Effect of Peanut Shell Biochar on Dynamic Changes of Nutrient Elements and Heavy Metals during Sewage Sludge Composting

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Abstract. The effect of peanut shell biochar (PB) addition on thermophilic compost of sewage sludge (SS) with wheat straw was investigated. Four treatments were designed with different concentrations of PB0% (CK), PB10% (H1), PB20% (H2), PB30% (H3) (on dry weight of compost basis). The pH value, electrical conductivity (EC), total nitrogen (TN), total phosphorus (TP), total potassium (TK), and the different speciation of Cu and Zn were determined. After 30-days of compost, the growth rate of EC values of four treatments were 113.20%, 98.98%, 89.62% and 79.82%, respectively, and they were 1.31%, 4.63%, 5.06% and 6.51%, respectively for pH value, the loss rate of TN was 18.96%, 16.25%, 12.51% and 12.44%, respectively, and they were 63.59%, 81.21%, 91.14% and 94.05% of the TK. The maximum passivation rate of Cu was 9.72%, when PB adding was 30%. As for Zn, only 30% PB adding can reduce the activation of Zn. Treatments with PB had a lower value of EC and a higher value of pH than CK, and contributed to the increase of the contents of TN, TP and TK, relatively. Bioavailability of Cu and Zn decreased with the increase of PB addition. It is suggested that in the range of the study, the addition of 30% PB was the optimal choice which had the most effective effect on improving composting nutrient and reducing the bioavailability of heavy metals Cu and Zn.

1. Introduction

Sewage sludge (SS) is a by-product of wastewater treatment [1], which contains a large amount of N, P, K, pathogenic microorganisms, and harmful components such as heavy metals (HMs). With the rapid development of urbanization and industrialization in China, the amount of sewage treatment has also increased year by year, resulting in a large amount of sludge unprocessed timely and effectively. The annual sewage sludge production in China reached 30 million tons in 2015 [2]. Compost is one of the most effective ways for the utilization of sludge resource. Compost can improve the nutrient contents and reduce the bioavailability of HMs in the sludge [3]. But there is also a high bioavailability of HMs in the compost products which limits agricultural use, especially Cu and Zn. The speciation proportion of HMs can accurately reflect the bioavailability of the HMs, their speciation is fractionated by BCR (Community Bureau of Reference) method [4], which are exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction, respectively. Among them, exchangeable and reducible HMs are often called bioavailable HMs, because they can enter the plant cells easily [5]. The addition of several amendments were utilized to improve the
passivation ability of compost. The commonly used amendments are fly ash [6], lime [7], medical stone [8], zeolite [9], bentonite [10], phosphate rock [11], biochar [12] and so on.

As we know, the production of peanut in Henan province, China has been growing. The peanut shells have become an attractive feedstock for biochar production because these are inexpensive and easily available [13]. Except for a small part of peanut shells used as fuel and feed, most of them are not effectively utilized. PB is produced by peanut shell under anaerobic and high temperature conditions. It has a porous structure, large specific surface area, and contains a large number of functional groups such as carboxyl groups and phenolic hydroxyl groups to adsorb HMs [14]. Meanwhile, high potassium contents of PB can also improve nutrient contents of compost products.

The aims of this study were to explore the effects of PB as an amendment during the SS composting process. The variations of N, P and K contents during the process and the influence of bioavailability of Cu and Zn were investigated for the beneficial utilization of SS.

2. Material and Methods

2.1. Feedstock Materials

The experiment was done from March 26, 2018 to April 24, 2018 in the Henan Agricultural University. SS was got from the Wulongkou Sewage Treatment Plant in Zhengzhou, Henan province. Wheat straw (WS) was collected from a farm in Zhengzhou and chopped 2–5 cm. PB was got from Shangqiu Sanli New Energy Company. The ATMO was a kind of thermophilic aerobic strain which was purchased from Henan Jinhui Agricultural Technology Co., Ltd. The physical and chemical properties of the materials are given in Table 1.

| Material                          | Sewage sludge | Wheat straw | Peanut shell biochar |
|-----------------------------------|---------------|-------------|----------------------|
| Moisture content (%)              | 80.11         | 8.52        | 3.78                 |
| pH                                | 7.62          | 6.51        | 9.30                 |
| Electrical conductivity (mS·cm⁻¹) | 1.20          | 1.60        | 3.72                 |
| Total carbon content (mg·g⁻¹)     | 340.10        | 420.50      | 320.00               |
| Total nitrogen content (mg·g⁻¹)   | 53.00         | 6.60        | 8.80                 |
| Total potassium content (mg·g⁻¹)  | 106.9         | 11.36       | 34.05                |
| Total phosphorus content (mg·g⁻¹) | 25.44         | 2.48        | 0.51                 |
| Total copper content (mg·kg⁻¹)    | 356.40        | 17.28       | 72.29                |
| Total zinc content (mg·kg⁻¹)      | 280.56        | 71.26       | 160.59               |
| C/N Ratio                         | 6.43          | 63.76       | 37.13                |

