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Role of phosphoric acid in the bioavailability of potentially toxic elements in hydrochars produced by hydrothermal carbonisation of sewage sludge

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ABSTRACT

The effect of phosphoric acid addition to the feed-water on the speciation and transformation behaviour of potentially toxic elements (PTEs) in the hydrothermal carbonisation (HTC) of sewage sludge was explored. Over 70% of each of the PTEs (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn) was in the directly bioavailable and potentially bioavailable fraction in the raw sludge, and especially Cu and Zn at 97.5 and 98.6%, respectively. Through the HTC process the directly bioavailable and potentially bioavailable fractions of PTEs in the sludge hydrochar clearly decreased, and the residual fraction in the hydrochar showed an observable increase. Further stabilisation of PTEs in hydrochar occurred during HTC with the addition of phosphoric acid solution to the feed-water. As the concentration of phosphoric acid in the feed-water increased the percentages of the residual fraction of Cd, Cr, Ni, Pb and Zn in hydrochars each exceeded 80%, but different PTEs behaved differently with increasing phosphate molar ratio in the feed-water. When the molar ratio of phosphate was 15%, the percentages of the residual fractions of Cd, Mn and Zn reached their maximum values in accordance with the changing trend in aromaticity of the hydrochar. Moreover, a large number of phosphate mineral crystals effectively occluded the PTEs in hydrochar. In conclusion, the addition of phosphoric acid to the feed-water during HTC further deactivated PTEs leading to a substantial decline in the potential environmental risk associated with the land application of the sewage sludge.

1. Introduction

Sewage sludges are by-products generated during wastewater treatment processes and are rich in organic materials and plant nutrients such as nitrogen, phosphorus and potassium (Tian et al., 2013). They can be reused as fertilisers after conventional composting (Leng et al., 2015) or as feedstocks for energy production in incineration plants (Vardon et al., 2012). However, sewage sludge contains many potentially toxic substances such as potentially toxic elements (PTEs) and organic pollutants and pathogens (Tian et al., 2013). The release of these toxic and harmful substances in the fertilisers or in the fly-ash to the environment can represent a substantial risk to the environment and to human

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health via the food chain (Zhai et al., 2016). In addition, the amount of sewage sludge produced continues to increase annually. Therefore, seeking a safer means of disposal of the sewage sludge that can make full use of the useful ingredients and also greatly reduce the environmental risk, e.g. the PTEs, has become a focus of attention (Chen et al., 2012; Kirchmann et al., 2017). The total PTE content is a simple and direct index for environmental risk assessment (Zorpas et al., 2008). However, it is widely held that the mobility, ecotoxicity and bioavailability of PTEs in the environment depends more upon their chemical speciation than upon the total PTE content (Huang and Yuan, 2016; X. Yuan et al., 2011), and can be assessed using the modified BCR sequential extraction scheme (Chen et al., 2008; Devi and Saroha, 2014). Based on the BCR method (Long et al., 2009; Sungur et al., 2014), the chemical speciation of PTEs is classified into four fractions: the exchangeable and acid-soluble (F1), the reducible (F2), the oxidisable (F3), and the residual (F4) fractions (Huang and Yuan, 2016). The bioavailability and mobilization of PTE fractions decrease in the sequence F1 > F2 > F3 > F4 (Chen et al., 2015) and can be integrated into three categories (Huang and Yuan, 2016), namely the directly toxic and bioavailable species (F1 + F2), the potentially toxic and bioavailable species (F3), and the non-toxic and non-bioavailable species (F4) (Ščančar et al., 2000). Therefore, reducing the F1 and F2 fractions and part of the F3 fraction and increasing the F4 fraction of PTEs in sewage sludge as much as possible is a valuable technique in the treatment of PTE pollution and the use of sewage sludges.

Hydrothermal carbonisation (HTC) might be a promising strategic approach to the sustainable management of sewage sludges and has been extensively revisited recently. It can deliver a useful product in landscaping and horticulture or as a functionalised carbon material for environmental protection (Álvarez et al., 2017; Wang et al., 2018a, b), and more importantly which can immobilise PTEs in the resultant hydrochars (Chanaka Udayanga et al., 2018). Recent studies on HTC of sewage sludge find that changes in the carbonisation conditions and parameters (e.g. temperature, time, catalyst and additives) can change the total contents and chemical forms of the PTEs (Chen et al., 2008; Huang et al., 2011; Leng et al., 2014; Shi et al., 2013a, 2013b). Shi et al. (2013b) report that the concentrations of PTEs in hydrochars decreased with the addition of increasing amounts of rice husk. Shi et al. (2013a) found that the total PTE content and the residual fraction (F4) of all PTEs except Cd in hydrochars increased as the reaction temperature increased. An increase in the feed-water pH also had a positive effect on the accumulation of Cd, Ni, Pb and Zn in hydrochars (Zhai et al., 2016). However, acting as a solvent, a reactant or even a catalyst, the feed-water is a very important factor controlling all the parameters but its properties other than its pH are usually ignored (Makela et al., 2016; Peterson et al., 2008; Zhai et al., 2016).

