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Chemical forms of heavy metals in pyrolytic char of heavy metal-implanted sewage sludge and their impacts on leaching behaviors

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ABSTRACT

In this paper, we introduced a new sewage sludge (SS) recycle method, in which heavy metals were implanted into sewage sludge and then they underwent co-pyrolysis. Three-step sequential extraction procedure (BCR) was conducted to evaluate the four chemical forms of heavy metals in pyrolytic char, namely, acid-soluble fraction, reducible fractions, oxidizable fraction and residual fraction; and the fractionation results were compared with the leaching results of the concerned metals to explore the heavy metal speciations formed during co-pyrolysis. Experimental results indicated that Cu implanted into sewage sludge could influence the speciation distribution of Cr, Ni, Pb and Zn in pyrolytic char, as a result the leaching of heavy metals could be influenced. The sum of oxidizable fraction and residual fraction of Cr was deceased by ~10%; the sum of Ni was increased by at least 13%; the sum of Zn was almost unchanged; the sum of Pb showed an overall increase trend. At the same time, the contents of Cu in oxidizable and residual forms decreased with Cu implantation. Pyrolysis temperature also affected the distribution of heavy metal speciation. High temperature contributed to the immobilization of Pb and Zn by significantly increasing the sum of oxidizable fraction and residual fraction. However, high temperature showed the less effect on the stabilization of Cr and Ni, and even had the negative impact on the suppression of Cu release. The leaching levels of Cu and Zn were related to the percentages of residual fractions, suggesting that the acid-soluble fraction, reducible fractions, and oxidizable fraction were unstable and prone to be extracted.

1. Introduction

Pyrolysis is the thermal degradation of material in the absence of air or in an oxygen-deficient atmosphere. The three major products of pyrolysis are gas, liquid (oil and tar), and carbonaceous residue (char) [1]. In recent years, pyrolysis carbonization, as an alternative disposal method for sewage sludge (SS), has gained the increasing attention worldwide [2–3]. Heavy metals are the most toxic chemicals released during these processes [4–5]. The pyrolysis process enables heavy metals in SS to be concentrated mostly in the resultant char [6–7].

Pyrolytic char with immobilized heavy metals has the following application options: agronomic application [8–10], activated carbon, and catalyst [11]. Yuan et al. [12] concluded that SS char has the potential to amend degraded soil and improve crop yield. The presence of heavy metals restricted sewage sludge application in agriculture [13]. Heavy metals such as zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), and chromium (Cr) are principal elements which restricted the usage of sludge for agricultural purposes and their potential accumulation in human tissues and biomagnifications through the food chain led to human health risk and environmental problems [14–15]. In addition, under the deactivated conditions of the activated carbon or catalyst, whether the attached heavy metals cause additional pollution is still unknown. Therefore, heavy metals in pyrolytic char remain a challenge in the innocuous treatment and resource utilization of sludge pyrolytic residues. The mobility of heavy metals, their bioavailability and related eco-toxicity to plants, depend strongly on their specific chemical forms or binding ways [16]. The evaluation of sewage sludge toxicity by chemical speciation and biological testing is therefore very important [17]. In particular, the speciation of heavy metals during the sludge disposal process was analyzed by some researchers. Pan et al. [18] studied the different fractions from different carbon materials produced through the pyrolysis of SS with corn straw. He et al. [19]

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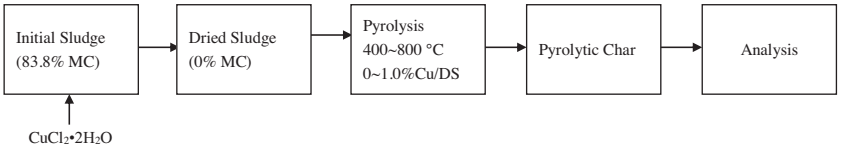
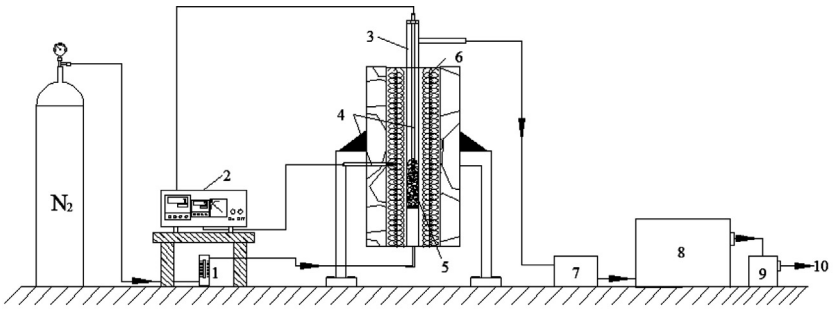


Fig. 1. Flow diagram of heavy metals-implanted SS carbonization.



