Sorption of polycyclic aromatic hydrocarbons by biochars of wheat straw with different pyrolysis temperatures

Zheng Ding, Fan Zhang, Ning Sun and Jie Chi*
School of Environmental Science and Engineering, Tianjin University, Tianjin, 300350, China
*Corresponding Author’s e-mail: cjiechi@163.com.

Abstract: This study investigated the sorption kinetics of a model solute (phenanthrene and pyrene) with a series of biochars prepared from wheat straw at 100-700 °C (referred as BC100-BC700) to probe the effects of biochars produced at different pyrolysis temperatures on sorption of phenanthrene and pyrene. The samples were characterized by the elemental compositions, Fourier transform IR spectroscopy, and Brunauer-Emmett-Teller-N₂ surface areas. The results showed that the sorption parameters (N and lgKᵢ) are linearly related to sorbent aromaticity and the total surface areas, which increase with the pyrolysis temperature. Sorption mechanisms of biochars are evolved from partitioning-dominant at low pyrolysis temperatures to adsorption-dominant at higher pyrolysis temperatures.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are a kind of persistent organic pollutants which are carcinogenic, teratogenic and mutagenic. They are ubiquitous and have been identified in a variety of environmental media [1]. Biochars are carbon-rich materials obtained by biomass pyrolysis at relatively low temperatures (<700 °C) under limited or no oxygen conditions. The substances receive increasing attention for uses in soil amendment, soil fertility and carbon sequestration [2,3]. Studies reported that carbonaceous materials (CM), such as activated carbon and biochar, could bind soil-bound hydrophobic organic compounds (e.g. PAHs) very strongly due to their great sorptive capacities [4,5]. By decreasing concentrations of organic pollutants in porewater, CM amendment to soils could reduce bioavailability of these compounds to plants and earthworms, and thereby reduce their transfer from the soil matrix into the terrestrial food-chain and also alleviate phytotoxicity [6,7]. At the same time, the uptake of a compound by a biochar depends on the composition and the surface structure of the biochar that is affected by the pyrolytic temperature.

In this study, phenanthrene and pyrene were used as the model compounds. Wheat straw was chosen as the original feedstock for its abundance to prepare different biochars at the pyrolysis temperature of 100-700 °C. The objectives were to explore the effects of biochars produced at different pyrolysis temperatures on sorption of phenanthrene and pyrene in water. The mechanisms were discussed.

2. Materials and Methods
2.1 Preparation and characterization of biochars
Wheat straw was collected from Anhui Province in China. After air-dried, wheat straw chips were pyrolyzed under an oxygen-limited condition at 100, 200, 300, 400, 500, 600 and 700 °C for 4 h in a muffle furnace. After cooled down to room temperature, the charred solids were passed through a 0.178...
mm sieve and were referred to as BC100, BC200, BC300, BC400, BC500, BC600 and BC700, respectively.

Elemental (C, H, N) analyses were conducted using an elemental analyzer (Elementar, Germany). The content of O was determined by a mass balance. Ash content was measured by heating the samples at 800 °C for 4 h. Fourier transform infrared (FTIR) spectra were recorded in the 400-4000 cm⁻¹ region by FTIR spectrometer (Bruker Vector 22) with a resolution of 2 cm⁻¹. The surface characteristics of biochars were measured by a NOVA-2000E surface area analyzer. The total surface areas (SA) was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume (V_{total}) was estimated from a single N₂ adsorbed point at a N₂ relative pressure of 0.99.

2.2 Kinetic Sorption Experiments
Phenanthrene and pyrene were chosen as model sorbates. All sorption isotherms were obtained in 5 mmol/L CaCl₂ to simulate environmental water, with 200 mg/L NaN₃ added to inhibit the degradation by incidental bacteria. Relative initial concentrations ranged from 0.20 to 2.60 mg/L for phenanthrene, and 0.04 to 0.45 mg/L for pyrene to saturate potential adsorption. Biochar to water ratios were 5 mg per 40 mL for BC100-BC400, 2 mg per 40 mL for BC500 and BC600, 2 mg per 80 mL for BC700, respectively. The vials were placed on a rotating shaker and agitated in the dark at 110 rpm for 3 days. The solution was separated from solids by centrifugation at 4000 rpm for 20 min. 2 mL supernatants were taken to determine the concentration of phenanthrene and pyrene by high performance liquid chromatography (Waters).

