



# Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon



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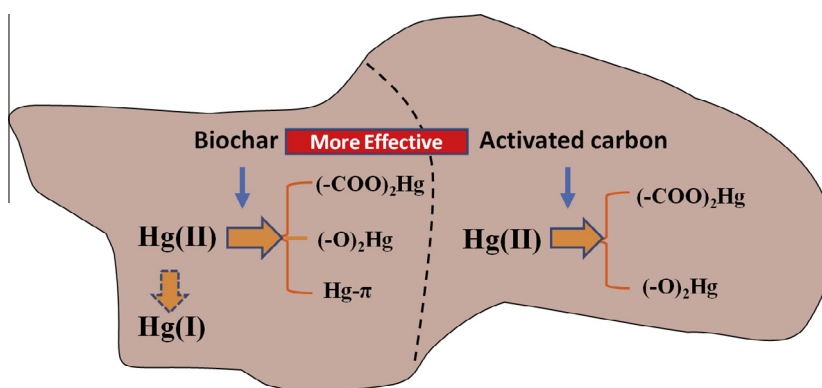
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## HIGHLIGHTS

- Biochars showed higher effectiveness for Hg(II) sorption than activated carbon.
- Hg(II) sorption by biochar was mainly attributed to the C=C or C=O induced Hg- $\pi$  binding.
- Formation of  $(-\text{COO})_2\text{Hg}$  and  $(-\text{O})_2\text{Hg}$  were responsible for the Hg(II) sorption by activated carbon.
- Biochar can be a substitute of activated carbon for removal of Hg from wastewater.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Two biochars were produced from bagasse and hickory chips (referred to as BB and HCB, respectively) and evaluated for their sorption ability of Hg(II) in aqueous solution. A commercial activated carbon (AC) which is commonly used for Hg(II) removal was included for comparison. Both biochars showed higher sorption capacities than AC, following the trend of BB > HCB > AC. The sorption of Hg(II) by BB and AC was mainly attributed to the formation of  $(-\text{COO})_2\text{Hg}^{\text{II}}$  and  $(-\text{O})_2\text{Hg}^{\text{II}}$ . As a result, the adsorption capacity of Hg(II) by BB decreased 17.6% and 37.6% after  $-\text{COOH}$  and  $-\text{OH}$  were blocked, respectively and that of Hg(II) by AC decreased 6.63% and 62.2% for  $-\text{COOH}$  and  $-\text{OH}$  hindered, respectively. However, blocking the function groups had little effect on the Hg removal by HCB since sorption of Hg(II) by HCB was mainly resulted from the  $\pi$  electrons of C=C and C=O induced Hg- $\pi$  binding. Further X-ray photoelectron spectroscopy analysis indicated the possibility of reduction of the Hg(II) to Hg(I) by phenol groups or  $\pi$  electrons during the removal of Hg(II) by both biochars. In conclusion, biochar is more effective than activated carbon in removing Hg(II) and there exists a high potential that biochar can be a substitute of activated carbon for removal of Hg(II) from wastewater.

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## 1. Introduction

Mercury is one of the most toxic metals as it can easily pass the blood–brain barrier and affect the fetal brain even at low environmental concentrations [1,2]. According to the standards in China,

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the tolerance discharge limit of Hg(II) in wastewater is  $50.0 \mu\text{g L}^{-1}$  (GB8978-1996) and the upper concentration limit for Hg in surface water is only  $1.0 \mu\text{g L}^{-1}$  (GB3838-2002) [3]. Many studies have shown the effectiveness of carbonaceous materials, especially activated carbon (AC) for Hg removal from aqueous solution [4–7] due to their availability of sorption-specific extensive surface area and microporous structure [8]. It was proposed that Hg(II) can be bound to the sorbent surface through complexation with functional groups [9], electrostatic interaction [9] or ion exchange [10]. Precipitation and reduction reactions were other two important mechanisms for Hg(II) sorption from solution [3,11,12].

Biochars produced from crop residues, wood chips, animal manure, etc. have the AC-like structure and property [13]. Since 2005, biochar has received considerable interest as a recalcitrant carbon stock and consequently as a soil amendment to improve soil fertility, crop production, and nutrient retention [14,15]. Therefore, carbon sequestration of biochar will provide additional benefits if biochar can be used for the sorption of Hg(II) in the water. Brazilian pepper biochars [2] and camel bone charcoal [16] can effectively remove Hg(II) from wastewater with sorption capacities of  $15\text{--}25 \text{ mg g}^{-1}$  and  $28.3 \text{ mg g}^{-1}$ , respectively. Kong et al. [3] and Boutsika et al. [17] found that biochars derived from soybean stalk and malt spent rootlets could also efficiently remove Hg(II) from aqueous solution. However, most of the studies have focused on the effect of different experimental conditions (varying treatment time, metal ion concentration, adsorbent amount, pH, solution temperature, etc.) on the sorption ability. Little work has been done on the underlying mechanisms of the sorption of Hg(II) by biochars.

In this study, two biochars were produced from bagasse and hickory chips and evaluated for the sorption effectiveness of Hg(II) in the aqueous solution. A commercial activated carbon was included as a sorbent for comparison. The underlying mechanisms of Hg(II) sorption by biochars and activated carbon were illustrated, especially for the roles of functional groups since functional groups such as hydroxyl and carboxyl groups were considered to play an important role in heavy metal sorption by carbonaceous materials [18].

