

Short Communication

Nutrients and Heavy Metals in Biochar Produced by Sewage Sludge Pyrolysis: Its Application in Soil Amendment

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Abstract

The production of sewage sludge has been sharply increasing by municipal sludge treatment plants in China. Sewage sludge is a difficult waste to manage not only due to the high quantities produced but also due to its high concentration of heavy metals and pathogens. The pyrolytic conversion of sewage sludge to biochar and then applied to the land is a sustainable management option. Therefore, the aim of this work is to evaluate the characteristics of nutrients and heavy metals in biochar from sewage sludge pyrolysis, and pot experiments were carried out with different treatments consisting of infertile and contaminated soils. The results showed that the content of major plant nutrients (N, P, K) in sewage sludge biochar meets agricultural requirements. The concentrations of heavy metals (Cu, Pb, Zn, Cd, and Cr) were evidently increased in biochar, but those of available heavy metals were decreased. The sewage sludge biochar can improve soil fertility and enhance plant growth while not increasing plant uptake of heavy metals, and remedied contaminated soil by reducing the plant availability of heavy metals.

Keywords: sewage sludge, pyrolysis, biochar, nutrient, heavy metal

Introduction

Sewage sludge, an inevitable major byproduct of wastewater treatment, is being produced massively in China with dramatic increases of municipal wastewater. Generally, municipal sewage sludge is treated by land application [1, 2]. Raw sewage sludge, which contains valuable nutrients such as nitrogen, phosphorus, organic matter and essential trace elements, can improve soil physical properties and increase the dry matter yields of many crops as effective fertilizers. However, the concomitant toxins, especially heavy metals, jeopardize soil-plant systems and may further threaten human health [3, 4].

Practically, Pyrolytic conversion of sewage sludge into biochar excels conventional incineration processes with respect to fuel economy, nutrient recovery, and control of heavy-metal emissions [5, 6]. Most studies on the pyrolysis of sewage sludge refer to energy and fuel quality, and removal of water pollutants using solid fraction as adsorbents [7-9]. However, the effects of sewage sludge biochar on soil, plant nutrients, and the content and bioavailability of heavy metals in plants have seldom been studied hitherto. Therefore, we aim to investigate the production of biochar from sewage sludge, to characterize plant nutrients and heavy metals, and to evaluate the potential application of the biochar as a feasible fertilizer for agricultural land by improving soil productivity, releasing heavy metals, and remedying contaminated soils.

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Table 1. General properties of potting soils.

Soil type	pH	C%	N%	P (g·kg ⁻¹)	K (g·kg ⁻¹)	Cu (mg·kg ⁻¹)	Pb (mg·kg ⁻¹)	Zn (mg·kg ⁻¹)	Cd (mg·kg ⁻¹)	Cr (mg·kg ⁻¹)
Infertile soil	6.4	0.92	0.08	0.140	0.96	38.1	40.5	63.4	0.211	91.2
Polluted soil	6.9	2.41	0.22	0.589	3.44	290	1309	2210	5.72	237

Materials and Methods

Sewage Sludge

Sewage sludge was sampled from Xinzhuang Urban Wastewater Treatment Plant (Guiyang), in which municipal wastewater was subjected to secondary treatment by an activated sludge system. Activated sludge was dewatered by anaerobic digestion and belt-filter press, air-dried, crushed, passed through a 2-mm sieve, and stored in airtight plastic bags until pyrolysis.

Pyrolysis of Sewage Sludge

Pyrolysis should be performed by simultaneously considering biochar yield, heavy metal stability, structure, and energy efficiency [10, 11]. In this study, the sewage sludge sample was pyrolyzed in a fixed bed laboratory pyrolyzer for 30 min to produce biochar, with the temperature being increased up to 450°C at the rate of 5°C/min. The resultant biochar was then removed from the pyrolyzer, cooled in a desiccator, weighed, and stored in airtight plastic containers.

Pot Trial

After pyrolysis, most nutrients in sewage sludge were retained in the biochar, thus theoretically allowing plant growth and adsorption of heavy metals. In this regard, infertile yellow soils in Guiyang and polluted soil around a zinc-lead mine were sampled as the potting soils, air-dried and filtered with a 2 mm sieve, with relevant parameters shown in Table 1. Chinese cabbage (*Brassica pekinensis* R) was cultivated in cylindrical plastic pots (about 20 cm tall and 18 cm in diameter), to which were added 3 kg dry soils each. Factorial randomized block design was used with four treatments and three replications. The four treatments were:

- (i) infertile soil with sewage sludge biochar (ISB) (mass ratio, 3:1)
- (ii) infertile soil (IS)
- (iii) polluted soil with sewage sludge biochar (PSB) (mass ratio, 3:1)
- (iv) polluted soil (PS).

Fifteen plump, uniform seeds were planted in each plastic pot and irrigated with distilled water, and those germinated were recorded. The plants were harvested 30 days after seeding, and their average heights and biomasses (fresh matter weights) were measured. Then they were subjected to enzyme deactivation at 105°C, oven-drying at 60°C and grinding to determine the contents of heavy metals during plant growth.

