage sludge incineration also result to serious air pollutions [5]. Pyrolysis is an alternative choice to sewage sludge disposal due to some specific advantages, for instance, the pyrolysis temperature may decompose organic pollutants and kill pathogens, oxygen-limited atmosphere restrains the generation of pollutants released in the incineration process [6,7].

Syngas, bio-oil and solid residue are the three different pyrolysis products. Syngas and bio-oil can be used as fuel or industrial chemicals [8,9], and the solid residue (biochar) has been regarded as a very promising soil amendment since the remarkable discovery of “terra preta” soils in Amazonia [10]. The biochar has significant effect on soil sustainable fertility because the former could improve soil organisms, soil water retention [11–13] and soil aggregation and aeration, reduce acidity, enhance nutrient retention and availability [14,15], and abate the bioavailability of some detrimental substances, such as heavy metals [16,17], pesticide residues and organic contaminants [18,19].

Extensive studies [17,20–22] have shown that the effects of biochar on improving soil fertility depend on its physical and chemical properties, such as being rich in aromatic carbon and difficult to decompose chemically and biologically, having high porosity, being alkaline and containing plentiful nutrients. Among the pyrolysis conditions, such as temperature, residence time and heating rate, temperature has the largest effect on physical and chemical properties of biochar. The previous researches on biochar derived from cottonseed hulls indicated that elevating temperature increased the specific surface area [17], and could reduce biochar acidity [20,21]. However, a higher CEC (cation exchange capacity) was

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observed in biochars derived from poultry litter, peanut hulls and pine chips at a lower pyrolysis temperature [22].

As shown above, most of the researches were about biochars derived from agricultural and forestry residuals. However, still some attention was paid on sewage sludge biochar, considering about its great nutrient elements contents. For example, Méndez et al. investigated pH, BET surface area, porosity, CEC, EC (electrical conductivity), and heavy metal content of sewage sludge biochar at two pyrolysis temperatures of 400 and 600 °C [23]. Hossain et al. also investigated the influence of temperature on production of wastewater sludge biochar and evaluated the properties required for agronomic applications in a temperature range of 300–700 °C [24]. Apart from biochars derived from various biomass residuals, a strong interest point of sewage sludge biochar was its heavy metal toxicity. Various leaching methods, such as TCLP (toxicity characteristic leaching procedure), BCR (Community Bureau of Reference) sequential extraction procedure were used to test its environmental toxicity, after all, a great percentage of heavy metals originally contained in sewage sludge still remained in biochar [3,23–26]. Nevertheless, the investigation on sewage sludge biochar was still scarce, it was necessary to conduct more researches to understand the effect of temperature on biochar physical and chemical properties, especially to evaluate the leaching toxicity of heavy metal presented in biochar. In this study, the pyrolysis experiments were conducted using sewage sludge to investigate the influence of temperature on biochar yield, pH, constituents, pore structure, dissolved salts content, nutrients content and heavy metal content. Additional, (diethylenetriaminepentaacetic acid) DTPA leaching was applied to analyze the availability of trace nutrient elements. TCLP was applied to analyze the leaching toxicity of heavy metals in the biochar, in order to determine the biological safety of biochar application as a soil amendment.

2. Material and methods

2.1. Sewage sludge materials

A digested sewage sludge sample was collected from the dewatering room in an urban wastewater treatment plant with improved anaerobic–anoxic–oxic process treatment in Guangzhou, China, and the main properties of the sewage sludge sample are listed in Table 1. The sewage sludge sample was first separated from other impurities, such as glass fragments and plastic bags, and then dried in a convection laboratory oven at room temperature until it qualified for pulverization. The sewage sludge sample was then ground to 1–2 mm fine particles, stirred and mixed in mortar to ensure that it was homogeneous and representative for the subsequent experiment. Finally, the sewage sludge sample was dried again overnight at 105 °C in a convection laboratory oven and stored in airtight plastic bags until pyrolysis.

2.2. Pyrolysis apparatus and procedures

All the biochars were produced using a horizontal quartz reactor (60 cm length × 5 cm i.d.) placed in an electrical laboratory furnace equipped with a temperature controller with a range of room temperature to 1000 °C and an accuracy of 1 °C. A gas cylinder, needle valve and rotameter were employed to maintain an oxygen-free atmosphere in the reactor. The first conical flask loaded with an ice water mixture was used to collect the condensable materials (bio-oil and water), and the second conical flask loaded with sodium hydroxide solution was used to absorb acidic gas and purify the gaseous materials (syngas).

