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# Effects of Pb on pyrolysis behavior of water hyacinth

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ABSTRACT

Heavy metal contaminated biomass derived from biosorption is widespread and the disposal of the biomass needs to be paid more attention to avoiding second pollution. In this study, pyrolysis of Pb contaminated water hyacinth (Pb-WH) in a fixed-bed was investigated. The results indicated that the presence of Pb could increase the yield of pyrolytic bio-oil maximumly by 56% with only 0.6% lower of high heating value (HHV), while decreased the char and gas yield with a little higher concentration of $H_2$. The increased amount of carboxylic acids and decreased aromatics were responsible for the slightly decrease of HHV. The remained char was analyzed by flame atomic absorption spectrometry and X-ray diffraction analysis, showing that more than 82% of the Pb in the Pb-WH was kept in the char in the form of PbO and PbS. It is proposed that $Pb^{2+}$ stabilized the carboxyl or carbonyl groups and changed the position of chemical bond scission of aliphatic components formed via depolymerization of hemicellulose and NDS rather than decarboxylation at initial stage, thus forming more fatty acids by decreasing $CO_2$ concentration and promoting $H_2$ to release.

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## 1. Introduction

With increasing industrialization and economic development, the environmental and health issues resulting from heavy metal contaminated wastewater have attracted great attention. In order to sanitise wastewater a lot of techniques have been developed. Among these, biosorption is a promising and low-cost method, which is a remediation process for pollutant removal and/or recovery from wastewater by inactive biomass [1–4]. The large scale application of biosorption generates quantities of heavy metal contaminated biomass. Thus the disposal of biomass is receiving more attention.

Direct combustion of the biomass has been carried out worldwide since the ancient times. During the combustion, many toxic pollutants may produce, for example, polycyclic aromatic hydrocarbons and dioxins. Moreover, the absorbed heavy metals would be released to the environment again after the violent burning. Therefore, some mild thermal conversion methods such as pyrolysis to produce fuel products are more preferable to the direct combustion. Under mild pyrolysis conditions, the toxic pollutants can be condensed and collected while the heavy metals would be kept in the char in maximum.

A few literatures concerning pyrolysis as a tool for processing heavy metal contaminated biomass are available. Fast pyrolysis of heavy metal contaminated birch and sunflower was applied with controlled temperature and reaction parameters. It shows that an optimal pyrolysis temperature must be selected to avoid volatilizing the heavy metal out of the char. The heavy metals could be well kept in the char below 400 °C, however, sand matrix or fumed silica matrix must be used to help keeping the heavy metals not to release to the condensable or gas products above 400 °C [5,6]. Koppolu et al. [7–9] prepared "Synthetic hyperaccumulator biomass" to mimic the metal concentration in actual hyperaccumulators, and found that the heavy metals did increase the yield of condensable or gas products and the catalytic activities of the metals were different, however, only Ni, Zn, Cu, Co or Cr contaminated biomasses were investigated in their work. Liu et al. [10] specifically studied the effect of Cu on the pyrolysis of biomass by fast pyrolysis and found an appropriate amount of Cu could increase the yield of tar but decrease the yield of gas. Large amount of the Cu could be kept in the char, and the higher the temperature was, the more the Cu released to the gas or condensed products. Stals et al. [11] studied flash pyrolysis of heavy metal contaminated hardwoods originating from phytoremediation and found that the pyrolysis oil did not contain considerable amounts of heavy metals. However, in this work, the contents of heavy metals in the feeds were quite low, in which Pb was only 14.4–26.3 ppm. Therefore, it is hard to draw such a conclusion that the heavy metals could be well kept in the char by the fast pyrolysis. Moreover, the effect of Pb is not

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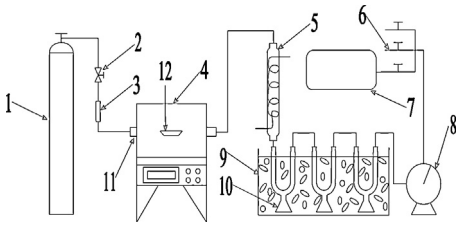


**Fig. 1.** Schematic diagram of the fixed-bed reactor setup. (1, $N_2$ gas source; 2, flow control valve; 3, rotor flow meter; 4, horizontal tube furnace; 5, graham condenser; 6, three-pole connection value; 7, gas collector; 8, wet type gas meter; 9, iced-water bath; 10, liquid collector; 11, quartz tube; and 12, quartz boat).

well investigated for its microscale content. To our knowledge, with the development of the modern industry, a large number of rivers, lands and sea areas are polluted with Pb, which seriously threatens the health of human beings by food chains [12]. It is realized that phytoremediation can be an applicative method to recover the polluted soils and waters.

Water hyacinth is a fast growing plant even in the polluted waters, and can absorbed Pb effectively. Pb concentrations in the water hyacinth can be higher than 1.0% (wt%) in heavy metal contaminated sites [13,14]. Therefore, water hyacinth can be an effective biomass for recovering Pb from the polluted waters and then the pyrolysis of the Pb contaminated water hyacinth should be investigated. In this work, Pb contaminated water hyacinth samples with a series Pb concentrations were prepared and their pyrolysis behaviors were studied for understanding more about the effect of the Pb. In order to investigate the forms of the Pb kept in the char, samples with Pb concentration higher than 1.0% was prepared for sensitive enough to X-ray diffraction (XRD). The characteristics of the produced bio-oils and gas and the transformation of Pb during the pyrolysis were also studied.