## 2. Materials and methods

### 2.1. Preparation and characterization of biochar and activated carbon

The biochars used in this study were obtained from two waste biomasses, bagasse and hickory chips, through a slow pyrolysis process. The details on biochar preparation can be found in a previously published paper [19]. Briefly, the dried bagasse and hickory chips were heated at  $450^\circ\text{C}$  for 2 h in a stainless steel reactor in a Muffle Furnace under the  $\text{O}_2$ -limited condition. The residue left in the reactor after heating was C-rich solid and called as biochar [14]. The biochars derived from bagasse and hickory chips were referred to as BB and HCB, respectively. Activated carbon (AC) used in this study was produced from coconut shell and purchased from Fisher Scientific Co. The resulted biochars and activated carbon were ground to pass through a 20-mesh ( $\phi = 0.84\text{-mm}$ ) sieve for later characterization and sorption experiment.

The specific surface area (SSA) of biochar and AC was detected by  $\text{N}_2$  adsorption isotherms at 77 K using a Micropore Analyzer (ASiQ, Quantachrome, USA). The surface elements of C, H, and O were measured by X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI). The content of surface acid groups were determined using a modified Boehm titration [20]. To determine the ash content, biochars or AC were heated at  $900^\circ\text{C}$  in a muffle oven under air atmosphere for 4 h. The zero point of charge ( $\text{pH}_{\text{zpc}}$ ) was determined using the mass titration method described by Noh and Schwarz [21].

### 2.2. Hg(II) sorption by biochar and activated carbon

About 30 mg biochar or activated carbon was added to a range of Hg(II) solutions ( $100 \mu\text{g L}^{-1}\text{--}5 \text{ mg L}^{-1}$ ) in 40 mL Pyrex centrifuge tubes. The mercury contaminated electrolytic solution was prepared by spiking the  $1000 \text{ mg L}^{-1}$  mercury standard solution (Assurance Grade, SPEX CertiPrep) with simulated freshwater solution (1 mM  $\text{NaHCO}_3$ , 10 mM  $\text{NaNO}_3$  and 50 mM HEPES) and mixing thoroughly for 10 min. The pH of the vials was then adjusted using either 0.1 N NaOH or 0.1 N  $\text{HNO}_3$ , obtaining solution pH at 6. Previous studies have reported optimum sorption of mercury at pH 6 or near values [22,23]. The vials were capped with Teflon line caps and the caps were then wrapped with parafilm. The samples were then shaken for 24 h at  $25^\circ\text{C}$  in a tumbling box to reach equilibrium. Upon removal from the shaker, sample pH was measured. The solid and liquid phases of the sample were separated by centrifugation at 3500 rpm for 15 min. The supernatant was filtered with a plastic syringe through a 13-mm Whatman GD/X syringe filter into a HDPE centrifuge tube. The filtrate was acidified to 2%  $\text{HNO}_3$  and then analyzed for Hg concentration using an inductively coupled plasma mass spectrometer (ICP-MS) (ELAN DRC-e, Perkin Elmer). The solid phase was dried with freeze dryer for about 24 h and then characterized by XPS.

### 2.3. Hg(II) sorption by biochar and activated carbon with blocking of carboxyl and hydroxyl Groups

Carboxyl (Re-COOH) and hydroxyl groups (Re-OH) are generally accepted as the main groups contributing to coordination between heavy metals and the sorbent surfaces [18]. Therefore, to estimate their contribution to Hg(II) sorption by biochars and activated carbons, these groups were blocked using the methods described by Gardea-Torresdey et al. [24], Chen and Yang [25], and Lu et al. [18]. In brief, anhydrous  $\text{CH}_3\text{OH}$  was used to block the carboxyl function groups while blocking of the hydroxyl groups was performed with HCHO. These sorbent with the blocked functional groups were freeze-dried, and thus employed for the Hg(II) sorption experiments as described in Section 2.2.

### 2.4. XPS analysis

Biochar and activated carbon before and after reacting with  $5 \text{ mg L}^{-1}$  Hg were analyzed by XPS. The valence state of the Hg sorbed onto biochars and activated carbon was analyzed by XPS (PHI 5000, ULVAC-PHI). The XPS used for analysis is equipped with a monochromatic Al  $K\alpha$  X-ray source (1486.6 eV) and is operated at a base pressure of  $8 \times 10^{-8}$  Pa with pass energy of 23.5 eV. The X-rays are focused onto a spot size of  $10 \mu\text{m} \times 100 \mu\text{m}$  on each sample. All survey and high resolution scans were taken with the charge neutralizer operating at 30 V to avoid any charging caused by any insulating components of the samples. The calibration of the spectra binding energy was performed with the C1s peak of the aliphatic carbons at 284.8 eV.

## 3. Results and discussion

### 3.1. Characteristics of biochars and activated carbon

The selected properties of biochars and activated carbon are listed in Table 1. Biochars and activated carbon had high  $\text{pH}_{\text{zpc}}$  (8.5–9.9). The ash content of all the three sorbents was low (<8%), especially that of HCB (2.32%). AC had a much larger surface area ( $922 \text{ m}^2 \text{ g}^{-1}$ ) than the two biochars ( $12.9$  and  $15.3 \text{ m}^2 \text{ g}^{-1}$  for HCB and BB, respectively). AC is usually produced at higher temperatures ( $>800^\circ\text{C}$ ) than the biochars used in this study ( $450^\circ\text{C}$ ),

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