



# Speciation and environmental risk assessment of heavy metal in bio-oil from liquefaction/pyrolysis of sewage sludge



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## HIGHLIGHTS

- Bio-oils were obtained from sewage sludge by liquefaction and pyrolysis.
- High total concentration of Cu, Cr, Pb, Zn, Cd, Ni in bio-oils were observed.
- Exchangeable and leachable Zn and Ni in bio-oils were found undesirably high.
- Bio-oils were quantitatively assessed to possess very high risk to the environment.
- Bio-oils from SS should be pretreated or upgraded before utilization.

## ARTICLE INFO

### Article history:

Received 17 March 2014

Received in revised form 22 July 2014

Accepted 4 October 2014

Handling Editor: S. Jobling

### Keywords:

Bio-oil

Heavy metal

Risk assessment

Pyrolysis

Liquefaction

## ABSTRACT

Liquefaction bio-oil (LBO) produced with ethanol (or acetone) as the solvent and pyrolysis bio-oil (PBO) produced at 550 °C (or 850 °C) from sewage sludge (SS) were produced, and were characterized and evaluated in terms of their heavy metal (HM) composition. The total concentration, speciation and leaching characteristic of HMs (Cu, Cr, Pb, Zn, Cd, and Ni) in both LBO and PBO were investigated. The total concentration and exchangeable fraction of Zn and Ni in bio-oils were at surprisingly high levels. Quantitative risk assessment of HM in bio-oils was performed by the method of risk assessment code (RAC), potential ecological risk index (PERI) and geo-accumulation index (GAI). Ni in bio-oil produced by pyrolysis at 850 °C (PBO850) and Zn in bio-oil by liquefaction at 360 °C with ethanol as solvent (LBO-360E) were evaluated to possess very high risk to the environment according to RAC. Additionally, Cd in PBO850 and LBO-360E were evaluated by PERI to have very high risk and high risk, respectively, while Cd in all bio-oils was assessed moderately contaminated according to GAI.

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## 1. Introduction

Sewage sludge (SS) is the main waste generated in the urban wastewater treatment process. It is a complex heterogeneous mixture of organic compounds, macronutrients, micronutrients, organic micropollutants, microorganisms, parasitic eggs and heavy metals (HMs) (Chen et al., 2008) and can be served as renewable energy source. Sludge-to-energy technologies such as pyrolysis and liquefaction, are gaining increasing attention worldwide

(Manara and Zabaniotou, 2012; Tyagi and Lo, 2013). However, the pyrolysis or liquefaction of SS may result in secondary environmental pollution if it is treated improperly. HM is one of the most toxic chemicals that may emerge during these processes (Devi and Saroha, 2014; Hwang et al., 2007; Waqas et al., 2014; Yuan et al., 2011).

Several studies have been focused on the behavior of HMs in SS during liquefaction or pyrolysis (Devi and Saroha, 2014; He et al., 2010; Trinh et al., 2013; Yuan et al., 2011). The pyrolysis/liquefaction process can enable HMs in SS to be concentrated mostly in one of the main products, bio-char (Trinh et al., 2013; Yuan et al., 2011). In our previous liquefaction study, most of the HMs (over 80% of Cu, Pb, Cr, and Cd and 70–80% of Zn and Ni) in SS were remained in liquefaction residues (bio-chars) after liquefaction

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(Yuan et al., 2011). In a pyrolysis study, significant release of HMs with low boiling points (e.g., As, Hg, Cd, and Se) from SS occurred during pyrolysis above 550 °C, whereas HMs with high boiling points (e.g., Pb, Co, Ni, Cu, Zn, and Sr) mostly remained in the bio-char (Trinh et al., 2013). During the pyrolysis/liquefaction process, HMs in SS distributed into bio-char with large portion, whereas the hazards of HMs in processed residues were markedly mitigated. According to the quantitative evaluation of the potential ecological risk and pollution degrees of HMs (Pb, Zn, Cu, Cd, Cr and Ni) in liquefaction residues, the mobility and leachability of HMs in residues were well suppressed compared to those of SS (Huang et al., 2011). The pyrolysis study of pulp/paper sludge also indicated that the increasing pyrolysis temperature enhanced the stabilization of HMs in the bio-chars and the potential risk of heavy metal pollution in the bio-chars was significantly reduced (Devi and Saroha, 2014). Meanwhile, the leachable concentrations of HMs in bio-char based on toxicity characteristic leaching procedure (TCLP) decreased sharply with increasing pyrolytic temperatures (Devi and Saroha, 2014). Considering the conservation of mass during these processes, bio-oil, the other main product of liquefaction/pyrolysis, may have taken away part of the toxic fractions of the HMs in SS. But the HM distributed to the liquid bio-oils during these processes were overlooked in the previous studies.