## 2. Materials and methods

### 2.1. Materials and samples preparation

The WH biomass was collected from a lake near Huaqiao University in Xiamen, China. The biomass was first chipped and air-dried. After drying it was cut into 0.16 mm with a high-speed rotary cutting mill. Prior to use, the biomass was dried at 105 °C. The components of water hyacinth was determined by the method of Van Soest. Water hyacinth is composed of cellulose (8.58%), hemicellulose (43.29%), lignin (10.12%), neutral detergent solute (NDS, 37.70%) and acid-insoluble ash (0.31%). NDS include protein, fat, sugar, etc.

Adsorption experiments were conducted in a series of 250 mL flasks at 25 °C. A certain amount of WH and 100 mL of $Pb(NO_3)_2$ solution were mixed in the flasks in different concentrations and shaken in a constant temperature bath oscillator with an frequency of 150 rpm for 24 h. Then, the mixture was separated by filtration. The obtained solid was dried at 105 °C and then sieved again to collect the particles with a size of 0.16 mm for further use.

### 2.2. Pyrolysis of WH and Pb-WH

Fig. 1 depicts the experimental fixed-bed reactor setup. The pyrolysis experiments were performed in batches with 15 g samples in a horizontal tube reactor, constructed of quartz. High purity $N_2$ was used as the sweep gas (240 ml/min). The sample was heated till a preset final temperature (275–550 °C) with a heating rate of 30 °C/min and maintained for 10 min, after which the experiment was terminated. A condenser was connected to the output of the reactor and the bio-oil was condensed in a collector. The char collected in the reactor was weighed at the end of experiment. The gas ($CO_2$, CO, $H_2$, and $CH_4$) was collected to a gas collector. The gas yield was calculated based on the analysis of the mole fraction and cumulative production volume, combined with the molecular weight (1 mol is equivalent to 24.45 L for the gas at room temperature and ambient pressure). The yield of bio-oil was calculated by subtraction.

**Table 1**
Samples digestion procedure.

| Time (min) | Power (W) |
|---|---|
| 5 | 700 |
| 25 | 1000 |
| 15 | 0 |

### 2.3. Analytical methods

The Pb concentration in the Pb-WH, char and bio-oil samples was determined by flame atomic absorption spectrometry (FAAS, TAS-990). Before measurement, the samples were digested with a microwave digestion system (Multiwave 3000) as follows: 200 mg of the sample was carefully weighed in a PTFE vessel and 5.00 ml of $HNO_3$ was added, and then a microwave program according to Table 1 was applied. After digestion, samples were diluted with purified water to 50.0 ml. The Pb concentration in the digested solution was determined.

XRD was used to analyze the existing form of Pb in the chars of Pb-WH. XRD pattern was recorded using a SmartLab 3 kW diffractometer to scan over the angular $2\theta$ range of 10–80° with a scanning speed of 5°/min.

The released gaseous product was analyzed by gas chromatography (GC-9160) after removing moisture. During the process, the gaseous product was separated using a TDX-01 packed column (1 m × 0.3 mm) and detected by a thermal conductivity detector (TCD). Ar was used as the carrier gas and the temperature of TCD and oven were 100 °C and 60 °C, respectively.

The bio-oils were dissolved in trichloromethane ($CHCl_3$) and analyzed by gas chromatography/mass spectrometry (GC/MS, GCMS-QP2010). Ar was employed as the carrier gas at a constant flow rate of 1.5 mL/min, and a split of the carrier gas (1:10) was used. The temperature of the GC–MS injection port was 250 °C. The GC oven temperature was programmed from 40 °C to 140 °C at 12 °C/min and to 190 °C at 8 °C/min, and then to 250 °C at 8 °C/min and keep in 250 °C for 3 min. The injection volume was 1 μL/min. HHVs of the bio-oils were determined using a ZDHW-2A automatic bomb calorimeter.

## 3. Results and discussion

### 3.1. Pyrolysis performance of Pb-WH and WH

Yields of pyrolytic products of WH and Pb-WH (6.0 wt%) are shown in Fig. 2. The char yields of both WH and Pb-WH pyrolysis monotonously decrease with the increasing temperature, while the gas yield of WH shows an fluctuation trend with the increase of temperature and the gas yield of Pb-WH changes slightly from 275 °C to 375 °C and then increases from 375 °C to 550 °C. This result is opposite with those reported in literatures [15,16]. Bio-oil yields of both WH and Pb-WH increase with the pyrolysis temperature increasing from 275 °C to 450 °C and then decrease when the pyrolysis temperature is up to 550 °C. The maximum oil yields for both WH and Pb-WH are obtained at 450 °C, which are 37.5% and 58.5%, respectively. The maximum oil yield of Pb-WH is about 47% higher than that of WH. The bio-oil yields of Pb-WH are higher than those of WH at all temperatures, whereas the char and gas

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