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Effect of hydrothermal carbonization on migration and environmental risk of heavy metals in sewage sludge during pyrolysis

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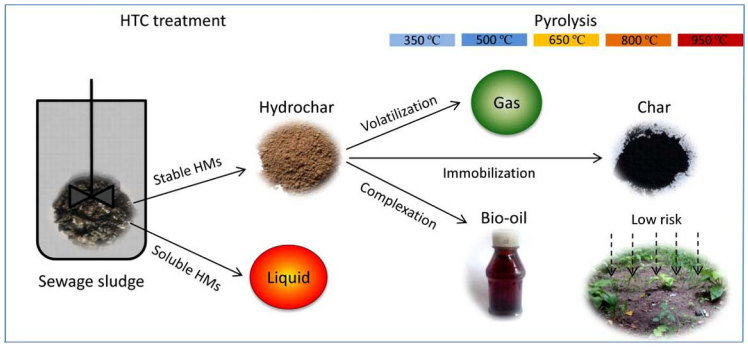
GRAPHICAL ABSTRACT



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ABSTRACT

The heavy metals distribution during hydrothermal carbonization (HTC) of sewage sludge, and pyrolysis of the resultant hydrochar was investigated and compared with raw sludge pyrolysis. The results showed that HTC reduced exchangeable/acid-soluble and reducible fraction of heavy metals and lowered the potential risk of heavy metals in sewage sludge. The pyrolysis favored the transformation of extracted/mobile fraction of heavy metals to residual form especially at high temperature, immobilizing heavy metals in the chars. Compared to the chars from raw sludge pyrolysis, the chars derived from hydrochar pyrolysis was more alkaline and had lower risk and less leachable heavy metals, indicating that pyrolysis imposed more positive effect on immobilization of heavy metals for the hydrochar than for sewage sludge. The present study demonstrated that HTC is a promising pretreatment prior to pyrolysis from the perspective of immobilization of heavy metals in sewage sludge.

1. Introduction

It was reported that more than 20 million tons of sewage sludge (80% of moisture) was generated in 2013 in China, accompanying with an average annual growth of 13% (Yang et al., 2015). Sewage sludge is the inevitable byproduct from wastewater treatment with abundant of nutrient (nitrogen, phosphorus and potassium), the organic matrix as well as the embedded pollutants including pathogens, organic matter dioxins and PAHs, and heavy metals (HMs) (Singh and Agrawal, 2008). These pollutants will bring environmental risk such as HMs can

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accumulate in the organism and then enter into human body through food chains if the sewage sludge is not in proper treatment. With gradual restriction of traditional disposing methods including sea dumping and sanitary landfill, thermochemical technologies including hydrothermal carbonization (HTC) and pyrolysis have been developed to meet the demand of efficient and environmental benign disposal of the increasing sewage sludge.

Pyrolysis is generally conducted at higher temperature (> 400 °C) under inert atmosphere which can convert sewage sludge into alternative fuels (chars) and chemical feedstock (bio-oil), and greatly decrease the volume and fully kill the pathogens (Garlapalli et al., 2016). The chars obtained by pyrolysis are generally alkaline and are of micropores as well as nutrient contents, correspondingly, the chars derived from pyrolysis of sewage sludge have been applied as soil conditioner recently years (Song et al., 2014; Van Wesenbeeck et al., 2014). Nevertheless, the toxic HMs are concentrated during pyrolysis due to its higher thermal stability than organic matter and this will bring potential risk to environment and plant if the chars are applied into soil. The toxicity of HMs in the chars under various pyrolysis conditions has been extensively investigated and it indicates that pyrolysis promotes the transformation of mobile fraction of HMs to stable forms (Shao et al., 2015). Jin et al. (2016) found Cu, Zn, Pb, Cr, Mn, and Ni exited mainly in oxidizable and residual forms in the chars derived from pyrolysis of sewage sludge at the temperature ranging from 400 to 600 °C. Similar observation was also reported by Devi and Saroha (2014) that bioavailability and eco-toxicity of the HMs in chars were significantly reduced as the mobile and bioavailable HMs fractions were transformed into the relatively stable fractions and increasing pyrolysis temperature favored this conversion found by Yuan et al. (2015a). In addition, the leachable contents of Ba, Cd, Cu, Ni, Pb and Zn were found to be reduced after pyrolysis, suggesting the potential and direct ecological risk was substantially lowered (Chen et al., 2014). However, pyrolysis is usually used in the conversion of dry biomass and not suitable for the high moisture sewage sludge because of the high energy intensive drying process.

