Supplementary Information

Cd(II) Sorption on Montmorillonite-Humic acid-Bacteria Composites

Huihui Du[1,2], **Wenli Chen**[1,*], **Peng Cai**[1,2], **Xingmin Rong**[1,2], **Ke Dai**[1,2], **Caroline L. Peacock**[3], **Qiaoyun Huang**[1,2,*]

[1]State Key Laboratory of Agricultural Microbiology, Huazhong Agricultural University, Wuhan 430070, China

[2]Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze River), Ministry of Agriculture, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

[3]University of Leeds, School of Earth and Environment, LS2 9JT, UK

*Corresponding Author: phone: +86 27 87671033; fax: +86 27 87280670; email: wlchen@mail.hzau.edu.cn; qyhuang@mail.hzau.edu.cn

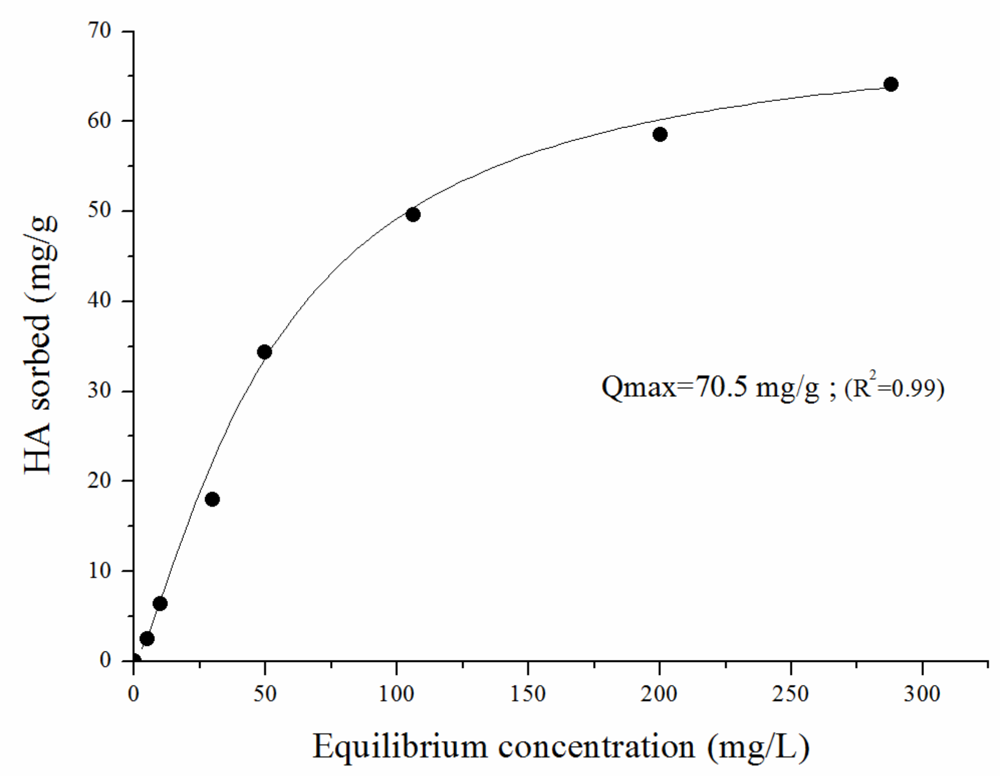

Figure S1. Equilibrium adsorption of humic acid on montmorillonite in the presence of 0.01 mol L^{-1} KNO_3 at pH 5 and 28 ℃.

ITC data analysis

The ITC data analysis was conducted using Origin 8.5 software based on the methods described by Garcia-Valls & Hatton[45]. In the present study, the heat is related to the interaction enthalpy (ΔH) by

$$\Delta Q = \Delta H\,(\Delta n_M)\,V_{\text{cell}} \tag{1}$$

Where Δn_M (mmol g^{-1}) is the changes of the total Cd bound to different components following the given injections. V_{cell} denotes the volume of the solution being titrated. The total heat released after a given number, t, of injection can be obtained by summing all the ΔQ value to give

$$Q_b = \sum_{j=1}^{t} \Delta Q_j = \Delta H\,[\mathrm{M}]_b\,V_{\text{cell}} \tag{2}$$

where $[M]_b$ (mmol g^{-1}) represents the total adsorbed Cd after t injection. Since the sorbents may bind more than one Cd ions, the following reaction stoichiometry is used to account for Cd adsorption

$M + L \leftrightarrow ML \ldots\ldots k_1 = [ML] / [M] [L]$

$M + ML \leftrightarrow M_2L \ldots\ldots k_2 = [M_2L] / [M]^2 [L]$

……

$M + M_{n-1}L \leftrightarrow M_{n-1}L \ldots\ldots k_n = [M_nL] / [M]^n [L]$ (3)

where n denotes the total number of binding sites on different components and the equilibrium constant is conditional at each pH value, then we can write

$$k_i = \frac{[M_iL]}{[M]^n [L]} = K^i \quad (4)$$

where K^i (L $mmol^{-1}$) is the global constant (β_i). Then, after some algebraic manipulation, the average fraction of Cd binding sites occupied can be shown

$$\Phi = \frac{\sum_{i=1}^{n} i[M_iL]}{\sum_{i=0}^{n}[M_iL]} = \frac{\sum_{i=1}^{n} ik_i[M]^i[L]}{\sum_{i=0}^{n} k_i[M]^i[L]} = \frac{\sum_{i=1}^{n} iK_i[M]^i}{\sum_{i=0}^{n} K_i[M]^i} = \frac{nK[M]}{1+K[M]} \quad (5)$$

The total Cd concentration is

$$[M]_T = [M] + [M]_b = [M] + [L]_T\Phi = [M] + [L]_T\frac{nK[M]}{1+K[M]} \quad (6)$$

This equation is a quadratic in [M], which can be solved to yield the free concentration of Cd in solution as a function of the total Cd and different components concentrations. The concentration of bound metal ions can then be determined to be

$$[M]_b = [M]_T - [M] = [M]_T + \frac{(1 + nK[L]_T - K[M]_T) - \sqrt{(1 + nK[L]_T - K[M]_T)^2 + 4K[M]_T}}{2K} \quad (7)$$

Therefore, the total heat released or adsorbed when the sorbents have been titrated with Cd solution when the total sorbent and Cd concentration are $[L]_T$ and $[M]_T$, respectively, is

$$Q_b = \Delta H\left([\mathrm{M}]_T + \frac{\left(1 + nK[\mathrm{L}]_T - K[\mathrm{M}]_T\right) - \sqrt{\left(1 + nK[\mathrm{L}]_T - K[\mathrm{M}]_T\right)^2 + 4K[\mathrm{M}]_T}}{2K}\right)V_{cell} \quad (8)$$

The relevant thermodynamic parameters, n, K, and ΔH can then be determined as those values giving the best fit of this expression to the cumulative heat release curves. The ΔG can be calculated by: ΔG = -RT lnK, where T is the absolute temperature (301 K), R is the universal gas constant, and K represents the equilibrium binding constant. ΔS is derived from $\Delta G = \Delta H - \mathrm{T}\Delta S$.