2.2. Experimental Design and Sampling

There are 4 treatments in this experiment. The weight of PB added was according to the three substrates’ total weight (10%, 20%, 30%, respectively). WS was mixed with SS in the ratio of SS: WS (W/W, wet weight) 0.84:1 to get the C/N ratio 25:1 in a 5L capping compost device (Size: height 15 cm and inner diameter 20.6 cm), which was placed in the temperature-controlled incubator at 60°C for 30 days. The treatments were turned uniformly on days (0, 5, 10, 15, 20, 25, 30) to provide enough air for composting. The moisture content was adjusted to approximately 65%, and the ATMO strain was added at a wet mass ratio of 10 g/kg.

When the treatments were turned, 40 g samples were collected from each treatment which were divided into two parts, one was stored at 4°C to analyze electrical conductivity (EC) and pH, and the other was air-dried to analyze the contents of Total N (TN), Total P (TP), Total K (TK) and Cu and Zn speciation. All data reported were means of three replicates.

2.3. Analytical Methods

EC and pH were measured by pH/EC meter according to Lu’s methods [15]. TP and TK was detected using the Bao’s methods [16]. TN was measured using the Dignac’s methods with a vario EL cube.
elemental analyzer (Elementar, Germany) [17]. Cu and Zn were detected using BCR method by AAS (Atomic Absorption Spectrometer) [4].

2.4 Statistical Analysis
Statistical analysis was performed by EXCEL 2016 software. Figures were performed using Origin-2016. ANOVA analysis was performed using SPSS 22.0 software to compare the least significance difference (LSD) at p<0.05.

3. Results and Discussion

3.1 EC and pH

The EC value is an indicator of the soluble salt content during the compost, and also a very useful parameter to determine compost characteristics [14]. High EC value is undesirable because it inhibits plant growth and reduces the water and nutrients transportation into the plants. It can be seen from figure 1a that the EC values in four treatments were increased after the composting, the final EC values were 3.51, 3.11, 2.78 and 2.28 mS/cm, respectively. The result illustrated that the PB decreased the EC value of the compost. Generally, the EC value of less than 4.0 mS/cm of compost has been considered safe for future use. Compared with the initial value, the final EC values in CK, H1, H2, and H3 treatments was increased by 113.20%, 98.98%, 89.62% and 79.82%, respectively. It was explained that the decrease of EC during the initial phase might be due to the volatilization of CO₂, NH₃ and other gases under high temperature conditions and the large of compounds were consumed by microbial metabolic. Meanwhile, the PB can adsorb some soluble salts, resulting in the decline of soluble salt in the treatments. Compared with CK and H1, EC values of H2 and H3 reached the minimum faster, maybe due to the more salt ions adsorbed by PB during the composting. The increase of EC value after 15 days might be related to microbial metabolism which generated organic acids and small molecule compounds.

The pH is an important compost attribution. Also, it is an important factor for determining the migration effect of HMs. The higher the value of pH, the lower the immobility of HMs [18]. As shown in figure 1b, after composting, the pH values in four treatments were all increased, and they were increased with more PB addition. The pH in four treatments increased sharply in the initial phase, but H2 and H3 reached the maximum faster than CK and H1. Then, the pH in all treatments displayed a rapid downward trend along with composting. At the end of the composting, the four pH values were 6.71, 7.01, 7.38 and 7.70, and they were increased by 1.31%, 4.63%, 5.06% and 6.51% in CK, H1, H2 and H3 compared with initial value. It was obviously that PB addition can improve the pH value. During the initial phase, the pH showed an increase trend with the NH₃ emission. Then, the pH values decreased, and the reasons were that lots of organic and inorganic acids were produced by the
decomposition of component. Besides, nitrifying bacteria produced parts of $H^+$ when completing nitrification [19].

3.2. Nutrient Elements
Nitrogen is an essential element which constitutes nucleic acids, proteins, amino acids and enzymes, etc. The change of nitrogen contents during composting mainly included nitrogen retention and nitrogen release. Figure 2a depicts the change of TN with different PB addition, the TN contents in four treatments displayed a downward trend. In the end, the contents reached 13.25, 13.24, 12.87 and 12.74 mg/g, respectively. The loss rates were 18.96%, 16.25%, 12.51% and 12.44%. It revealed that the treatments with PB can play a role in the nitrogen retention. The nitrogen was released in the form of $NH_3$ and $N_2O$ which generated with the action of microorganisms during the composting. The PB can adsorb gas effectively through its own pore structure, it was the process of physical adsorption [20]. It can also adsorb ammonia and nitrate through its own ionic bond, it was the process of chemical adsorption.