Phosphates can combine with more than 30 different elements in Nature to form more than 300 mineral phases that can exist in the environment for long periods of time. Phosphorylation of PTEs is performed to change their existing form by adding phosphate or phosphoric acid to reduce their activity, migration and percolation, thereby reducing their threat to the environment. Numerous studies have used water-washed fly ash with phosphoric acid or phosphate solution to transform available PTEs into insoluble metal phosphate compounds (Bournonville et al., 2004; Piantone et al., 2003). Bournonville et al. (2004) found that the formation of calcium phosphates can trap PTEs in a stable apatite mineral structure. Piantone et al. (2003) discovered that Pb and Zn in fly ash, initially distributed in the silicate and carbonate phases, were broadly redistributed in phosphate neoformations after carbonate dissolution, thus guaranteeing a more permanent stabilisation. Phosphorylation technology is also used to remediate soils contaminated with PTEs (Cao et al., 2009; Mignardi et al., 2012). Mignardi et al. (2012) used synthetic hydroxyapatite and natural phosphate rock to reduce PTE solubility, generally by about 84–99%. These studies were carried out at room temperature and at atmospheric pressure. The immobilization of PTEs by phosphorylation under the HTC process with higher temperature and self-generated pressure has been rarely reported (Wang et al., 2018a, b).

Hence, the objectives of the present work were (1) to explore the effects of the addition of different concentrations of phosphoric acid to the feed-water in the HTC process on the speciation and transformation behaviour of PTEs in the resultant sludge hydrochars, (2) to detect the role of the addition of phosphoric acid to the feed-water in the HTC process on changes in the aromaticity of the hydrochars and of the crystalline minerals formed in the hydrochars, and (3) to try to uncover the mechanisms by which PTEs are immobilized in hydrochar by addition of phosphoric acid to the feed-water during HTC processing of sewage sludge.

2. Materials and methods

2.1. Preparation of hydrochars

The sewage sludge used was sampled from the dewatering room in Lin'an Municipal Wastewater Treatment Plant in Hangzhou city, Zhejiang province, east China (119.72°N, 30.23°E), which uses triple-oxidation ditch technology for wastewater treatment and addition of polyacrylamide to dehydrate the sludge. The wet sewage sludge (water content 77%) was dried at 105 °C for at least 48 h in an oven, ground, passed through a 0.125 mm sieve, dried again to a constant weight and placed in sealed polyethylene bags and stored in a desiccator for further use.

An electrically heated bench-scale high-pressure reaction kettle (KCF-1, Jinghong Co. Ltd., Shanghai, China) was used for HTC of the sewage sludge. The inner pot (volume 1.0 L) was made of polyphenylene which can be stable in strongly acidic and strongly alkaline environments at a maximum temperature of 300 °C. Various concentrations of phosphoric acid solutions diluted to give a range of mass ratios between PO_4^{3-} and dried sludge of 0 (control), 5, 10, 15, 20 and 25% were used as the feed-water at pH values of 6.58, 1.54, 1.47, 1.35, 1.24 and 1.12, respectively. The solid:liquid ratio was 3:1 (w/v). Each treatment was replicated three times. The carbonisation experiments were carried out at 240 °C. The time required to heat the reactor from room temperature (~20 °C) to the target temperature was 80 min and the target temperature was held for 2 h. After natural cooling to room temperature, the hydrochars were obtained by solid-liquid separation with a 0.45-μm membrane filter, dried at 105 °C for 24 h, ground, passed through a 0.125 mm sieve and stored for further analysis.

2.2. Physicochemical analysis of sewage sludge and its hydrochars

An automatic elemental analyser (Vario EL cube, Hanau, Germany) was used to determine the total C, H, N and S contents of the raw sewage sludge and hydrochars by dry combustion at 1148 °C. The ash content in each sample was determined by heating samples at 800 °C for 4 h in a muffle furnace (Qi et al., 2017). The P content of all samples was determined using an ultraviolet spectrophotometer (Mapada UV-8000PC, Shanghai, China) at 700 nm (Wang et al., 2018a, b).

2.3. PTE analysis of the sewage sludge and its hydrochars

The raw sewage sludge and its hydrochars were digested in accordance with the US EPA 3050B method and inductively coupled plasma optical emission spectrometry (ICP-OES, Prodigy