Supporting Information

Adsorption of herring sperm DNA onto pine sawdust biochar: Thermodynamics and site energy distribution

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Principle and detailed derivation of wet surface area using ^{1}H NMR technology

The wet surface of biochar is covered by boundary water; hence, the amount of boundary water molecules can reflect the area of the wet biochar surface. In an adsorption system, the ^{1}H relaxation time of boundary water on the biochar surface (T_b, ms) is much shorter than that of free water (T_f, ~2600 ms), because of the association between water molecules and the mineral surface.

The corresponding relaxation rate (R_b and R_f, ms^{-1}) can be obtained by inverting the relaxation time:

$$R_b = 1/T_b \quad \text{(S1)}$$

$$R_f = 1/T_f \quad \text{(S2)}$$

The average relaxation time of water-containing biochar (T_{av}, ms) can be directly measured using a XiGo Nanotool operating at 13 MHz. The average relaxation rate (R_{av}, ms^{-1}) can be calculated as follows:

$$R_{av} = 1/T_{av} \quad \text{(S3)}$$

R_{av} is the relaxation rate of boundary water and free water weighted by their relative proportions:

$$R_{av} = \beta \times R_b + (1-\beta) \times R_f \quad \text{(S4)}$$

where β is the proportion of boundary water in total water. The enhancement in specific relaxation rate (R_{sp}) can be confined using Eq. (S5):

$$R_{sp} = R_{av} / R_f - 1 \quad \text{(S5)}$$

Substituting Eq. (S4) into Eq. (S5) gives Eq. (S6):

$$R_{sp} = \beta \times (R_b - R_f) / R_f \quad \text{(S6)}$$

Since R_b and R_f are constant for a given biochar, R_{sp} is proportional to β, which is the proportion of boundary water in total water at a certain biochar concentration, and further reflects the surface area of biochar exposed to water.

To verify the accuracy of this method, the measured wet surface area by Xigo Nanotools was compared with the actual area of well-suspended SiO_2 nanosphere. The relationship between R_{sp} and concentration (Ψ, g/mL) of SiO_2 nanosphere with diameters of 4 and 6 nm was shown in Figure S1. The slope was used to reflect the relative magnitudes of the wet surface area more accurately. As the result, the wet surface area of 4 nm SiO_2 nanospheres is 2.27 times higher than that of 6 nm SiO_2 nanospheres, when they are in the same weight. The ratio is very close to 2.25 (calculated by the formula for the area of a sphere), which confirms the accuracy of this method.

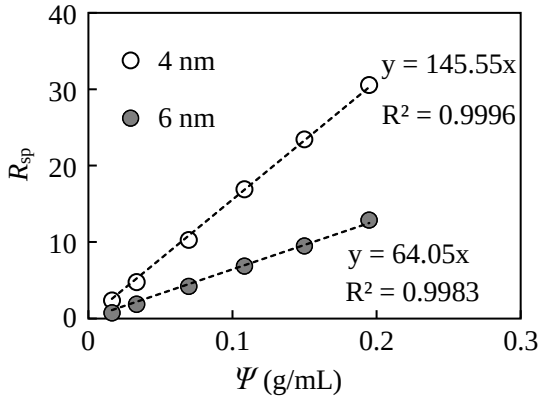

Figure S1. R_{sp} of well-suspended SiO_2 nanosphere with diameters of 4 and 6 nm for a series of nanosphere concentrations.

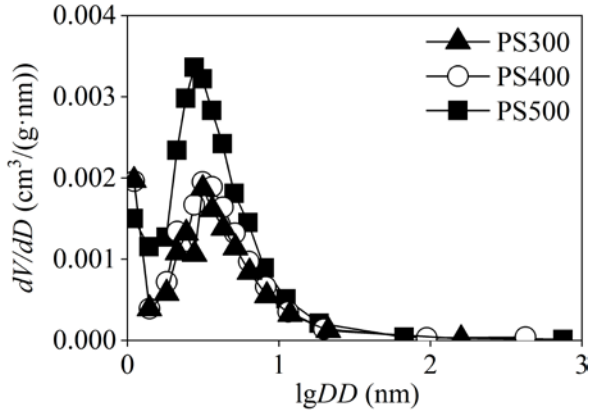

Figure S2. Pore size distributions of biochars prepared at 300 °C (PS300), 400 °C (PS400), and 500 °C (PS500).

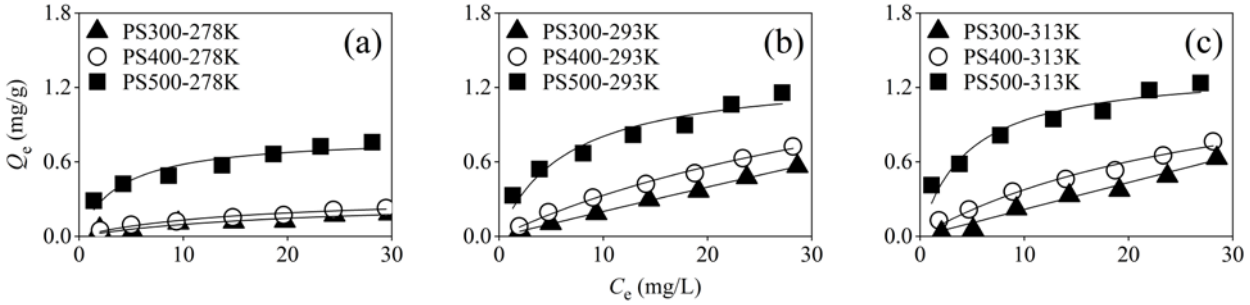

Figure S3. Isotherms of hsDNA adsorption on PS300 (▲), PS400 (○), and PS500 (■) at 278 K (a), 293 K (b), and 313 K (c) fitted with LM.