Phosphorus is an important nutrient for crop growth. As can be apparently seen from figure 2b, the TP content fluctuated up and down in the initial stage of composting, and increased rapidly in the later stage, showing an overall increasing trend. the TP contents in four treatments were 5.72, 6.27, 6.36 and 6.95 mg/g after composting. The growth rates were 19.72%, 42.03%, 62.26% and 89.99%, respectively. It was analyzed that the leachate produced during the initial phase would take away some of the phosphorus, resulting in a decrease in its content. And then, there came the degradation of organic matter and volatilization of the gas, resulting in relative concentration of TP [21]. the TP content increased.

As we know, potassium content is relatively high in plants. As shown in figure 2c, the TK contents in four treatments increased rapidly in the early stage, and then the growth rate was slowdown. Overall,
the TK contents showed an increasing trend. The final TK contents were 42.74, 48.57, 52.34 mg/g and 54.12 mg/g for CK, H1, H2, and H3 treatments, which increased by 63.59%, 81.21%, 91.14% and 94.05% compared with the initial level. Analysis showed that PB was rich in potassium, so the contents of TK increased with the increase of the addition of PB. In the early stage of composting, the "relative concentration" effect was caused by the degradation of organic matter in the material, resulting in a rapid increase in TK content. Whereas, due to the decline of the microbial activity in the late composting stage, the relative concentration was weakened, which led to a slow growth in TK content.

3.3. Speciation of HMs

As shown in figure 3a, along with composting, the proportion of exchangeable Cu increased in CK treatment, while it decreased in other treatments. The proportion of reducible Cu decreased in all treatments while residual Cu increased gradually. As for oxidizable Cu, it decreased slightly in H1 and H3 treatments, while it increased slightly in CK and H2. The oxidizable and residual Cu fraction were the major fraction in the compost. After composting, the bioavailable Cu accounted for 85.56%~90.06%, it decreased by 5.26%, 5.81%, 7.59% and 9.72% than it was before compost. It revealed that the passivation ability for Cu increased with the addition of PB. Except H1, the proportion difference of other treatments was significantly (p<0.05) higher than CK. Consequently, H3 treatment had a better effect on reducing the bioavailable Cu, this might be due to that organic matter was degraded continuously to form a large amount of humus, which was rich in carboxyl, hydroxyl, and enol-rich groups. Along with the PB addition, the pH value could increase to a certain extent, much hydroxide Cu could be generated. Consequently, it reduced the bioavailability of Cu.

As shown in figure 3b, the major phase of Zn was the reducible fraction, and the bioavailability was relatively strong. The final exchangeable Zn was higher than it was in initial phase, it revealed that Zn was activated, It was in line with the conclusion that Zeng Zhengzhong [22] reported that compost had a certain activation effect on Zn with sludge. Except CK, the difference of the reducible Zn decreased in other treatments. As for the oxidizable Zn, it decreased in CK treatment, and others increased, meanwhile, it increased with the addition of PB. The proportion differences of bioavailable Zn in four treatments were -18.39%, -3.27%, -0.16% and 2.03%, respectively. The proportion difference of bioavailable Zn between H1, H2 and CK was significant (p<0.05), indicating that PB addition could reduce the activation grade of Zn. The reason was that the solid phase organic matter was degraded, and exchangeable and reducible Zn were released during the composting [23]. Passivation effect for Zn in H3 was significantly (p<0.05) higher than CK. The complexation between Zn and humus was mainly by chelation and ion exchange, and the complexing-power was less than Cu with chelation [24]. As an alveolate adsorbent, PB can remove HMs with compost by complexation, ion exchange, surface precipitation and electrostatic adsorption. Meanwhile, the large specific surface area will also have a strong passivation of Zn. Consequently, with the increase of PB, the bioavailability of Zn was relatively reduced.
4. Conclusions
It is concluded that PB addition to SS reduced the EC value of the compost product and increased the pH value. Meanwhile, it reduced the loss rate of TN and increased the growth rate of TP in the compost product. PB treatment enriched potassium value of SS compost. The PB also reduced the bioavailability of Cu and Zn. In the study, the addition of 30% PB was the optimal application which improved nutrient content of the compost and reduced the bioavailability of Cu and Zn.

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6. Reference
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