



# Physi-chemical and sorption properties of biochars prepared from peanut shell using thermal pyrolysis and microwave irradiation<sup>☆</sup>



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## ABSTRACT

Microwave irradiation (MW) is an effective technique in heating and pyrolysis. This study compared the properties of peanut shell-biochars produced using MW and muffle furnace (FN). At the same pyrolysis temperature, MW biochars preserved more biomass (as indicated by their higher yields and higher abundance of functional groups) and possessed larger surface areas due to the high abundance of micropores. MW biochars generally exhibited higher adsorption of carbamazepine (CBZ) and bisphenol A (BPA) than FN biochars. However, their surface area-normalized sorption was lower, suggesting that the inner pores may not be fully available to CBZ and BPA sorption. We observed significant free radical signals in both types of biochars. Although CBZ and BPA did not degrade in the biochar sorption systems, the potential role of stronger free radical signals in MW biochars for organic contaminant control may not be overlooked in studies with other chemicals.

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## 1. Introduction

Biochars are carbon-rich materials produced through thermal decomposition of biomass under an oxygen-limit environment (Xiao et al., 2014; Yang et al., 2016b). These particles have shown great potential in carbon sequestration, acidic soil neutralization, nutrient accommodation, and soil fertility improvement (Lai et al., 2013; Qian and Chen, 2013). Consequently, biochars are recommended as soil amendments (Chan et al., 2007). In addition, biochars are potentially efficient adsorbents for organic contaminant removal (Mohan and Pittman, 2007). For example, biochars showed excellent adsorption (with the aspects of both capacity and affinity) to various contaminants, including heavy metals (Uchimiya et al., 2010), hydrophobic organic contaminants (Ghaffar et al., 2015; Wu et al., 2013) as well as ionic organic contaminants (Zheng et al., 2013). The surface area, inner pores, surface functional groups, and ash contents were all discussed for their contribution to the apparent sorption (Chen et al., 2008). Recently, investigators

have detected significant free radical signals in biochars (Liao et al., 2014). Degradation of organic contaminants by the free radicals in biochars was proved by the detected degradation byproducts as well as the low recoveries of the chemicals in the sorption systems (Yang et al., 2016a).

All the above-mentioned biochar properties and application potentials are greatly dependent on biochar generation techniques. Previous studies have compared biochars produced by different technique, such as microwave irradiation, conventional pyrolysis, and hydrothermal carbonization (Huang et al., 2013; Wu et al., 2013; Zhu et al., 2014). Among these techniques, microwave irradiation was proposed to be an effective, energy saving, and fast technique for biomass pyrolysis (Jones et al., 2002; Luque et al., 2012). Although this method may be limited in large scale field application, it could be beneficial in advanced application of biochars. The main difference between microwave irradiation and conventional thermal pyrolysis is the mechanism of heat generation (Menendez et al., 2010). Thermal pyrolysis is generally performed in kilns or electric furnaces, where the biomass is pyrolyzed indirectly through heat conduction and convection. However, the microwave irradiations supply energy directly to the biomass. The microwave energy is easily transformed into heat inside the particles by dipole movement and ionic conduction (Jones et al., 2002).

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In the presence of polar molecules, the electric field of the microwaves induces oscillation of specific molecules or atoms as they try to align themselves with the alternating field. Subsequently, the biomass is heated and pyrolyzed (Hu and Cheng, 2013). In the presence of charged particles, such as  $\pi$ -electrons in biomass, an electron shuttle with the electromagnetic field is induced. As the electrons cannot couple to the changes of the electric field, energy is transferred to heat due to the Maxwell–Wagner effect (Menendez et al., 2010).

Previous studies have successfully applied the MW technique for biochar and biofuel production (Li et al., 2016), and biochar activation or modification (Namazi et al., 2016). Furthermore, MW biochar properties have been extensively investigated (Zhu et al., 2015). However, these studies were focused on MW methodology, and comparison with biochars from other techniques was not carried out. In addition, studies seldom investigated how these properties were related to biochar interactions with pollutants. Liao et al. (2012) studied sorption properties of MW biochars to dyes, but they used furnace biochars modified by MW irradiation, not the original biomass for biochar production. Biochars produced from MW pyrolysis have higher surface area and pore volume than those from conventional heating processes (Luque et al., 2012; Menéndez et al., 2007; Zhu et al., 2015). Therefore, MW pyrolysis can provide a new technique for making more porous biochar, which can be used in sorption applications (Li et al., 2016).

The main objective of this study was to compare MW and FN biochar properties related to their interactions with pollutants. The compared properties were mostly focused on those determining biochars to be used in wastewater treatment, and thus included oxygen-containing functional groups, porous structure, surface area, reactivity, as well as sorption characteristics to organic contaminants. Carbamazepine (CBZ) and Bisphenol A (BPA) were selected as the adsorbates in this study because of their similar hydrophobicity and molecular mass, but different functional groups and molecular structure. In addition, both chemicals have attracted some research attention because of their health risks. CBZ is frequently used as an antiepileptic drug, and BPA is widely used for plastic production. They could not be removed completely using traditional water treatment technologies. Therefore, they may be discharged into the environment and cause health concerns (Zhang et al., 2008; Pan et al., 2008). Due to the enlarged area and the improved quality of the surface of MW biochars, a higher adsorption and thus removal efficiency of CBZ and BPA on the MW than on the FN biochars may be expected.

