Lower-Temperature Pyrolysis to Prepare Biochar from Agricultural Wastes and Adsorption for Pb²⁺

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Many agricultural activities generate large quantities of biomass wastes. Using these wastes to produce value-added products or energy has become very important in recent years. Heavy metals such as lead are among the most toxic chemical water pollutants from natural or anthropogenic sources. The goals of this work were to prepare three biochars from maize straw (BMS), sunflower straw (BSS), and wheat straw (BWS) under partial limited oxygen condition and to characterize their ability to adsorb Pb²⁺ from water. The sorption kinetics as well as the influence of solution pH and Pb²⁺ concentration was investigated. The three biochars had a good performance for Pb²⁺ adsorption. A greater adsorption efficiency was observed for BMS and BSS than for BWS. The physico-chemical properties of the biochars showed that the adsorption performance was correlated with preparation conditions, raw material types, higher total porosity, and micro-structure.

Keywords: Agricultural wastes; Biochar; Lower-temperature pyrolysis; Partial limited oxygen; Adsorption

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INTRODUCTION

Sorption is an effective method for the removal of metals from water. Activated carbon and biochar have been developed for this purpose. Activated carbon often shows superior performance as an adsorbent for heavy metal ions because of its rich pore structure and large specific surface area. However, the activation process is complex and introduces acidic or alkaline salts, which can be regarded as pollutants. Thus, biochar is a promising sorbent due to its environmental friendliness (Tan *et al.* 2016). Biochar requires a lower investment than conventional activated carbon, which makes it more sustainable. The accumulation of agricultural wastes (AW) and their burning for disposal is a major global environmental problem (Sobati *et al.* 2016), which has prompted the study of biochar made from agricultural wastes. In general, biochar is produced by pyrolysis under oxygen-limited conditions between 200 °C and 800 °C (Chen *et al.* 2016), but the major problem holding back the commercialization of biochar is the complexity of the process (Liu *et al.* 2015). This complexity is mainly related to the necessity of oxygen-limited conditions, which are achieved by evacuating or introducing an inert gas (*i.e.*, N₂, Ar.). In addition, the required higher pyrolysis temperature increases the cooling time (Jung *et al.* 2016).

The aim of this work was to prepare biochar under a partial limited oxygen environment at a lower temperature. In this study, maize straw (MS), sunflower straw (SS), and wheat straw (WS) were employed as the raw materials for biochar production. The biochar produced in a partial limited oxygen environment at lower temperature demonstrated good adsorption of Pb^{2+} from water with different concentrations of Pb^{2+} . The adsorption performance of the biochar derived from maize straw (BMS) and sunflower straw (BSS) was better than that produced from wheat straw (BWS).

EXPERIMENTAL

Materials and Equipment

Sunflower straw, maize straw, and wheat straw, which are by-products of agricultural crops, were harvested from Yuling, China, dried at 80 °C for 72 h in a blast oven (DHC-9053A, DAOHAN Industrial Co., Ltd., Shanghai, China), and crushed to 1 to 2 mm by a powder machine. The dry solids were sealed in a vacuum bag for carbonization.

Raw materials of about 25 g from sunflower straw, maize straw, and wheat straw were sealed in a crucible ($\varphi 90 \times 45$) and pyrolyzed in a box-type resistance furnace (SX-25-10, Shanghai Boluo Laboratory Equipment Co., Ltd., Shanghai, China) at 300 °C (10 °C/min⁻¹) for 45 min. The products resulting from sunflower straw, maize straw, and wheat straw were named BSS, BMS, and BWS, respectively; the yield for all samples was more than 30%. After cooling, the BSS, BMS, and BWS were sealed in vacuum bags.

Methods

The three types of carbon were characterized by several techniques. The proximate analysis of the samples was conducted by thermogravimetry (TG) coupled with a differential scanning calorimetry (DSC) (STA449F3, NETZSCH, Selbe, Germany), as previously described (Rashidi *et al.* 2012; Chowdhury *et al.* 2016a). In the TG analysis, 5 to 10 mg of each powder sample was sealed into a ceramic crucible ($\Phi 8 \times 5$) and heated under a 5 mL/min N₂ flow at 1300 °C with a heating rate of 10 °C/min. The phase identification of the samples was analyzed by X-ray diffraction (XRD) (X'Pert PRO, Almelo, Holland) (Chand *et al.* 2008). The morphology of the samples was characterized by scanning electron microscopy (SEM) (Zeiss EVO18, Oberkochen, Germany) (Chand *et al.* 2009).

The Water Absorption Performance (WAP) is also referred to as the water holding capacity. According to EBC guidelines (DIN ISO 14238-2011), $5\sim10$ g of the three biochars were immersed in water for 24 h, and then the three samples were placed on a sand-bed heaped by napkins for 2 h to remove excess water, respectively. Then, the saturated samples were weighed, dried at 40 °C, and then weighed again.

Surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR) analysis (Nicolet iS-10, Thermo Fisher Scientific). The samples were dried and crushed with KBr. The sample mixed with KBr was pressed to form transparent sheets. Spectra were measured in the range between 400 cm⁻¹ and 4000 cm⁻¹. Basic properties (apparent density, total porosity analysis, *etc.*) of three biochars were measured by high precision density tester (LH–120YE, Xiamen Qunlong Instrument Co., Ltd, Xiamen, China). The distilled water was added to the density meter sink up to the mark. From 5 to 10 g of the biochar was put into a weighing pan and the weight was recorded. Then the material was immersed in water and kept immersed for about 3 s. Then the samples was taken out, wiped off, and placed into the weighing pan again. Finally, the result was read from the instrument.



















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