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Effects of copyrolysis of sludge with calcium carbonate and calcium hydrogen phosphate on chemical stability of carbon and release of toxic elements in the resultant biochars

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HIGHLIGHTS

- Copyrolysis of sludge with phosphate and carbonate to obtain the resultant biochars.
- Exogenous phosphate and carbonate increase the chemical stability of biochars' carbon.
- High pyrolysis temperature increases chemical stability of carbon and toxic elements.
- Tessier's sequential extraction reveals speciation transformation of toxic elements.
- Chemic and thermal stability of carbon influences the release of toxic elements.

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ABSTRACT

The potential release of toxic elements and the stability of carbon in sludge-based biochars are important on their application in soil remediation and wastewater treatment. In this study, municipal sludge was co-pyrolyzed with calcium carbonate ($CaCO_3$) and calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$] under 300 and 600 °C, respectively. The basic physicochemical properties of the resultant biochars were characterized and laboratory chemical oxidation and leaching experiments of toxic elements were conducted to evaluate the chemical stability of carbon in biochars and the potential release of toxic elements from biochars. Results show that the exogenous minerals changed the physico-chemical properties of the resultant biochars greatly. Biochars with exogenous minerals, especially $Ca(H_2PO_4)_2$, decreased the release of Zn, Cr, Ni, Cu, Pb, and As and the release ratios were less than 1%. Tessier's sequential extraction analysis revealed that labile toxic elements were transferred to residual fraction in the biochars with high pyrolysis temperature (600 °C) and exogenous minerals. Low risks for biochar-bound Pb, Zn, Cd, As, Cr, and Cu were confirmed according to risk assessment code (*RAC*) while the potential ecological risk index (*PERI*) revealed that the exogenous $Ca(H_2PO_4)_2$ significantly decreased the risks from considerable to moderate level. Moreover, the exogenous minerals significantly increased the chemical stability of carbon in 600 °C-pyrolyzed biochars by 10–20%. These results indicated that the copyrolysis of sludge with phosphate and carbonate, especially phosphate, were effective methods to prepare the sludge-based biochars with immobilized toxic elements and enhanced chemical stability of carbon.

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1. Introduction

Biochar, a carbon-rich material, is generally prepared from various biomass through pyrolysis/carbonization under oxygen-limited conditions at relatively low temperatures (300–700 °C) (Ahmad et al., 2014; Mohan et al., 2014). It has been used as low-cost adsorbents for organic and inorganic contaminants in wastewater and as soil amendment to increase soil carbon (C) and mineral nutrients (Singh et al., 2010; Bogusz et al., 2015; Inyang et al., 2016). It is also an effective way for carbon sequestration

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for waste biomass (Meyer et al., 2012).

Agricultural waste, wood materials, biological sludge, manure, and other organic wastes have been investigated to prepare biochars (Ahmad et al., 2014; Mohan et al., 2014). Sewage sludge is the main byproduct of municipal wastewater treatment (Luostarinen et al., 2009) and the disposal of a large amount of municipal sewage sludge has become one of the major bottlenecks restricting the healthy development of wastewater treatment (Zhang et al., 2015). For example, over 3000 tons of sludge containing 80% moisture was produced in 656WWTPs in 70 cities of China and the proportion of resource recycling (recycled building materials, compost) is only 25%, whereas landfilling, combustion, and untreated sludge takes up 50%, 10%, and 15%, respectively (Zhang et al., 2016). The recycling of sludge is a very tough task and more methods for recycling have to be developed. The pyrolysis of sewage sludge into biochars not only expands low-cost resourcing utilization of municipal sludge as soil amendments and sorbents for wastewater treatment but also increases carbon sequestration (Zielińska et al., 2015; Inyang et al., 2016). Sewage sludge generally contains a lot of mineral elements such as K, Mg, P and toxic elements such as Cd, Pb and As (Table S1, the supporting information). Yang et al. (2014) reviewed the current status and developing trends of the contents of heavy metals in sewage sludges in China (Yang et al., 2014). Contents of heavy metals and As in most of the sludge samples were generally lower than their threshold values in national mandatory standard of China for disposable sludge (GB 24188-2009) (Table S1). However, these elements may enrich in the resultant biochars (Zielińska and Oleszczuk, 2015). For example, contents of some toxic elements in sludge-based biochars (Table S2) were higher than their threshold values in national mandatory standard of China for soil (GB 15618-1995) (Table S1). Release of certain soluble elements from biochars during applications may occur in soil remediation and wastewater treatment (Singh et al., 2010; Smith et al., 2012). The release of some nutrient elements (e.g., K^+, Mg^{2+}, and PO_4^{3-}) may benefit for crop growth during their land application (Xu et al., 2013a; Chintala et al., 2014). However, the release of toxic elements may result in secondary contamination (Waqas et al., 2014). Therefore, investigations have been conducted to evaluate the release of both nutritious elements and toxic elements from sludge biochars (Liu et al., 2014; Van Wesenbeeck et al., 2014) and single leaching experiments and sequential extraction procedures have been used to investigate the mobility, bioavailability and fractionation of nutritious elements and toxic elements in the resultant biochars (Rao et al., 2008). For example, the water-soluble toxic elements in biochars were assessed by using the pH-dependent water leaching experiment (Wu et al., 2016). The research into the transformation of toxic elements in sludge during the pyrolysis process showed that the toxic elements were more immobile in the resultant biochars than that in the raw sludge (Liu et al., 2016). No mandatory standards for heavy metals and As in biochars are set up all-over the world, so further researches should be carried out to evaluate their release before large-scale application of biochars as soil amendments and sorbents for wastewater treatment.