Recently, concerns have started to emerge on the potentially adverse environmental impacts of biofuels in consideration of toxic components in them (Bellas et al., 2013; Bluhm et al., 2012; Khan et al., 2007; Mezher et al., 2013). Bio-oil produced by liquefaction/pyrolysis has been regarded as one of the promising candidates in some districts to replace petroleum fuels for power generation, heat, or for extraction of valuable chemicals (Xiu and Shahbazi, 2012). However, bio-oil with high HM content would cause environmental pollutions during its marketing, storage and combustion. Environmental pollution from oil spills and waste fuel products dumping were taken place during marketing of fuel products (Adeniyi and Afolabi, 2002; Boughton and Horvath, 2004). Evidence of leakage from more than a million of the underground storage tanks and the leakage-contaminated soil were identified (Rauckyte et al., 2006). TCLP leachability of toxic metal in used engine oil indicated that Pb exceeded 5 ppm concentration level, which qualified it as a hazard (Rauckyte et al., 2006). Metallic species are also generally undesirable in automotive fuels because they are associated with engine corrosion, metal deposits on engine parts and poor fuel performance caused by oxidative decomposition (Dantas et al., 2010). Bio-oil with high HM content, if used as fuel for combustion or burning, would cause metal emissions into the atmosphere. HMs like As, Cd, Cr, Ni, and Pb found in urban atmosphere can be partly due to the combustion of fuels (Betha and Balasubramanian, 2013; Pacyna et al., 2007; Wang et al., 2003) and some of these elements have been reported to be linked with adverse human effects (Lim et al., 2007). To evaluate the environmental quality of the bio-oil derived from SS by liquefaction/pyrolysis and the environmental impact of its utilization, and to assess the environmental friendliness of the liquefaction and pyrolysis processes, it is necessary to make progress on the study of HM characteristics in the bio-oil.

The water-free bio-oils obtained from liquefaction and pyrolysis of SS were rather high viscosity, and even more like semisolid with extremely poor flow characteristics (Huang et al., 2013; Tian et al., 2011). In addition, the densities of liquefaction/pyrolysis bio-oil could be as high as 0.91–0.93 g cm<sup>-3</sup> for it contains heavy fractions (Tian et al., 2011; Huang et al., 2013). Thus, in this study, bio-oil was regarded as solid matter and simple sequential extraction procedure and risk assessment methods were implemented to it.

Liquefaction bio-oil (LBO) in this study was obtained from SS by liquefaction at 360 °C with typical polar protic solvent ethanol

(LBO-360E) and dipolar aprotic solvent acetone (LBO-360A), respectively. Pyrolysis bio-oil (PBO) was obtained from pyrolysis of SS at two common reaction temperatures 850 °C (PBO850) and 550 °C (PBO550), respectively. TCLP was employed for leaching test and qualitative toxicity assessment of the bio-oils. The speciation of HM in bio-oil was obtained by a simplified sequential extraction procedure modified from the Community Bureau of Reference (BCR) sequential extraction procedure. According to the assayed results, HM contamination degrees in bio-oils were quantitatively evaluated by employing risk assessment code (RAC), geo-accumulation index (AGI) and potential ecological risk index method (PERI), respectively.

## 2. Materials and methods

### 2.1. Materials

Dewatered SS sample was obtained from a municipal sewage treatment plant in Changsha, Hunan Province. The sample was dried in an oven at 105 °C for 24 h, followed by grinding and screening into fractions of particle diameter 30–120 meshes (0.12–0.60 mm). Then the meshes were stored in an airtight container at room temperature.

### 2.2. SS characterization

Prior to the experiment, the elemental composition of SS was analyzed by an elemental analyzer (Vario EL III, German) and the amount of combustible and ash in biomass samples were analyzed by burning them at 600 °C for 30 min according to (Huang et al., 2013). As shown in Table 1, the content of oxygen was 17.41% and ash as high as 39.2%, which may attribute to the abundant metallic compounds existed in the raw SS. The pH of SS was measured using a pH meter (PHBJ-260, China) by mixing SS with water and the solid/water (w/v) ratio was 1:5.

0.5 g of SS sample was digested by 13 mL HNO<sub>3</sub>–HClO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> (v, 30%) (5: 3, v/v) mixture on a hot plate and thereafter dissolved in 5% HNO<sub>3</sub> for heavy metal total concentration determination according to (Yuan et al., 2011). The BCR extraction procedure was performed to analyze the speciation of HMs in SS, presented in sequence: step one, acid soluble/exchangeable fraction (F1, exchangeable metal and carbonate-associated fractions); step two, reducible fraction (F2, fraction associated with Fe and Mn oxides); step three, oxidizable fraction (F3, fraction bound to organic matter); step four, residual fraction (F4). The details of the procedure were reported in our previous study (Yuan et al., 2011). The total concentration and each fraction of Cu, Cr, Pb, Zn, Cd and Ni in SS were detected by high-performance Inductively Coupled Plasma Optic Emission Spectrometer (ICP-OES, ICAP 6300, US).

### 2.3. Experimental procedure

#### 2.3.1. Production of bio-oil

PBO: pyrolysis of SS was carried out in a horizontal tubular furnace (China). In each experiment, 20 g of raw dried SS was placed into the quartz reactor carefully, and nitrogen (99.9%) was used as the purge gas at a rate of 200 mL min<sup>-1</sup> to maintain an inert atmosphere. The temperature was increased from room temperature to the target temperature (550 °C or 850 °C) at a constant heating rate 25 °C min<sup>-1</sup>, and held at the set temperature for 120 min. Bio-oil was collected by a trap system consists of a series of glass condensers in which water was used as the cooling solvent. After each test, bio-oil was evaporated under reduced pressure at 90 °C to remove the water content, and then cooled to room temperature and collected carefully.

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