## 2. Materials and methods

### 2.1. Materials

The biochar precursor material, peanut shells, was obtained from a local market in Yunnan, China. These peanut shells were dried in an oven at 60 °C, and then crushed and sieved through a 60-mesh sieve. The pretreated raw materials were used for biochar preparation. Analytical grade reagents CBZ and BPA were obtained from Beijing Chemicals Reagent Company (Beijing, China). Selected physico-chemical properties of CBZ and BPA are given in the Supplementary material (Table S1).

### 2.2. Biochars preparation

Biochars were prepared in a microwave irradiation (MW) unit or a muffle furnace (FN). In order to minimize their contact with air, the particles were placed in and fully occupied a ceramic crucible, covered and then placed into the pyrolysis device. The feedstock was pyrolyzed with a heating rate of 10 °C·min<sup>-1</sup>, held for 2 h at 200 °C,

400 °C or 600 °C. All the processes were carried out under nitrogen atmosphere until the temperature decreased to room temperature. Specifically, MW biochars were produced in a MW unit of 2.450 GHz at 500 W. To avoid the impact of dissolvable minerals and organic matter to the apparent sorption experiment, the treated particles were repeatedly washed with hot and cool distilled water until constant pH. In general, the pH of biochars ranged from 6.4 to 8.5, as summarized in Table S2. The particles were then dried in an oven at 105 °C ( $\pm 5$  °C) over night and stored in brown bottles for subsequent use.

### 2.3. Characterization of biochars

Biochar surface areas and porous structures were determined by N<sub>2</sub> adsorption at 77 K using a volumetric gas adsorption instrument (Autosorb-1C, Quantachrome, USA) (Peng et al., 2012). Elemental composition analysis was performed using a Vario Micro cube elemental analyzer (Elementar Company, Germany). X-ray photoelectron spectroscopy (XPS) measurement (PHI 5000 Versaprobe-II) brought about quantitative evaluation of the surface elemental composition (C, O and N) for the investigated biochars. The morphology of biochars was observed by scanning electron microscopy (SEM), equipped with an EDX Thermo Fisher Noran System 7 (Thermo Fisher Scientific, Waltham, MA, USA). The functional groups were studied with Fourier transformed infrared spectroscopy (FTIR, Varian 640-IR, USA). The FTIR spectra were recorded at room temperature in the wave number range of 400–4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution. The detailed methods of the above-mentioned techniques are provided in supplementary materials.

All the particles were also subject to EPR measurement. Briefly, 2 mg of particles were loaded into a micropipette (from Germany, 1.0 mm in i. d. 1.5 mm in o. d. and 125 mm in length) and sealed with vacuum grease at one tip. These loaded samples were monitored for free radical signals on an EPR spectrometer (Bruker, A300–6/1, X-band) with a single cavity, a modulation of 100 kHz and microwave frequencies of 9.2–9.9 GHz. The typical parameters for EPR measurement were as follows: the sweep width was 100 G, the modulation amplitude was 1.00 G, and the resolution in the X axes was 1024 points. The EPR microwave power was set specifically to 31 dB (or 0.131 mW) and the sweep time was 81.92 ms.

### 2.4. Adsorption experiments

CBZ (50 mg/L) and BPA (50 mg/L) were separately dissolved in background solution (0.02 M NaCl and 200 mg/L NaN<sub>3</sub>) as stock solutions. The stock solutions of CBZ or BPA were diluted using the background solution to 9 concentrations spanning in the range of 1–50 mg/L. The adsorption experiments were conducted in glass vials and the solid:aqueous ratios (w:w) were in the range of 1:200–1:2000 based on our preliminary experiments. All the vials were kept in the dark and were shaken in an air-bath shaker at 25 °C for 7 d. This time period was sufficient to reach apparent equilibrium for both chemicals according to our preliminary study. Each condition has two replications. After equilibrated for 7 d, all the vials were placed overnight and centrifuged at 3000 g for 10 min. The solution pH at equilibrium was measured using a pH meter. The supernatants were subject to quantification of solute concentration.

The sorption kinetics of CBZ and BPA with the initial aqueous-phase concentration of 7.07 mg/L was investigated for biochars produced at 600 °C. The same concentrations of CBZ and BPA solution without solid particles were used as the initial concentration references. The solid:aqueous ratios (w:w) were fixed at 1:1000. The sorption kinetics experiments were carried out in 40 mL vials with Teflon-lined screw caps. At the selected time points (2, 4, 6, 12,

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