Stability of biochars is another important property for their applications. Previous studies show that an increase of the pyrolysis temperature increases considerably the aromaticity and the condensed graphitic structure of the resultant biochars and therefore they are less prone to oxidation, indicating higher stability (Hossain et al., 2011; Chen et al., 2016; Li et al., 2017). For example, molar ratios of H/C have been used to estimate the aromaticity of biochars and with the increase of the pyrolysis temperature the ratios of H/C decreased, indicating more condensed aromatic structures and graphitic structure (Wang et al., 2013). It was also reported that endogenous minerals influenced carbon stability, surface electrochemistry and ion exchange properties of the resultant biochars (Li et al., 2014b; Zhao et al., 2014; Zhao et al., 2015). In fact, sludge biochars have higher contents of minerals or ashing than the biochars derived from agro-forestry biomass feedstocks (Mohan et al., 2014). Although researches have been done on the stability of the resultant biochars after mineral addition (Li et al., 2014b; Zhao et al., 2014; Zhao et al., 2015), further investigations should be done on the stability of carbon in biochars and the potential release of both nutritious elements and toxic elements of sludge biochars after the addition of exogenous minerals under different pyrolysis temperature.

In this study, two commercially available minerals, calcium carbonate ($CaCO_3$), and calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$] were utilized as additives and mixed with municipal sewage sludge for biochar production. Pyrolysis temperature was 300 and 600 °C, respectively. Physicochemical properties of the resultant biochars were characterized using various methods. The release of soluble elements from the biochars was measured, the fractions of toxic elements were extracted by Tessier's sequential chemical extraction, and the carbon stability was evaluated by chemical oxidation of hydrogen peroxide and potassium dichromate. Otherwise, the risk assessment code (*RAC*) and the potential ecological risk index (*PERI*) were used to evaluate the environmental risk of toxic elements in the resultant biochars. The overall objective of this study was: 1) to investigate the influence of the exogenous minerals and pyrolysis temperature on the chemical stability of carbon and the release of nutrients and toxic elements from the resultant biochars, and 2) to discuss the relationship between carbon stability and immobilization of toxic elements in the resultant biochars. The simple treatment to decrease toxic elements' release from the sludge-based biochars is helpful to its large-scale application as soil amendments and sorbents for wastewater treatment.

2. Materials and methods

All the chemical reagents used were of analytic grade except as noted and solutions were prepared using deionized (DI) water (18.3 MΩ*cm). Potassium nitrate (KNO_3), hydrochloric acid (HCl), hydrofluoric acid (HF), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the labware was soaked in dilute nitric acid at least overnight, thoroughly flushed with tap water, and washed three times with deionized (DI) water.

2.1. Preparation of biochars

Dewatered municipal sewage sludge was obtained from a sewage treatment plant in Nanjing. The moisture content of sewage was measured in laboratory and it was about 78%. First, the dewatered sludge was diluted by tap water, and then minerals ($CaCO_3$ and $Ca(H_2PO_4)_2$) were mixed with the dilute sludge at the ratio of 8% (w/w) (dry weight). The mixtures were placed outdoors and air dried. The air-dried samples were placed into a muffle furnace (CIMO, SX_2-4-10, China) and pyrolyzed by purging with nitrogen at peak temperature of 300 and 600 °C, respectively. The temperature was raised at a rate of 10 °C min^{-1} and held at the peak for 2 h. The obtained biochars were sieved with 18-mesh and 60-mesh nylon sieves to gain 0.250–1.00 mm fraction. Biochars prepared by unmodified sludge were marked as SSB3, and SSB6, respectively. Biochars prepared by $CaCO_3$-added sludge were marked as 8C/SSB3, and 8C/SSB6, respectively. $Ca(H_2PO_4)_2$-added sludge biochars were marked as 8P/SSB3, and 8P/SSB6, respectively. These resultant samples were stored in a drying oven for

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