3. Results and Discussion

3.1 Characterization of biochars
The basic physicochemical properties of BC100-BC700 are listed in Table 1. Atomic ratios of H/C and O/C reflect the aromaticity and polarity of biochars. With increasing pyrolysis temperature from 100 to 700 °C, H/C and O/C ratios decreased from 2.06 to 0.14 and from 0.90 to 0.05, respectively, exhibiting higher aromaticity and lower polarity for biochars produced at high temperature as a result of carbonization. As shown in Table 1, the SA is small for low production temperature biochars (BC100-BC300, 1.46-2.06 m²/g), which is related with their non-porous structure (i.e. micropore volume was negligible). This is due to the presence of a significant amount of the residual plant organic matter because the decomposition peaks of hemicelluloses and cellulose were at 318 and 362 °C [8]. When biochars were produced at temperature higher than 400 °C, the SA increased dramatically (BC400-BC700, 41.4-376.0 m²/g), exhibiting a more developed nanopore structure. The main reason is the further enhanced evolution of volatile matter and the loss of organic constituents under higher pyrolysis temperature [9].

Table 1. Yield, elemental composition and ratios, ash content, BET-N₂ surface area (SA) of biochar samples

| Sample | Ash (%) | Yield (%) | pH | C (%) | H (%) | N (%) | O (%) | (N+O)/C | O/C | H/C | SA(m²/g) |
|--------|---------|-----------|----|-------|-------|-------|-------|---------|-----|-----|----------|
| BC100  | 7.04    | 96.69     | 6.12 | 44.75 | 7.67  | 0.42  | 40.12 | 0.68    | 0.67 | 2.06 | 1.46     |
| BC200  | 5.65    | 83.75     | 6.68 | 48.64 | 7.66  | 0.51  | 37.54 | 0.59    | 0.58 | 1.89 | 1.61     |
| BC300  | 10.13   | 42.13     | 7.31 | 66.28 | 5.11  | 0.67  | 17.80 | 0.21    | 0.20 | 0.93 | 2.06     |
| BC400  | 14.14   | 32.67     | 7.69 | 66.56 | 3.90  | 0.85  | 14.56 | 0.17    | 0.16 | 0.70 | 41.4     |
| BC500  | 18.67   | 26.70     | 8.12 | 73.05 | 2.79  | 0.77  | 4.73  | 0.06    | 0.05 | 0.46 | 254      |
| BC600  | 17.51   | 25.07     | 8.69 | 75.56 | 1.59  | 0.68  | 4.67  | 0.05    | 0.05 | 0.25 | 324      |
| BC700  | 19.65   | 24.24     | 9.30 | 75.34 | 0.90  | 0.62  | 3.49  | 0.04    | 0.03 | 0.14 | 376      |

* Elemental compositions and atomic ratios are on an ash-free basis. H/C: atomic ratio of hydrogen to carbon. O/C: atomic ratio of oxygen to carbon. (O+N)/C: atomic ratio of the sum of nitrogen and oxygen to carbon.
The FTIR spectra results are shown in Fig. 1. The peak assignments were the stretching vibration of O-H (3400 cm⁻¹), C-H for stretching vibration of aliphatic (2920 cm⁻¹), C=C of aromatic rings or C=O for stretching vibration of carboxylates, ketones and steroids (1610 cm⁻¹), C=C and O-H of aromaticity (1440 cm⁻¹ and 1375 cm⁻¹). The band at 1050-1110 cm⁻¹ is assigned to C-O stretching vibration of hydrocarbons [10]. It can be seen that all these bands clearly appeared in the spectra of BC100 and BC200, while the band intensities decreased markedly or even disappeared with the increase of pyrolysis temperature. For BC700, certain aromatic C=C ring stretching bands (around 1610 cm⁻¹) was preserved. These results suggested that aliphatic compounds decreased together with the development of fused aromatic ring structures in biochar with increasing pyrolysis temperature, which is attributed to the dehydration, dehydroxylation and demethoxylation [11].

Figure 1. FTIR spectra of the biochars.