Chemical Analysis

Soil pH was measured by adding 0.4 g dried carbonized sludge to 20 mL of water. The suspension was stirred for 24 h to reach equilibrium. Then the sample was filtered, and the pH of solution was measured. Total C and N were measured by a combustion method using a PE2400 elemental analyzer giving the mass percentages of carbon and nitrogen.

All samples (0.5 g) were digested by a 10 mL mixture of HNO₃ (65%, v/v), HCl (30%, v/v), and HF (40%, v/v) in a sealed Teflon vessel. Plant-available metals were extracted from the treated raw sewage sludge and biochar using diethylenetriaminepentaacetic acid (DTPA)-CaCl₂-triethanolamine. Ten grams of air-dried soil in 20 mL of DTPA-extracting solution was shaken for 2 h in a horizontal shaker with a stroke of 2.5 cm and a speed of 180 cycles·min⁻¹ [12]. After extraction was completed, the samples were collected for analysis. The concentrations of Cu, Pb, Zn, Cd, and Cr in all samples were determined using ICP-OES (Vista MPX, Varian Inc.). Quality assurance and quality control of metal analysis were assessed using duplicates, method blanks, and standard reference materials (SRM2710 and GBW-07603).

Total phosphorus (TP) and available phosphorous (AP) were determined by molybdenum antimony colorimetry. Total potassium (TK) and available potassium (AK) were determined by flame emission spectrometry. Hydrolyzable nitrogen (HN) was determined by alkaline hydrolysis and distillation [13].

Results and Discussion

Biochar Yield and Agronomic Properties

Pyrolysis process parameters such as temperature, residence time, and heating rate can affect the quality and quantity characteristics of biochar [11]. In this study, sewage sludge was converted at a relatively low pyrolysis temperature (450°C), allowing for biochar suitable for agricultural uses [6, 14]. Pyrolysis increased pH of the sewage sludge from 6.2 to 8.6; yielding biochar weighed 46.3% of the dry feed. Total C content in the biochar was reduced to 21.3%, while the fixed carbon yield was 39.9% (Table 2). Compared with previous studies, there were higher yields of biochar and fixed carbon herein at the same temperature mainly due to the slow pyrolysis [6, 15]. N, P, and K, as the major plant nutrients, were determined to assess whether

Table 2. Agronomic properties of sewage sludge and biochar.

Properties		Dried sewage sludge	Biochar
Biochar yield (%)			46.3
pH		6.2	8.6
C (%)		27.4	21.3
Total nutrients	N (%)	3.62	3.17
	P (g·kg ⁻¹)	8.7	15.4
	K (g·kg ⁻¹)	7.2	13.8
Available nutrients	N (%)	0.21	<0.03
	P (g·kg ⁻¹)	0.43	1.31
	K (g·kg ⁻¹)	2.19	2.47

the biochar was an eligible fertilizer for agricultural land. TN and AN (<0.03%) contents of biochar were lower than those of dried sewage sludge, which may be attributed to the volatilization of nitrogen during pyrolysis. Nitrogen can be removed through the losses of NH₄-N and NO₃-N fractions as well as volatile matter containing N groups at 200°C [10, 16]. Nevertheless, the plant availability of nitrogen in biochar remains unclarified. Total P and K contents of the biochar were increased by 77% and 97.1%, respectively. In addition, the available P and K contents also were elevated. AP content of the biochar was 3 times that of air-dried sewage sludge, while AK content was only increased by 12.8% after pyrolysis. Total N, P, and K content of the biochar was 6.1%, meeting the agronomic standards for gardens or parks of China (GB/T 23486-2009).

Heavy Metal Contents

The utilization of sewage sludge as fertilizer seems to be restricted because of the harmful components in the sewage sludge, such as heavy metals, pathogens, and toxic organics [4]. Pyrolysis is able to effectively kill pathogens and degrade toxic organics, although enriching heavy metals in biochar. Therefore, heavy metals mainly limit the application of sewage sludge in agricultural utilization.

Total and DTPA-extractable heavy metals in the sewage sludge and biochar are shown in Table 3. The concentrations of Cu, Pb, Zn, Cd, and Cr were significantly higher in biochar than those in sewage sludge. Retention rates ranged between 63.2-89.5%, with those of Cd and Cr being maximum (89.5%) and minimum (63.2%), respectively, mainly because the volatile heavy metals remained affected at pyrolysis temperatures. Heavy metals in biochar may not be entirely available for plant uptake. DTPA extraction method is used to estimate the readily available concentration of elements for plant uptake. In this study, the availabilities of heavy metals (Cu, Pb, Zn, Cd, and Cr) in biochar and sewage sludge were compared (Table 3). Compared with air-dried sewage sludge, total heavy metals were enriched in the biochar, but the amounts of DTPA-extractable ones were lower. Probably, on one hand, high-pH sewage sludge char tends to restrain heavy metal release. On the other hand, cadmium carbonate transforms into CdS that is more stable, and the carbonate and sulfide of copper form Cu₂S. Exchangeable-state Zn and Pb as well as carbonates produce corresponding oxides and sulfides during pyrolysis [5, 16-18]. Compared with control standards for pollutants in sludge from agricultural use of China (GB 4284-84), the biochar prepared in this study is a qualified fertilizer in practice.

