



Kinetics and mechanisms of hydrogen sulfide adsorption by biochars



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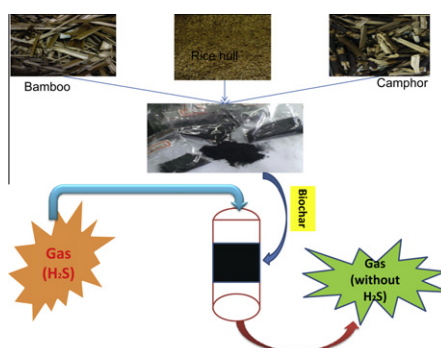
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HIGHLIGHTS

- ▶ Biochars derived from agricultural/forestry wastes were a promising adsorbent of H₂S.
- ▶ H₂S breakthrough capacity is related to local pH within the pore system of biochars.
- ▶ The adsorption kinetics of H₂S by biochars was modeled by Michaelis–Menten equation.

GRAPHICAL ABSTRACT



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ABSTRACT

Three different biochars as cost-effective substitutes for activated carbon (AC) were tested for their hydrogen sulfide (H₂S) adsorption ability. The biochars were produced from camphor (SC), bamboo (SB), and rice hull (SR) at 400 °C by oxygen-limited pyrolysis. The surface area (SA), pH, and Fourier transform infrared spectras of the biochars and AC were compared. The maximum removal rates and the saturation constants were obtained using the Michaelis–Menten-type equation. The three biochars were found to be alkaline, and the SAs of the biochars were much smaller than that of the AC. The H₂S breakthrough capacity was related to the local pH within the pore system of the biochar. The order observed in terms of both biochar and AC adsorption capacity was SR > SB > SC > AC. SR efficiently removed H₂S within the inlet concentration range of 10–50 μL/L. Biochars derived from agricultural/forestry wastes are a promising H₂S adsorbent with distinctive properties.

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1. Introduction

Hydrogen sulfide (H₂S) is one of the most common compounds that can be found in petrochemical plants, coal gasification plants, wastewater treatment plants, man-made fiber paper, and other production processes (Latos et al., 2011; Lebrero et al., 2011). This compound is extremely toxic to the central nervous system even at low doses and corrosive to concrete and steel (Burgess et al., 2001;

Lee et al., 2006). H₂S is a major air pollutant and also a cause of rain acidification.

Numerous studies on H₂S adsorption using activated carbon (AC) have been conducted because of the increase in deodorization problems (Bagreev and Bandoz, 2000; Bashkova et al., 2009). However, the manufacture of AC requires high temperature, high pressure, and an activation process (Boehm, 1994). Traditionally, only ACs impregnated with caustics were considered suitable materials. Although caustic-impregnated and catalytic carbons have been proven to work efficiently as H₂S removers, certain disadvantages with the application of such carbons have been observed, including (i) self-ignition at low temperature, (ii) low

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capacity for physical adsorption attributable to the filling of the pore system with the impregnate, (iii) special precautions are required for use with alkalis, and (iv) difficulties in regeneration after washing with water. All aforementioned factors directed the attention of numerous studies toward unmodified, as-received ACs.

As a precursor of AC, biochars have received considerable attention in the past decades (Azargohar and Dalai, 2006; Hayes, 2006; Renner, 2007; Moussavi and Khosravi, 2012). Biochar is the carbon-rich product of the thermal decomposition of organic material under a limited supply of O₂ and at relatively low temperatures (<700 °C) (Hale et al., 2011). Biochar has been known to act as a super-sorbent for organic contaminants in soil/sediment (Pandey et al., 1997; Sattar et al., 1991; Lou et al., 2012; Inyang et al., 2012). Biochar and AC differ primarily in their preparation method, source material, and the resulting physiochemical properties of the products. In contrast to AC, biochar use could be a cheaper remediation technology as the waste source materials would essentially be free, and the production of biochar at lower temperatures is more energy-efficient and less cost-intensive (Kumar et al., 2006) than AC production. A previous study reported on the potential of biochar derived from camphor to adsorb H₂S at various temperatures (100–500 °C) and demonstrated that the different sizes of biochars and the different pyrolysis temperatures for the camphor particle markedly affect H₂S adsorption. The biochar with particle size ranging from 0.3 to 0.4 mm possesses a maximum sorption capacity at a pyrolysis temperature of 400 °C (Shang et al., 2012). Further studies must be conducted to understand better the mechanisms of biochar H₂S adsorption because biochar characteristics depend not only on the pyrolysis temperature but also on biochar feedstock.

This study aimed to determine the efficiency of H₂S adsorption by three different biochars derived from camphor, bamboo, and rice hull at a pyrolysis temperature of 400 °C. A comparative study with AC was also conducted. Removal kinetics were used to evaluate the H₂S removal rate of biochars.