3.2 Sorption of phenanthrene and pyrene onto biochars.

The dependence of the amount of phenanthrene and pyrene sorbed onto BC100-BC700 were depicted in Figure 2. The isotherms fit the Freundlich equation, with the related parameters listed in Table 2. The isotherms of phenanthrene and pyrene on BC100 are practically linear, with respective Freundlich N=0.985 for phenanthrene and 0.992 for pyrene, the isotherms for BC200-BC700 display an increasing nonlinearity (Freundlich N were ranged from 0.631 to 0.271 and 0.827 to 0.261 for phenanthrene and pyrene, respectively). Similarly, the sorption ability of phenanthrene and pyrene on BC100 is lower, with Freundlich IgKf =0.74 for phenanthrene and 1.18 for pyrene, the isotherms for BC200-BC700 display an increasing sorption ability (Freundlich IgKf were ranged from 2.38 to 3.94 and 2.33 to 3.58 for phenanthrene and pyrene, respectively).

As mentioned above, aromaticity and SA of biochars were increased with increasing pyrolysis temperature, moreover, statistical analyses revealed that Freundlich N was positively correlated with the aromaticity of biochars (r=0.949, p=0.001, n=7 for phenanthrene and r=0.972, p=0.000, n=7 for pyrene), and IgKf was positively correlated with SA (r=0.923, p=0.009, n=6 for phenanthrene and r=0.894, p=0.016, n=6 for pyrene). The results showed that the nonlinear and sorption ability were increased with increasing pyrolysis temperature, due to the nanopore production and carbonization [12]. The partition of BC100-BC300 biochars originates from an amorphous aliphatic fraction, which is enhanced with a reduction of the substrate polarity; for BC400-BC700, the partition occurs with a condensed aromatic core that diminishes with a further reduction of the polarity. Simultaneously, the sorption mechanisms of PAHs by biochars exhibit a transition from partitioning-dominant to adsorption-dominant [8].
Figure 2. Sorption kinetics of phenanthrene and pyrene onto different biochars.

Table 2. Regression parameters of sorption isotherms of phenanthrene and pyrene to different biochars

| Samples     | linear Freundlich model for phenanthrene | linear Freundlich model for pyrene |
|-------------|-----------------------------------------|-----------------------------------|
|             | N          | lgK_f       | R^2   | N          | lgK_f       | R^2    |
| BC100       | 0.985      | 0.74        | 0.991 | 0.992      | 1.18        | 0.986  |
| BC200       | 0.631      | 2.38        | 0.996 | 0.827      | 2.33        | 0.989  |
| BC300       | 0.409      | 2.86        | 0.912 | 0.620      | 2.33        | 0.985  |
| BC400       | 0.481      | 2.81        | 0.994 | 0.484      | 2.56        | 0.989  |
| BC500       | 0.407      | 3.31        | 0.962 | 0.529      | 2.68        | 0.975  |
| BC600       | 0.383      | 3.32        | 0.915 | 0.388      | 3.04        | 0.929  |
| BC700       | 0.271      | 3.94        | 0.973 | 0.261      | 3.58        | 0.987  |

* The Freundlich parameters were calculated using the logarithmic form of the equation Q=K_f*C_e^N, where Q is the amount sorbed per unit weight of sorbent, mg/kg; C_e is the equilibrium concentration, μg/L; K_f [(mg/kg)/(μg/L)^N] is the Freundlich capacity coefficient, and N describes the isotherm curvature. R^2 is regression coefficient.

4. Conclusions

In this work, pyrolysis temperature-dependent sorption of PAHs in water was observed. The results showed that the aromaticity and the total surface areas of biochars were increased with increasing pyrolysis temperature. Correspondingly, Freundlich N and lgK_f were ranged from 0.985 to 0.271 and 0.74 to 3.94 for phenanthrene, from 0.992 to 0.261 and 1.18 to 3.58 for pyrene, respectively, indicated that the nonlinear and sorption ability of biochars were increased with increasing pyrolysis temperature. Moreover, statistical analyses revealed that Freundlich N was positively correlated with the aromaticity of biochars and lgK_f was positively correlated with SA. The sorption mechanisms of PAHs by biochars exhibit a transition from partitioning-dominant to adsorption-dominant.

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