Chemosphere 180 (2017) 93–99

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Contrasting effects of composting and pyrolysis on bioavailability and speciation of Cu and Zn in pig manure

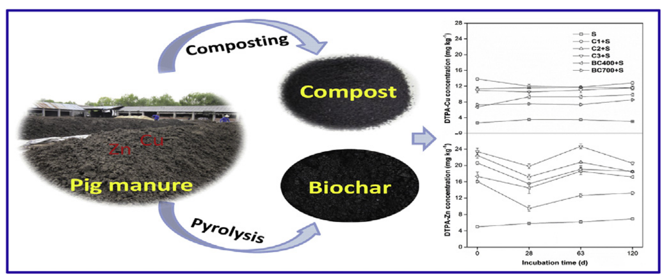
Jun Meng [a], Lu Wang [a], Libin Zhong [a], Xingmei Liu [a, *], Philip C. Brookes [a], Jianming Xu [a], Hongjin Chen [b]

[a] Institute of Soil and Water Resources and Environmental Science, Zhejiang Provincial Key Laboratory of Agricultural Resources and Environment, Zhejiang University, Hangzhou 310058, China
[b] Zhejiang Province Agriculture Department, Hangzhou 310028, China

HIGHLIGHTS

- Metal-contaminated manure was disposed by composting and pyrolysis processes.
- Bioavailability and speciation of Cu and Zn in compost and biochar was analyzed.
- Pyrolysis is a better manure treatment method compared to aerobic composting.
- Pyrolysis at higher temperature was recommended for immobilization of metals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
29 March 2017
Accepted 3 April 2017
Available online 3 April 2017

Handling Editor: X. Cao

Keywords:
Composting
Pyrolysis
Pig manure
Biochar
Metal speciation

ABSTRACT

The intensive and unregulated application of feed additives to commercial pig foods has resulted in high levels of Cu and Zn in pig manure. The aim of this study was to assess the impacts of composting and pyrolysis processes on the bioavailability and chemical speciation of Cu and Zn in pig manure products by single and sequential extractions, and to compare metal bioavailability in composts and biochar-amended soils in incubation experiments. Composting and pyrolysis processes can convert exchangeable and carbonate-bound Cu and Zn to organic matter and residual fractions, and significantly reduce the potential availability of metals in composts and biochars. The DTPA-Cu and Zn concentrations in soils amended with biochar BC700 were lower than in composts and soils amended with biochar BC400. It is suggested that 700 °C is the preferred pyrolysis temperature for the conversion of pig manure contaminated with heavy metals to biochar, in order to minimize environmental pollution.

1. Introduction

Large amounts of pig manure are generated from intensive pig production and most of it is applied as organic fertilizer to agricultural land (Zhou et al., 2005; Jin and Chang, 2011). However, with the development of the feed industry and livestock husbandry, the concentrations of several heavy metals in these manures have increased dramatically (Yao et al., 2006; Wang et al., 2013). In modern intensive pig production, feed additives such as Cu and Zn are commonly used in pig feed to minimize disease risk and

* Corresponding author.
E-mail address: xmliu@zju.edu.cn (X. Liu).

http://dx.doi.org/10.1016/j.chemosphere.2017.04.009
0045-6535/

improve the conversion rate of grain and feed (Li et al., 2007; Untea et al., 2011). However, this practice results in excessive amounts of Cu and Zn being almost completely excreted into feces and urine, which results in high concentrations of Cu and Zn in pig manure (Hsu and Lo, 2001; Cang et al., 2004; Tiquia, 2010). For example, Cu and Zn concentrations in manures collected from intensive pig productions in Jiangsu Province were as high as 1726 and 1506 mg kg^{-1}, respectively (Cang et al., 2004). Repeated applications of such manure to agricultural soils can result in the pollution of heavy metals in edible plants and soils (Shi et al., 2011; Legros et al., 2013; Xu et al., 2013). Total concentration of heavy metals may be a useful indicator of soil contamination, while associated with different forms of metals which have different impacts on soil-plant systems. Also, their availabilities for plant uptake are better correlated with different chemical forms or mechanisms of metal-organic matter chelation rather than the total metal concentration (Su and Wong, 2004; Zheljazkov and Warman, 2004; He et al., 2009). Raw animal manures may cause phytotoxicity due to their high concentrations of available heavy metals (He et al., 2009; Tiquia, 2010). Therefore, there is a need to find a viable approach to decrease the potential bioavailabilities of heavy metals in pig manure and thereby decrease the environmental risk of applying metal-contaminated manures to soil.