Hydrothermal carbonization (HTC) can convert biomass into useful homogenous hydrochar which is a promising candidate for energy production and carbonaceous materials at low temperature (150–350 °C) and autogenous pressure (Liu and Balasubramanian, 2014; Oliveira et al., 2013; Zhao et al., 2013). In addition to as alternative fuel, the hydrochar has high porosity compared to parent materials and can be regarded as bio-adsorbents (Jain et al., 2016). As the water plays a necessary role which induces a series of dehydration and carbonation during HTC process, no extra pretreatment such as drying treatment is needed even for biomass with high moisture content (Berge et al., 2011). Sewage sludge contains more than 80% of moisture even after mechanical dewatering and most of this water cannot be easily removed due to the high binding strength. Plenty research related to the application of HTC on sewage sludge disposal were conducted and it is confirmed the high efficiency of HTC in improving mechanical dewaterability of sewage sludge accompanied by the elevation of fuel properties (Wang et al., 2016a; Zhao et al., 2013). As a consequence, the energy consumption of following drying process prior to further energy conversion is substantially reduced in comparison with conventional pyrolysis and HTC has been widely applied as the pretreatment of sewage sludge disposal including pyrolysis (Wang et al., 2016a). In addition, several studies have reported that bioavailable HMs can be removed by transferring into liquid phase whereas the stable fraction are mainly retained in the hydrochar during HTC treatment of sewage sludge (Huang and Yuan, 2016; Huang et al., 2011; Leng et al., 2016; Shao et al., 2015; Zhai et al., 2014).

Taking consideration of the respective potentials of HTC and pyrolysis in sewage sludge disposal, the combination of these two technologies has been developed and the effects of HTC conditions as well as pyrolysis temperatures on the properties of hydrochar and its derived chars for specific application were investigated (Garlapalli et al., 2016; Zhu et al., 2015). However, the distribution of HMs during the pyrolysis of sewage sludge derived hydrochar has been investigated barely. To reveal the HTC treatment on the distribution of HMs, the pyrolysis of hydrochar and raw sewage sludge at various temperatures were performed and the HMs transformation during HTC process and pyrolysis process were evaluated in the present study. In addition, the potential ecological risk of HMs in chars was assessed. It was expected to track the distribution of HMs during the HTC and pyrolysis process and investigate the feasibility of HTC as pretreatment of sewage sludge pyrolysis from the point of environmental risk of HMs.

2. Materials and methods

2.1. Materials

The digest sewage sludge with 81% of moisture was obtained from a municipal wastewater treatment in Shandong Province. The sewage sludge was dried at 105 °C for 24 h and then crushed in the particles between 100 and 150 meshes. The dried sewage sludge (SS) particles were stored in airtight bags for use.

2.2. Experiment procedure

2.2.1. HTC treatment of sewage sludge

The HTC treatment of digest sewage sludge was conducted in a 2.5 L autoclave. The HTC procedure had been described in our previous study (Liu et al., 2017). Specially, about 1 kg of sewage sludge with 81% of moisture was placed in the autoclave without any pretreatment and then the reactor was heated up to 200 °C with a heating rate of 5 °C min^{-1} and maintained at final temperature for 30 min. A constant nitrogen gas was introduced into the reactor for several minutes to purge the air inside and guaranty the inert atmosphere. After The HTC treatment, the reactor was cooled down to the room temperature using an electric fan and the solid product was separated by centrifuge at 4000 rpm for 20 min. Then the solid product was dried at 105 °C for 24 h, followed by the crushing into particles in 100–150 mesh (so called the hydrochar). The liquid product was adjusted to pH 2 with HNO_3 for further analysis.

2.2.2. Pyrolysis of SS and the hydrochar

The SS and the hydrochar were pyrolyzed in a fixed-bed tubular furnace at various temperatures (350 °C, 500 °C, 650 °C, 800 °C and 950 °C, respectively). In each pyrolysis test, 3.0 g of SS/hydrochar was added into a quartz boat which was then placed inside the furnace which had reached up to desired react temperature. A 500 mL min^{-1} of nitrogen was injected into the reactor to maintain the oxygen-free atmosphere during the pyrolysis. The bio-oil generated during pyrolysis was condensed when it passed through bubbling bottles that contained dichloromethane in an ice bath. After 30 min of pyrolysis, the solid residue (chars) were collected and stored in the airtight bag for analysis while the bio-oil was stored at 4 °C after evaporating the solvents. The sample obtained from SS and the hydrochar pyrolysis at various temperatures was labeled as SS_x and HY_x, respectively, where x referred to the pyrolysis temperature. The ultimate analysis of the samples was conducted by an element analyzer (Vario EL III, Elementar).

2.3. Determination of HMs

2.3.1. BCR extraction and toxicity characteristic leaching test

The toxicity of HMs highly depends on their existing forms. Consequently, the speciation fractions including exchangeable and acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) forms of HMs were determined using BCR sequential extraction procedure and the extraction procedure can be found elsewhere (Wang et al., 2016b; Xiao et al., 2015).