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The comparison of the migration and transformation behavior of heavy metals during pyrolysis and liquefaction of municipal sewage sludge, paper mill sludge, and slaughterhouse sludge

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HIGHLIGHTS

- Both pyrolysis and liquefaction favored the migration of heavy metal.
- Increasing pyrolysis temperature could improve detoxification effect.
- Pyrolysis promoted mobile fractions transferred to the stable fractions.
- Risk level of Zn in slaughterhouse sludge was dropped obviously after treatment.

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ABSTRACT

Municipal sewage sludge, paper mill sludge, and slaughterhouse sludge were pyrolyzed and liquefied for the production of bio-char. The migration and transformation behavior of Cu, Cr, and Zn during pyrolysis and liquefaction of these sludges were studied. Pyrolysis and liquefaction promoted mobile fraction (F1 and F2) to stable fraction (F3 and F4). The results showed that pyrolysis and liquefaction largely affected the redistribution of Cu and Zn in raw materials. The environmental risk assessment results indicated that the environmental risk levels of Cu and Zn were significantly reduced in bio-char, and risk level of Cr was slightly decreased after pyrolysis or liquefaction. Both pyrolysis and liquefaction were promising detoxification technologies for the three sludges in terms of the mitigation of heavy metals toxicity. It was suggested that dewatered sludge could be reduced toxicity/risk before utilization by pyrolysis or liquefaction technology, especially for Cu and Zn in slaughterhouse sludge.

1. Introduction

In recent years, the production of sludge like municipal sewage sludge (MSS), paper mill sludge (PMS), slaughterhouse sludge (SS) has increased sharply due to the demand for better life and a consequence of more wastewater treatment plants. Meanwhile, increasing concern had been focused on the decrease of the sludge amount and its disposal. Descriptive statistics presented that the amount of MSS in China would increase from 30 million metric tonnes (at a moisture content of 80%) in 2012 to 34 million metric tonnes in 2015 (Feng et al., 2015). The global pulp/paper waste treatment market will be expected to increase by 60% between 2012 and 2020 (Meyer and Edwards, 2014). Moreover, the SS is gaining increasing attention worldwide (Liu et al., 2015). These sludges contained high concentration of heavy metals (HM), organic compounds, organic micropollutants, microorganisms, and eggs of parasitic organisms, and so on. Therefore, the accumulation of those sludges would pose growing environment problem and secondary environmental pollution if treated improperly. Many researchers have tried to find rational approaches (i.e. sludge landfill, cropland application, incineration, and ocean dumping) to deal with the existing development situation (Inguanzo et al., 2002). Thus, the production of bio-char from sludge was a promising tendency.

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Nomenclature

MSS	municipal sewage sludge
PMS	paper mill sludge
SS	slaughterhouse sludge
MLC	liquefaction char of MSS
PLC	liquefaction char of PMS
SLC	liquefaction char of SS
MPC550	pyrolysis char of MSS at 550 °C
MPC750	pyrolysis char of MSS at 750 °C
PPC550	pyrolysis char of PMS at 550 °C
PPC750	pyrolysis char of PMS at 750 °C
SPC550	pyrolysis char of SS at 550 °C
SPC750	pyrolysis char of SS at 750 °C

As bio-char produced could be used as effective adsorbents (Leng et al., 2015a,b), potential fertilizer (Illera et al., 2000), or a feedstock for energy production (Vardon et al., 2012). Reducing the toxicity of HM from the bio-char production of the sludge was one of the important preconditions before its utilization in agricultural or other field. The elimination of HM from the sludge and HM immobilization inside the sludges have been recognized to be effective (Shi et al., 2013). Recently, various methods such as bioleaching (Pathak et al., 2008), chemical extraction (Silva et al., 2005), and bioremediation (Gaur et al., 2014) have been used for HM removal from those sludges. But these methods were time-consuming and difficult to control the HM removal efficiency (Kistler et al., 1987).

