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Study on the effects of catalysts on the immobilization efficiency and mechanism of heavy metals during the microwave pyrolysis of sludge

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ABSTRACT

In order to enhance the immobilization of heavy metals in the bio-char during microwave pyrolysis, the immobilization efficiency and mechanism of heavy metals in the microwave pyrolysis of sludge with different alkaline catalysts were explored. Results showed that the leaching concentrations of heavy metals reduced greatly after pyrolysis, which were lower when catalyzed by CaO than those of Fe_2O_3. CaO was more favorable for the immobilization of Cr, Cu, Zn, Pb and Ni while Fe_2O_3 was more favorable for Cd. Different species distributions of heavy metals in the bio-char affected the leaching concentrations. Adding catalyst could significantly reduce the ecological risks of heavy metals in the bio-char, and CaO (RI = 15.17–20.43) had a better performance than Fe_2O_3 (RI = 16.88–21.79). When catalyzed by CaO, the formation of pores and co-crystal compounds in the bio-char determined the immobilization efficiencies of heavy metals.

1. Introduction

With the increase of the output of municipal sewage and treatment rates, the outputs of sewage sludge increase constantly, which causes great harms to human health and natural environment (Domínguez et al., 2006). The toxicity of sludge mainly results from the degradation-resistant organic matters and the heavy metals, among which, heavy metals are unable to be degraded by microorganisms but may enrich in the organisms through food chain to form other compounds with stronger toxicity, which causes severe contamination to the water, soils and atmosphere (Liu, 2007; Sánchez-Monedero et al., 2004). To date, amount of studies have been made on the removal and stabilization of heavy metals in the sludge, mainly focusing on the aspects of immobilization (cement, pitch and glass manufacturing) and incineration (Hii et al., 2014; Zhang et al., 2013), however, they all have obvious disadvantages. For example, as to immobilization, the volumes of the immobilized bodies increase a lot and the water-soluble heavy metals will be dissolved out. During incineration, plenty of poisonous and harmful gases will generate, and the treatment costs of the flue gas are high. To realize a proper treatment of the heavy metals contained in the sludge is still a key problem needed to be solved.

Microwave pyrolysis, as a new technology emerging in recent years, has been determined not only having the capability of effectively transformed the organic matters in the sludge into such energies as bio-gas (H_2 and CO) and bio-oil (Abubakar et al., 2013), but also can immobilize most of the heavy metals as Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+} and Pb^{2+} in the bio-char generated during the pyrolysis (more than 95%, and the others may exists in bio-oil or bio-gas, mainly the volatile) (Borges et al., 2014; Gan, 2000), which effectively reduces the generation of harmful gases, realizes the stabilization of heavy metals and further reclamation of sludge. In order to strengthen the immobilization of heavy metals in sludge into bio-char during the during the microwave pyrolysis, amount studies have been carried out on the influencing factors such as the microwave absorbing materials (Bu et al., 2012), pyrolysis temperatures (Cao et al., 2010; Tai and Jou, 1999), and so on. Studies have shown that temperature is one of the most important

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Table 1
Characteristics of sludge.

Proximate analysis (wt%)				Ultimate analysis[a,b] (wt%)			
Moisture	Ash[a]	Volatile	Fixed carbon	C	H	N	S
84.30	46.72	50.42	2.86	28.86	7.35	3.88	0.89
Heavy metals[b] (mg/kg sludge)		Cr	Cd	Cu	Zn	Pb	Ni
		126.2	33.4	591.4	3884.0	291.0	301.2

[a] Dry basis.
[b] Ash free basis.

operation conditions affecting the migration, transformation, and immobilization of heavy metals during the microwave pyrolysis of sludge, and the mechanisms and the optimal temperature on the immobilization of heavy metals in bio-char has been preliminarily illustrated by now (Abanades, et al., 2005; Caballero et al., 1997; Holbert and Lighty, 1998). With the increase of temperature, the structural properties of sludge changes, which enables the oxygen-containing functional groups to be removed from the surfaces of the solids, thus increasing the alkaline properties of bio-chars and leading to a good immobilization effects on the heavy metals (Huang and Yuan, 2016; Liu, 2007; Seames and Wendt, 2000).