Effect of Biochar on Plant Growth

Applying biochar to soils can increase the soil carbon pool, augment crop productivity, and reduce the bioavailability and phytotoxicity of heavy metals [19-21]. By focusing on the agronomic potential and security of sewage sludge biochar, we herein studied the impact of heavy metals on plant growth and bioavailability using Chinese cabbage as the agricultural crop in a glasshouse pot.

Table 4 shows the germination percentages, heights, and fresh matter weights of Chinese cabbage in all treatments. The 100% germination rates indicate biochar did not inhibit the germination of seeds. The average heights of PSB and ISB samples were highest at 16.6 cm and 15.7 cm, respectively, whereas those of IS and PS were only 8.1 cm and 10.2 cm respectively. The fresh matter weights of Chinese cabbage plant shoot varied significantly between the treatments, and the average fresh matter weights ranged

Table 3. Total and DTPA-extractable heavy metal contents in sewage sludge and biochar [mg·kg⁻¹].

Heavy metal	Dried sewage sludge	Dried sewage sludge(DTPA)	Sewage sludge biochar	Sewage sludge biochar (DTPA)	Present China MPC (GB 4284-84)	
					pH<6.5	pH≥6.5
Cu	79.3	1.3	124.8	0.8	250	500
Pb	38.2	1.7	67.5	0.4	300	1000
Zn	442	85.3	749	46.1	500	1000
Cd	2.13	0.17	4.12	BDL	5	20
Cr	67.5	3.2	92.2	2.8	600	1000

MPC – maximum permitted concentration, BDL – below detection limit

Table 4. Chinese cabbage growth and heavy metals uptake under different treatments.

Properties	ISB	IS	PSB	PS
Germination rate (%)	100	100	100	100
Plant height (cm)	15.7	8.1	16.6	10.2
Plant fresh matter weight (g)	164.2	51.1	179.3	98.2
Cu (mg·kg ⁻¹)	1.92	1.83	4.47	5.42
Pb (mg·kg ⁻¹)	0.54	0.61	0.91	2.1
Zn (mg·kg ⁻¹)	11.3	8.13	24.7	32.2
Cd (mg·kg ⁻¹)	0.06	BDL	0.37	0.54
Cr (mg·kg ⁻¹)	0.49	0.66	0.64	1.3

BDL – below detection limit, ISB – infertile soil with biochar, IS – infertile soil, PSB – polluted soil with biochar, PS – polluted soil

from 51.1 g to 179.3 g. PSB and ISB treatments exerted optimum growth-boosting effects due to the addition of biochar. The results suggest that sewage sludge biochar benefited infertile soil by augmenting the growth and yield of Chinese cabbage.

Uptake of Heavy Metals by Plant

The accumulation of heavy metals is of great concern in agricultural products owing to the potential threat to human and animal health [22]. Sewage sludge, which has variable compositions, contains toxic metals that limit land application due to food chain contamination. Although biochar can adsorb and deactivate contaminants in soils as well as restrict the migration of heavy metals, it may jeopardize the environment by accumulating the metals during pyrolysis. Therefore, the amounts of heavy metals in the applied biochar and their bioavailabilities in Chinese cabbage were studied using potting experiments (Table 4). Adding biochar in infertile soils did not significantly change the contents of heavy metals in plants, ruling out the odds of pollution owing to metal enrichment and being similar to the results of DTPA-extractable heavy metals. Besides, the heavy metal contents of PSB sample were significantly lower than those of polluted soil. Particularly, the contents of Pb and Cr were reduced by over 50%, and that of Cd was decreased by approximately 30%. Similarly, it has previously been reported that biochar was effective in metal immobilization, thereby reducing the bioavailability and phytotoxicity of heavy metals, especially decreasing soluble metals like Cd, Zn, and Pb in contaminated soil [21, 23].

Conclusions

Sewage sludge biochar has the potential to be used in agricultural production to satisfy the needs of plant growth and serve as a fertilizer. In this study, the yields of biochar and fixed carbon were 46.3% and 39.9%, respectively. In addition, pyrolysis increased total and available P and K concentrations, though those of total and available N were

decreased. In short, nutrients in the sewage sludge biochar meet relevant agronomic standards.

Moreover, pyrolysis resulted in obviously increased heavy metals (Cu, Pb, Zn, Cd, and Cr) contents of sewage sludge biochar, but heavy metal availability of them were lower than those of air-dried sewage sludge.

Applying sewage sludge biochar to infertile and polluted soils promoted the plant growth and increased the fresh matter weight of Chinese cabbage. Heavy metals were not prone to bioaccumulation in the plant, and the plant availability of heavy metals was reduced in polluted soil.

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