Pyrolysis and liquefaction technologies were widely used in sludge valorization, such as fluidized bed (Shen and Zhang, 2003), circulating fluidized bed (Zuo et al., 2013), spouted bed reactors (Alvarez et al., 2015), and continuous-flow processing systems (Elliott et al., 2014). Furthermore, pyrolysis and liquefaction were two effective techniques to immobilize HM in biomass (sludge). Immobilization of HM decreased the direct toxicity or leachable fraction of HM in biomass, resulting in significant environmental risks reduction. Currently, pyrolysis, a thermal process conducted in an inert atmosphere, is becoming popular to dispose solid waste. It reduced the solid waste volume while at the same time, generated valuable by-products and made the final waste chemically stable (Hu et al., 2006). The pyrolysis process was commonly conducted from 300 °C to 900 °C to convert sludge into fixed carbon, ash, bio-oils, and combustible gases depending on the final temperature and the heating rate (Fytili and Zabaniotou, 2008). Liquefaction, another effective technique for HM mitigation, is also ideal for processing biomass or solid waste since solvent was used as the reaction medium under high temperature (250–350 °C) and pressure (5–15 MPa). It was reported that liquefaction solvent had an effect on the redistribution of HM in bio-char during the MSS liquefaction and the increased temperature promoted the migration of HM toward bio-oil (by-product) (Leng et al., 2014).

Various studies had been reported in the literature on the mobility reduction of HM in the bio-char produced from MSS (Leng et al., 2014; Li et al., 2012; Yuan et al., 2015; 2011). Kistler et al. (1987) studied the transformation behavior of HM (Cr, Ni, Cu, Zn, Cd, Pb, and Hg) during the pyrolysis of MSS and found that the HM in the bio-char was highly immobile due to its alkaline properties. Devi and Saroha (2014) got the conclusion that the HM (Cd, Cr, Cu, Ni, Pb, and Zn) became enriched in bio-char matrix after pyrolysis of PMS at different temperatures (200–700 °C). High liquefaction temperature (180 °C) tended to inhibit the HM (As, Cr, and Cu) recovery and low liquefaction temperature (120 °C) resulted in higher residue content (Pan, 2010). However, the total concentration and speciation of HM distributed to the treated bio-chars during pyrolysis or liquefaction process for SS were overlooked in the previous researches and the comparison of pyrolysis and liquefaction technologies during disposing sludge were rarely studied.

The main objectives of this study are as follows:

(1) To study the fractionations of Cu, Cr, and Zn in bio-chars from pyrolysis and liquefaction of MSS, PMS, and SS.
(2) To evaluate the environmental risk of bio-chars from pyrolysis and liquefaction of sludges.
(3) To compare the transformation and migration behavior of HM between pyrolysis and liquefaction, and between different sludges.

2. Materials and methods

2.1. Sample collection and pre-treatment

The MSS, PMS, and SS were collected from three different wastewater treatment plants in Changsha, China. The sample was dried in an oven at 105 °C for 24 h to make sure the water content less than 1%. Then, the dried sample was ground and screened into fractions of particle diameter 80–200 meshes. The obtained sample was kept in a desiccator for future use. The pH value of the sample was obtained by the method reported in Chen et al. (2014b). The mixing ratio of sample and deionized water was 1:10 (w./v.).

2.2. Pyrolyzer and pyrolysis process

A special, horizontal and lab-scale pyrolyzer (SK-G08123K, China) was applied to conduct pyrolysis experiment. The pyrolysis chamber was comprised of a quartz tube (internal diameter = 72 mm, length = 1000 mm) and an electrically heating furnace with a programmable temperature controller. Temperature profiles were obtained using a thermocouple positioned at the center of reactor.

Three types of sludge were utilized for lab-scale pyrolysis experiment. In each pyrolysis run, 2.0 g dried sludge was inserted into a quartz tube, in which nitrogen gas of 99.99% purity was purged for 5 min to wipe out the air before pyrolysis and a 100 mL min^{-1} gas purge was maintained during the entire pyrolysis process. The furnace temperature was programmed to rise from room temperature to 500 °C at heating rate of 5 °C min^{-1}, then the designed pyrolysis temperature (550 °C or 750 °C) attained at heating rate of 10 °C min^{-1}. Pyrolysis process was maintained for 30 min at the designed temperature.

The resultant bio-chars of MSS, PMS, SS at 550 °C (750 °C) were labeled MPC550 (MPC750), PPC550 (PPC750), and SPC550 (SPC750), respectively. The produced bio-chars were stored in a desiccator at room temperature for further use.

2.3. Liquefaction autoclave and liquefaction process

Liquefaction experiments of samples (MSS, PMS, and SS) were conducted in a 500 mL airtight autoclave (GSA-0.5, China) at specified reaction temperature under the pressure of 5.0 ± 0.5 MPa. In