200 ± 1 g of the sewage sludge sample was used in each pyrolysis experiment, and different temperatures (300, 400, 500, 600, and 700 °C) were studied, respectively. Experimental procedures are described below. For an inert oxygen-free atmosphere, about 1000 mL min^{-1} flow rate of purified nitrogen (99.999%) was flushed for 30 min after loading the sewage sludge sample in the horizontal quartz reactor. The reactor was placed in the electrical laboratory furnace and the nitrogen was turned off when the desired pyrolysis temperature was reached. With each experiment, the condensable matter was quenched and collected in the first flask, and the syngas was discharged into the atmosphere after it was purified in the second flask. The horizontal quartz reactor was removed from the electrical laboratory furnace until no syngas was emitted (the criterion was that the gas bubbles were less than 5 min^{-1} in the first flask), and the nitrogen was turned on again until the reactor was cooled to ambient temperature, then the biochar was recovered from the quartz reactor for subsequent tests. The bio-oil also was collected and dehydrated for subsequent heavy metal detection.

Table 1
Means and standard deviations for yield, proximate analysis, H/C, O/C, pH, EC, specific surface area and pore volume of sludge sample and biochars at various temperatures.

	Description	SS	300 °C	400 °C	500 °C	600 °C	700 °C
Yield	Mean (%)		83.3	74.0	69.5	67.1	65.0
	SD		±2.9	±2.6	±2.3	±2.3	±2.1
Ash	Mean (%)	55.7	65.8	75.5	80.6	83.8	86.8
	SD	±2.4	±2.3	±1.8	±2.6	±1.7	±1.4
VM	Mean (%)	39.7	27.4	16.0	10.2	8.6	5.5
	SD	±1.8	±1.6	±1.4	±1.0	±0.8	±0.4
	FC	Mean (%)	4.6	6.8	8.5	9.2	7.6
7.7							
	SD	±0.4	±0.6	±0.7	±0.9	±0.6	±0.7
O/C	Mean	0.56	0.33	0.32	0.09	0.06	0.05
	SD	±0.011	±0.011	±0.010	±0.010	±0.010	±0.010
pH	Mean	5.67	6.66	7.40	7.50	8.10	8.40
	SD	±0.22	±0.23	±0.24	±0.22	±0.25	±0.26
EC	Mean (dS m^{-1})	16.4	7.75	3.53	2.55	1.69	1.56
	SD	±0.21	±0.16	±0.15	±0.13	±0.11	±0.10
SSA	Mean (m^2 g^{-1})	11.85	14.37	22.68	24.53	26.66	26.70
	SD	±0.15	±0.18	±0.17	±0.18	±0.19	±0.19
PV	Mean (mL g^{-1})	0.775	0.108	0.132	0.139	0.144	0.159
	SD	±0.010	±0.011	±0.012	±0.011	±0.013	±0.014

SS: sludge sample; SD: standard deviation; VM: volatile matter; FC: fixed carbon; SSA: specific surface area; PV: pore volume.

2.3. Equipment and methods for analysis

Nitrate and ammonium nitrogen were measured in 2.0 mol L^{-1} KCl (1:5) by UV–vis spectrophotometer (8500, Techcomp, China) according to the indophenol blue method [27]. The pH was measured in a supernatant of aqueous solution (solid–water ratio was 1:5) with a digital pH meter (PHB-4, Leici, China). A simultaneous thermal analyzer (STA409PC, Netzsch, Germany) was used to obtain proximate analysis of the sewage sludge sample and biochars. The elemental composition of the sewage sludge sample and biochars was determined using an elemental analyzer (Vario EL cube, Germany), and oxygen content was determined by the difference. The DTPA-extractable trace nutrient elements were measured in a buffered DTPA solution of 0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$ and 0.1 mol L^{-1} $C_6H_{15}NO_3$ according to Chinese Standard *NY/T 890–2004*. EC was the current conduction capability of the sewage sludge sample and biochar solutions, and it was measured using a conductivity meter in the supernatant of solution (solid–water ratio was 1:5) after which was shaken at 200 rpm for 5 min and filtered [28]. Heavy metals were measured using ICP-AES (USA Thermo Jarrell Ash Corporation), after 0.1 g