Adding alkaline catalysts to the pyrolysis of sludge may be another choice. Studies have shown that the alkaline catalysts can react with the heavy metals in the sludge to change the migration and transformation properties of the heavy metals during the traditional heating pyrolysis process, thus influencing its thermochemical behaviors (Chen et al., 2015). As to the microwave pyrolysis of sludge, for the inside-out heat conducting mode (Hu et al., 2016), the migration and transformation behaviors and immobilization efficiency during the process of microwave pyrolysis of sludge comes to be a complex process with the actions of different kinds of alkaline catalysts. To date, many studies have been carried out on adding catalysts to the microwave pyrolysis to increase the quality and quantity of biofuel (bio-oil and bio-gas) generated (Mohamed et al., 2016). However, the characteristics and the heavy metals immobilized in the bio-char have been neglected usually. Whether and how the immobilization of heavy metals in the bio-char during microwave pyrolysis can be improved, no relevant reports have been found by now.

Therefore, two different alkaline catalysts (CaO and Fe_2O_3) were selected to study their positive effect on the immobilization of heave metals during the microwave pyrolysis of sludge in this work. The effects of CaO and Fe_2O_3 on the leaching concentration and the morphological transformation of the six kinds of heavy metals in the bio-char in the microwave pyrolysis of sludge under different temperatures were studied and compared firstly. Then, the ecological risks index of the bio-char with different catalysts were calculated and compared, in order to assess the immobilization performance of heavy metals in the bio-chars. At last, the chemical compositions, the crystalline structures and the morphologies of the dried sludge and the bio-char were analyzed to explore the immobilization mechanism of heavy metals during microwave pyrolysis of sludge with different catalyzing conditions.

2. Materials and methods

2.1. Raw sludge

The sludge used in this work was obtained from a wastewater treatment plant located in Shenzhen, China. The industrial analysis and elemental analysis results of the sludge were shown in Table 1. During the drying process, the raw sludge was dried at the temperature of 105 °C for 12 h till a constant weight. The dry sludge (DS) samples were cooled at room temperature, and then ground with a mortar into a particle size of 1 mm for analysis.

Table 2
Indices for the ecological risk assessment (Chabukdhara and Nema, 2012).

E_r	Potential ecological risk of single heavy metal	RI	Potential ecological risk of sludge/bio-char
$E_r < 40$	Low	$RI \leq 50$	Low
$40 \leq E_r < 80$	Moderate	$50 < RI \leq 100$	Moderate
$80 \leq E_r < 160$	Considerable	$100 < RI \leq 200$	Considerable
$160 \leq E_r < 320$	High	$RI > 200$	High
$E_r \geq 320$	Very high		

2.2. Microwave pyrolysis

The experimental device with the controlled experimental conditions reported in Ma et al. (2017) was used for the microwave pyrolysis of sludge. In this work, 30 g raw sludge and 3 g catalysts (CaO or Fe_2O_3) were mixed and pyrolyzed in the quartz tube at a final pyrolysis temperature range of 500–900 °C. The power knob was adjusted according to the displayed temperature to maintain the final temperature of the pyrolysis at a constant. The nitrogen gas was used to maintain an inert environment. The whole period for the pyrolysis of sludge 10–15 min. After pyrolysis, the bio-gas generated was collected by a 2-L air bag, the bio-oil generated was obtained after the removal of dichloromethane with a rotary evaporator, and the residual bio-char were collected from the quartz tube for further analysis of the heavy metals.

2.3. Analytical methods

2.3.1. Total amount of heavy metals

The DS and bio-char samples were digested using a microwave digestion system to measure the total amount of heavy metals. After digestion, the concentrations of heavy metals in the digestion solutions were examined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) and an inductively coupled plasma mass spectrometry (ICP-MS).

2.3.2. Leaching concentrations of heavy metals

The toxicity characteristic leaching procedure (TCLP) method was used to measure the leaching concentrations of the heavy metals in the DS and bio-char samples at the room temperature. In the experiments, the glacial acetic acid was diluted with the distilled water to prepare 1 L leaching agent with a pH of 2.65. The leaching agent was poured into a polyethylene oscillator bottle and mixed with 5 g DS or bio-char samples, after that, the bottle was closed, fastened and fixed on a rotary with a speed of 30 r/min. At last, the mixed solution inside the bottle was taken out and filtered with a 0.45 μm membrane. The filtered liquid was then analyzed by the ICP-AES and ICP-MS to measure the content of heavy metals.