2. Methods

2.1. Materials

Shell-derived AC is a commercial product purchased from Changzhou Bihai Environmental Protection Technology Co., Ltd. Three different biochars were produced from agricultural/forestry wastes such as camphor (SC), rice hull (SR), and bamboo (SB). The wastes were cut into small pieces, washed, and baked in the oven at 60 °C for 48 h. The pieces were then ground into small particles by using a crusher. The sizes of the particles were determined to be between 0.3 and 0.4 mm after screening. The waste was pyrolyzed at 400 °C under an O₂-free atmosphere in a ceramic fiber muffle furnace. The heating rate was initially set at 10 °C/min and increased to the selected pyrolysis temperature, with a holding time of 5 h at the final temperature. The samples were cooled by ventilation to 30 °C with nitrogen gas.

2.2. Physicochemical characteristics

The pH of the carbon surface was measured in deionized water with a 1:5 (wt/wt) ratio. Samples were thoroughly mixed and allowed to equilibrate for 1 h. The pH was measured with a digital pH meter. Carbon and nitrogen contents were determined by elemental analysis–stable isotope ratio mass spectrometer (Vario EL III/Isoprime, Germany). The ash content of the biochars and AC was measured as follows: the samples of the biochars and AC were placed into crucibles. The crucibles were placed into a muffle furnace and baked at 900 °C for 2 h and then cooled down at room temperature. The ash content was obtained by calculating the

difference between the mass of the biochars and AC before and after baking.

2.3. Measurement of H₂S breakthrough curves

To evaluate the removal capacity of biochars, H₂S adsorption experiments were performed at room temperature using a laboratory-scale apparatus (Fig. 1). The three biochars were packed into quartz glass columns (inner diameter = 12 mm; height = 300 mm). The biochar bed was 150 mm high, with a bulk density of 0.12 g/cm³ and a porosity of 35%. The quartz sand was packed above and below the biochar bed. The source gas containing 50 μL/L H₂S and 500 μL/L water vapor was passed through the column of the adsorbent at 40 mL/min. The inlet H₂S concentration was changed from 10 to 50 μL/L by diluted compressed air. The load of H₂S into the columns was changed by controlling the inlet concentration and/or space velocity. The outlet H₂S was collected by airbags every 2 min and monitored using gas chromatography (GC). The test was stopped at the breakthrough concentration of 50 μL/L. After every test, excess H₂S was absorbed using a sodium hydroxide solution. The adsorption capacity of each biochar was calculated by integration of the area above the breakthrough curves. From the H₂S concentration in the inlet gas, flow rate, breakthrough time, and mass of biochar were also calculated.

2.4. GC chromatography

The concentration of H₂S in the exhaust gases from the biochar bed was monitored using a Shimadzu GC (Model GC-2010). The separation was conducted at CNW (a German company) CD-1 column (bonded dimethyl siloxane = 100%, length = 30 m, internal diameter = 0.32 mm, and df = 5.00 μm). The GC oven heating procedure was conducted as follows: (1) initial heating temperature of 80 °C for 2 min; (2) temperature increased to 150 °C at 20 °C/min; and (3) temperature held at 150 °C for 18 min. The injector temperature was 80 °C. An FPD detector with a sulfur filter and an opening temperature of 220 °C was used.

2.5. Fourier transform infrared (FTIR) analysis

The FTIR spectra of the biochar samples were obtained using diffuse reflectance FTIR spectroscopy. The biochars were ground to 0.1 and 0.5 mg of each sample was placed onto the Ge window of a Nicolet 5700 FTIR with an attenuated total reflectance attachment (OMNI Sampler Nexus). Spectra were obtained over 256 scans with a KBr beam splitter, set at a resolution of 4 cm⁻¹, ranging from 4500 to 650 cm⁻¹ and with an aperture size of 34 cm. The reflectance was measured and analyzed using OMNIC v7.1 with Happ–Genzel apodization and Mertz phase correction.

3. Results and discussion

3.1. Characterization of the biochars

The physicochemical characteristics of the three different biochars and AC used in this experiment are shown in Table 1. Biomass type significantly affects pH and SA. The SA of the biochars and AC ranged from 20.35 to 850.00. All biochars were alkaline, whereas AC was neutral. The highest pH was 10.56 for SR, and the lowest was 7.05 for AC. These values are typical for most biochars generated at high temperature (Lehmann and Joseph, 2009). Higher SR pH suggests potential to adsorb acidic H₂S (Dudka and Adriano, 1997). Among the biochars, the highest SA was 115.34 for SR, which was 7.3 times lower than that of AC. AC is a high-surface-area carbon, which is most often produced by physical and

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