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Effect of pyrolysis temperature on characteristics and aromatic contaminants adsorption behavior of magnetic biochar derived from pyrolysis oil distillation residue

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HIGHLIGHTS

- Magnetic biochars were easily synthesized by pyrolyzing distillation residue.
- Pyrolysis temperature showed a pronounced effect on magnetic biochar properties.
- Adsorption of aromatic contaminants on magnetic biochars were investigated.
- Adsorption mechanisms associated with biochar properties and target contaminants.

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ABSTRACT

The magnetic biochars were easily fabricated by thermal pyrolysis of $Fe(NO_3)_3$ and distillation residue derived from rice straw pyrolysis oil at 400, 600 and 800 °C. The effects of pyrolysis temperature on characteristics of magnetic biochars as well as adsorption capacity for aromatic contaminants (i.e., anisole, phenol and guaiacol) were investigated carefully. The degree of carbonization of magnetic biochars become higher as pyrolysis temperature increasing. The magnetic biochar reached the largest surface area and pore volume at the pyrolysis temperature of 600 °C due to pores blocking in biochar during pyrolysis at 800 °C. Based on batch adsorption experiments, the used adsorbent could be magnetically separated and the adsorption capacity of anisole on magnetic biochars was stronger than that of phenol and guaiacol. The properties of magnetic biochar, including surface area, pore volume, aromaticity, grapheme-like-structure and iron oxide (γ-Fe_2O_3) particles, showed pronounced effects on the adsorption performance of aromatic contaminants.

1. Introduction

The fast pyrolysis technology has been considered as a promising process since it offers a feasible method to convert waste biomass into liquid pyrolysis oil. Unfortunately, the pyrolysis oil consists of a large number of unstable oxygen-containing compounds, and it is difficult to directly apply the pyrolysis oil in existing equipment (Li et al., 2016c, 2015b). Therefore, it is very necessary to upgrade pyrolysis oil.

Distillation offers a feasible and effective way to obtain the high-grade fuel and high-value chemicals from the biomass pyrolysis oil. Most researches have been conducted to the production of the volatile fraction, in which the distillates have been achieved in various applications either as an energy or chemical source (Capunitan and Capareda, 2013; Zhang et al., 2013b). In fact, approximately 30–50 wt.% solid residue as a by-product was parallel formed after distillation of pyrolysis oil, which can be seen in the previous studies (Capunitan and Capareda, 2013; Zheng and Wei, 2011). In order to achieve comprehensive utilization of pyrolysis oil, the parallel generated distillation bottom (or distillation residue) should be concerned.

Unfortunately, there were by far very few studies have focus on the application of the distillation residue derived from pyrolysis oil. Zhang et al. (2013b) made distillation residue a source of renewable chemicals using co-pyrolysis. Elkasabi et al. (2015) applied the bio-oil distillate bottoms (distillation residue) as a feedstock to further upgrade for the production of calcined coke.

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In recently published paper, the distillation residue was utilized as solid fuel to co-fire with lignite, in which the waste was recycled (Li et al., 2016b). In fact, the development of magnetic biochar from biomass (especially agricultural waste) have been attracted many researchers (Kundu et al., 2015; Thines et al., 2017). These magnetic biochar showed a remarkable application as an adsorbent for various wastewater treatments, which may be due that the magnetic biochars not only can adsorb the contaminants from aqueous solutions, but also can be easily isolated with external magnets after adsorption. Two publications reported the production of magnetic bio-char derived from palm oil empty fruit bunch as the raw material by using microwave heating technique (Mubarak et al., 2014, 2016). Thines et al. (2016) focused on the conversion of the durian's rind into magnetic biochar in the presence of three different metallic salts by employing a novel vacuum condition in an electrical muffle furnace. Noraini et al. (2016) employed a novel method for the preparation of magnetic biochar from sugarcane bagasse by microwave-assisted pyrolysis at a microwave power of 600 W. Wei et al. (2016) obtained magnetic biochar composite from shell as raw material by using co-precipitation method in the presence of $FeCl_3$ and $FeSO_4$. However, there is no study on the application of pyrolysis oil distillation residue for the synthesis of magnetic biochar using for the adsorption of aromatic contaminants from aqueous solution in the literature. Various aromatic pollutants in aqueous solution were a threat to human health. And adsorption was one of the convenient method for the organic contaminants removal from aqueous solution.

In this work, a novel magnetic biochar has been easily fabricated using the discarded material, the rice straw pyrolysis oil distillation residue, with impregnated $Fe(NO_3)_3$. The pyrolysis of the impregnated distillation residue was carried out at 400, 600 and 800 °C. The effect of pyrolysis temperature on the characteristics of magnetic biochars were investigated comprehensively in the study. In addition, batch adsorption experiments were conducted to investigate the adsorption capacity of the magnetic biochars to various aromatics (i.e., anisole, phenol and guaiacol). It is anticipated that the feasible method presented here can achieve the comprehensive utilization of the distillation by-product of pyrolysis oil.