Currently, the conversion of animal manures into valuable end products and energy is carried out through biological or thermal treatment methods. Aerobic composting is an economical and eco-friendly way of transforming animal manures into more stabilized humic substances that can be used as plant nutrients and soil conditioners (Kuhlman, 1990; García-Gómez et al., 2005). Previous studies examined the changes in metal concentrations and fractions in composting systems (Hsu and Lo, 1999; He et al., 2009; Singh and Kalamdhad, 2013). Composting resulted in changes in heavy metal fractions and decreased the concentrations of bioavailable metals (He et al., 2009; Chen et al., 2010). Pyrolysis is a method for the thermal decomposition of biomass under anaerobic conditions at elevated temperatures to produce biogas, oil, and solid biochar (Lehmann, 2007; Uras et al., 2012; Al-Wabel et al., 2013). Pyrolysis of animal manures at high temperatures has the potential to reduce their volume, recover energy, kill pathogens and sequester carbon (Cantrell et al., 2008; Ro et al., 2010; Troy et al., 2013). The pyrolysis process may increase the immobilization of heavy metals in the pyrolysis residue (biochar). Previous studies have reported on the availabilities of heavy metals in biochars derived from sewage sludge (Lu et al., 2013; Zhai et al., 2014; Jin et al., 2016) and pulp-mill sludge (Devi and Saroha, 2014). However, little information is available on the contrasting effects of composting and pyrolysis on the changes of Cu and Zn speciation and bioavailability in pig manure. There is also a lack of information on the bioavailability of Cu and Zn in agricultural soils amended with heavy metal contaminated pig manure composts and biochars produced at different pyrolysis temperatures. Therefore, a rigorous study should be carried out to assess the bioavailabilities of Cu and Zn in pig manure during the composting and pyrolysis processes, and the potential risks of the release of Cu and Zn from the composts and biochars when applied in agricultural soils.

The aims of this study were (1) to investigate the changes in Cu and Zn speciation and bioavailability during the aerobic composting and pyrolysis of pig manure, (2) to compare the water soluble and DTPA availabilities of Cu and Zn in soil amended with raw pig manure, immature (composted 21 days) and mature (composted 84 days) composts and (3) the availabilities of Cu and Zn in biochars derived from heavy metal contaminated pig manure prepared at different pyrolysis temperatures. The results from this study will enable us to determine the most appropriate composting and pyrolysis regimes for the disposal of pig manure containing high concentrations of Cu and Zn to agricultural land.

2. Materials and methods

2.1. Composting procedure and sampling

Materials employed for composting in this study were a mixture of pig manure and sawdust. Selected physicochemical properties of each raw material are listed in Table 1. Pig manure was mixed with sawdust at a 4:1 ratio on a fresh weight basis, giving an initial C/N ratio of 20. A total of 3 piles of raw pig manure plus sawdust were made in an indoor concrete area. Each pile was mechanically turned every 4 days during the composting period (84 days). Samples from each pile were collected for separate analysis at 10 random locations and bulked within each compost pile, to give three replicates at each sampling time at days 0, 3, 7, 14, 21, 28, 35, 49, 63 and 84. After sampling, they were transported to the laboratory and stored at 4 °C. Subsamples of the three replicate air-dried compost samples per treatment were crushed to pass through a 60-mesh sieve and stored separately in plastic bags until use.

2.2. Pyrolysis processes

The dried and ground raw pig manures were placed into ceramic crucibles with tight-fitting lids to produce biochar. The pyrolysis temperature was raised to 400, 500, 600 and 700 °C at a rate of 10 °C min^{-1} and then held constant for 2 h (Dai et al., 2014). The resultant biochars were assigned codes BC400, BC500, BC600 and BC700 depending on their pyrolysis temperature. All biochar samples were crushed to pass a 100-mesh sieve and stored in a desiccator for subsequent chemical analysis.

2.3. Analytical methods

For the determination of total Cu and Zn in compost and biochar, 0.25 g of each crushed sample was weighed and digested with concentrated HF-HNO_3-$HClO_4$ acids (Dai et al., 2013). Water-soluble and DTPA-extractable fractions of the compost and biochar samples were measured to indicate the bioavailable concentrations of the metals. Water-soluble Cu and Zn concentrations were extracted by shaking the samples with distilled water at a 1:10 ratio (w/v) at 200 rpm for 2 h. DTPA-Cu and Zn were obtained by shaking the samples at a 1:5 ratio (w/v) at 200 rpm for 2 h with a DTPA complexing solution (0.005 M DTPA+0.01 M $CaCl_2$+0.1 M TEA, pH 7.3) (Chen et al., 2010; Lu et al., 2013). Speciation of Cu and Zn were

Table 1
Selected physicochemical properties of sawdust and pig manure.

Properties	Sawdust	Pig manure
Moisture (%)	20.66 ± 1.46	79.73 ± 0.29
pH	5.79 ± 0.01	7.39 ± 0.13
EC (mS cm^{-1})	0.10 ± 0.01	7.19 ± 0.44
Ash content (%)	0.91 ± 0.04	31.52 ± 0.46
Organic matter (%)	79.77 ± 0.36	55.14 ± 1.05
Total Kjeldahl Nitrogen (g kg^{-1})	0.90 ± 0.01	30.86 ± 0.44
Total phosphorus (g kg^{-1})	0.42 ± 0.16	12.56 ± 0.39
Total potassium (g kg^{-1})	1.95 ± 0.09	11.02 ± 0.31
Total Cu (mg kg^{-1})	1.79 ± 0.20	652.01 ± 1.02
Total Zn (mg kg^{-1})	10.03 ± 0.61	1089.34 ± 96.21
W-Cu (mg kg^{-1})[b]	ND[a]	121.45 ± 8.34
W-Zn (mg kg^{-1})	ND	103.88 ± 8.16
DTPA-Cu (mg kg^{-1})	ND	411.50 ± 11.38
DTPA-Zn (mg kg^{-1})	ND	708.53 ± 96.79

[a] ND, not detected.
[b] W-, Water soluble metal.