1.Flowmeter 2.Temperature controller 3. Tubular reactor 4. Thermocouple 5.Samples 6.Pyrolysis furnace 7.Bio-oil condenser 8.Combustor 9.NaOH solution absorption 10.Exhaust gas

Fig. 2. The system diagram of samples pyrolysis.

revealed that the variation in low pyrolysis temperature did not effectively contribute to the distribution of metal speciation in the residues and concluded that pyrolysis could enhance the stability of metals when the temperature was high enough.

Consequently, it is essential to estimate the fractionation of metals in the char obtained according to a new SS disposal method because the disposed SS may be applied on cropland. In the study, Cu was considered as the representative of heavy metals in SS to study the effects of implanting concentration and carbonization temperature on the fractionation of heavy metals in pyrolytic char. Cu, Zn, Pb, Ni, and Cr were selected as the target heavy metal elements to evaluate their fractionation in the sludge char. A sequential extraction procedure recommended by the Community Bureau of Reference (BCR) was adopted in the fractionation of heavy metals in sewage sludge and the char produced after pyrolysis. It is expected that the combined analysis of heavy metal speciation distribution can help to explain the metal immobilization effect of the new method and provide the reference to the further disposal for the SS pyrolytic residues.

2. Materials and methods

2.1. Samples and chemicals

The dewatered SS was sampled from an urban wastewater treatment plant with the improved anaerobic–anoxic–oxic process treatment in Shanghai and the moisture content (MC) of raw sludge was 83.8%. In this study, the powder reagents ($CuCl_2{\cdot}2H_2O$) supplied by Sinopharm Group Chemical Reagent Co. was dissolved in distilled water. The Cu^{+2} solution and raw sewage sludge was stirred together for 1 h by a vortex stirrer (D2004W, 700 r min^{-1}). Mixed samples were dried to constant mass at 105 °C in a drying oven for approximately 24 h and then broken into small pieces. Finally, the samples were stored in air-tight plastic bags until their use in pyrolysis. Due to the volatility of $CuCl_2$, the volatile ratio of Cu during the process of carbonization could be conveniently tested.

All the chemicals used in this study, including $CuCl_2{\cdot}2H_2O$, HF, HNO_3,$HClO_4$, HAc, NH_2OH_3 HCl, H_2O_2, and NH_4Ac, were of analytical grade and purchased from Sinopharm Group Chemical Reagent Co.

2.2. Pyrolysis carbonization

The carbonized experiment was conducted in a laboratory-level tubular reactor made of stainless steel and the operation temperature could be adjusted by a controller (XST-191). Then, 100 g of sludge sample was used in each batch. Different pyrolysis temperatures (400, 500, 600, 700, and 800 °C for 0.5% Cu/dried sludge (DS)) and implanting concentration (0%, 0.5%, 0.6%, 0.8%, and 1.0% pyrolyzed at 650 °C) were studied. In order to remove the oxygen in the reactor, nitrogen gas was purged into the reactor at a flow rate of about 1000 mL/min for 30 min before pyrolysis. When syngas was no longer emitted in each experimental batch, the vertical reactor loaded with sludge samples was taken out. The volatiles evolved from the samples were burned in a combustor. The bio-oil was condensed and collected in the condensers and the combustion products were discharged directly into atmosphere after purification by NaOH solution absorption. Finally, the char was recovered

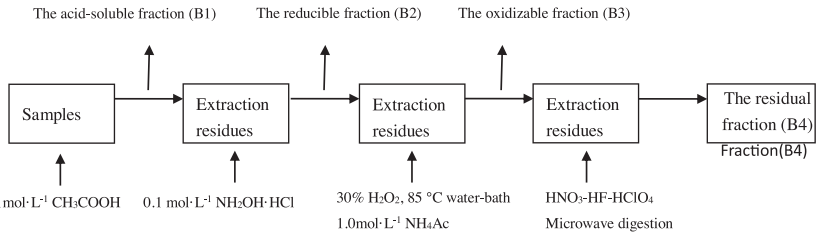


Fig. 3. BCR sequential extraction method scheme.