2. Materials and methods

2.1. Materials

The rice straw pyrolysis oil studied in this work was kindly provided by Shaanxi Yingjiliang Bio-energy Corporation, China. The bio-oil was produced in a downstream circulating fluidized bed reaction by flash pyrolysis of rice straw (500 °C/s and 500 °C for the heating rate and reaction temperature, respectively). The pyrolysis oil poured into a round-bottom flask was distillated at a certain temperature (140, 180, 220 and 250 °C) for 30 min. Then, the distillate bottom was obtained. The distillation residue was the distillate bottom. The detail experimental procedure about the distillation was described in the reported paper (Li et al., 2015a). The iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), guaiacol, anisole and phenol were obtained from Aladdin-reagent, China.

2.2. Preparation of magnetic biochar

In this study, the magnetic biochar was synthesized using pyrolysis oil distillation residue as raw material. The distillation residue was initially washed with DI water and ethanol to remove impurities, respectively, and dried in an oven at 80 °C for 12 h under air atmosphere. The dried distillation residue was then grinded to 200 mesh. Subsequently, the grinded distillation residue (5 g) was immersed into the prepared $Fe(NO_3)_3$ solution (2.02 g $Fe(NO_3)_3$ in 20 mL of DI water). After stirring for 2 h, the sample was dried at 80 °C for 12 h under air atmosphere. The obtained material was pyrolyzed for 2 h under nitrogen (N_2) flow of 100 mL/min^{-1} at a heating rate of 10 °C/min. The pyrolysis temperature were 400 °C, 600 °C and 800 °C, respectively. The obtained magnetic biochars (MB) were grinded to 200 mesh, washed with DI water, filtered, dried (60 °C, 4 h) in a vacuum oven, and sealed in a container before use. In this study, MB 400, MB 600 and MB 800 were the magnetic biochars prepared at the pyrolysis temperature of 400 °C, 600 °C and 800 °C, respectively.

2.3. Characterization

Ultimate analyses were performed on the elemental analyzer (Vario micro cube, Elementar, Germany). Thermogravimetric analysis was analyzed by TG (TG 209 F3, Netzsch, Germany). For each experiment, approximately 5 mg of sample was processed and heated up to 900 °C at heating rate of 10 °C/min under nitrogen or air atmosphere. The DSC analysis of samples (MB 400, MB 600 and MB 800) were performed on the DSC analyzer (DSC 2, Mettler-Toledo, Switzerland) under nitrogen purge of 80 ml/min and at the heating rate of 10 °C/min. The surface area, pore volume, and pore size of the magnetic biochars were determined with an instrument (V-Sorb X800, Gold app instruments, China). The surface morphology of magnetic biochars were studied by scanning electron microscopy (S-4800, Hitachi, Japan). Chemical functional groups of magnetic biochars were analyzed using FTIR (FTS6000, Bio-rad, US). The crystallinity and structure of the magnetic biochars were analyzed through XRD (D8-Advance, Bruker, Germany) with Cu Kα radiation (λ = 1.542 Å) at 40 kV and 40 mA and scanned from 10 to 90° at a rate of 0.5°/s. The magnetic properties of MB 400, MB 600 and MB 800 were evaluated using Vibrating Sample Magnetometer (VSM).

2.4. Batch adsorption experiments

Adsorption of aromatics (anisole, phenol and guaiacol) were conducted using batch adsorption approach. The adsorption experiments were performed over the initial aromatics concentration range from 3 to 35 mg/L. About 0.0090 g magnetic biochar was weighed to each 50 mL tube and then 30 mL aromatics solution with one specific concentration was added. The mixtures were shaken for 24 h at 298.15 K on the shaker, which is sufficient for reaching equilibrium. Then, the samples were centrifuged for 5 min at 4000 rpm and filtered using a 0.22 μm nylon membrane filter. The aromatics concentrations were determined using an ultraviolet–visible (UV–vis) spectrophotometer (TU 1900, Purkinje General Instruments Co. Ltd., China) at 269 nm (for anisole), 270 nm (for phenol) and 274 nm (for guaiacol). The magnetic biochars were obtained for characterization after adsorption of phenol over the initial aromatics concentration of 35 mg/L.

3. Results and discussions

3.1. Characterization of magnetic biochar

3.1.1. Ultimate analysis

The elemental composition of the magnetic biochars (MB 400, MB 600 and MB 800) were investigated and presented in Table 1. The results showed that the carbon contents of magnetic biochar decreased with the pyrolysis temperature increasing from 400 °C to 800 °C. It may be attributed that higher pyrolysis temperature led to the larger loss of volatiles in distillation residue. In addition, the H/C atomic ratio could be applied to evaluate the aromaticity of