Electronic Supplementary Material

Simple combination of humic acid with biogenic hydroxyapatite achieved highly efficient removal of methylene blue from aqueous solution

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1. Mathematical models

The pseudo-first-order (eq. 1) [1], pseudo-second-order (eq. 2) [2], and intra-particle diffusion model (eq. 3) [3] were used to simulate the adsorption kinetics.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = k_p t^{1/2} + C \quad (3)$$

where q_e (mg/g) is the amount of adsorbate adsorbed per unit adsorbent at equilibrium; q_t (mg/g) is the amount of MB adsorbed at time t; k_1 (1/min), k_2 (g/(mg·min)), and k_p (mg/(g·min$^{-1/2}$)) are the rate constants for the pseudo-first-order, pseudo-second-order and intra-particle diffusion models, respectively; C (mg/g) is the intercept which provides an idea of the boundary layer thickness. Herein, the initial adsorption rate (v_0) is calculated as: $v_0 = k_2 q_e^2$ for the pseudo-second-order model.

Langmuir (4) [4], Freundlich (5) [5] and Sips (also known as Langmuir-Freundlich) isotherm models (6) [6] were used to describe the adsorption of MB on the HA-bHAP adsorbent:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$q_e = \frac{q_m (K_S C_e)^{1/n}}{1 + (K_S C_e)^{1/n}} \quad (6)$$

where K_L (L/mg), K_F [mg/g(L/mg)$^{1/n}$] and K_S (L/mg) are the equilibrium constants of Langmuir, Freundlich and Sips models, respectively; q_e(mg/g) is the adsorption capacity at equilibrium; C_e (mg/L) is the equilibrium concentration of HA in solution; q_m (mg/g) is the maximum adsorption capacity, and $1/n$ is the heterogeneity factor. If

the value of K_S or C_e approaches to zero, Sips isotherm equation follows the Freundlich isotherm model, while the value of 1/*n* equal or close to 1, the Sips isotherm equation reduced to the Langmuir isotherm.

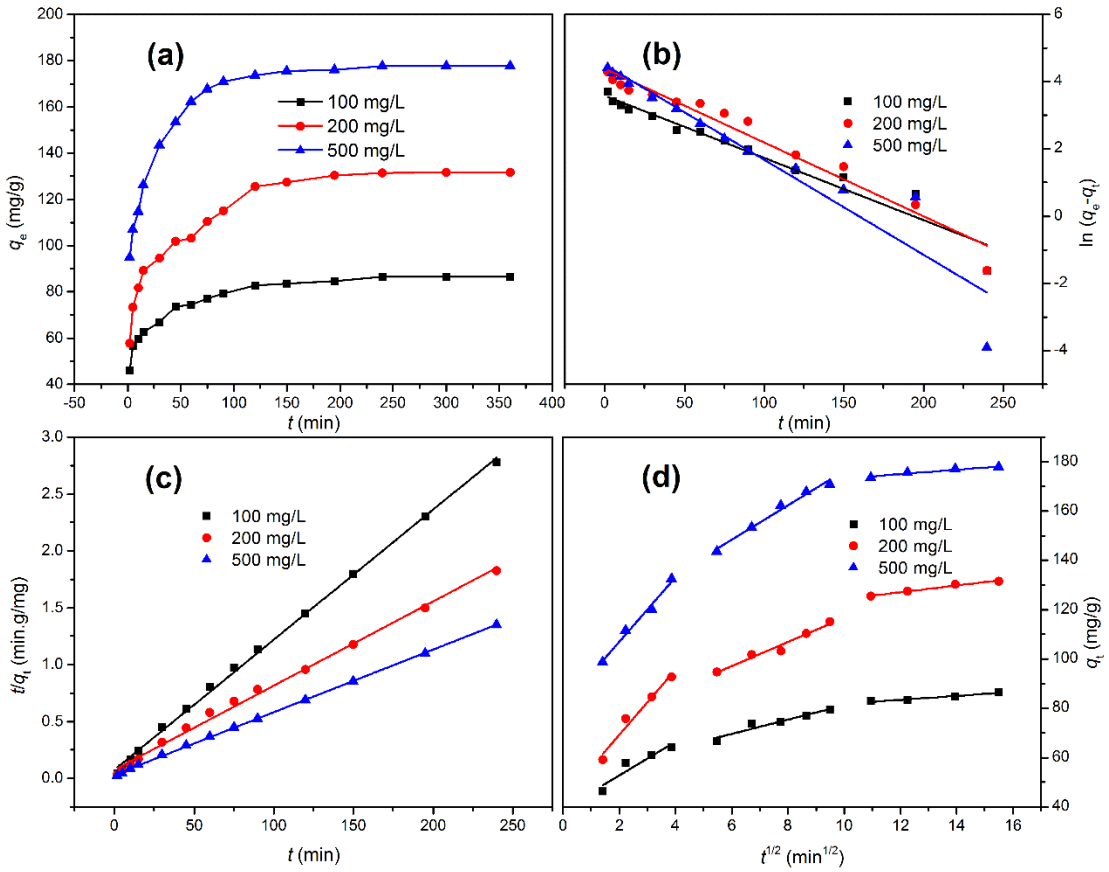

Figure S1. (a) Effect of contact time and initial metal concentration on adsorption capacity of MB onto HA-bHAP; the fitting of different kinetic models for MB adsorption onto HA-bHAP at different initial concentrations ((b) pseudo-first-order, (c) pseudo-second-order, (d) intra-particle diffusion). (Adsorption conditions: adsorbent dosage = 1.0 g/L, initial pH = 7.0, and temperature = 298 K).

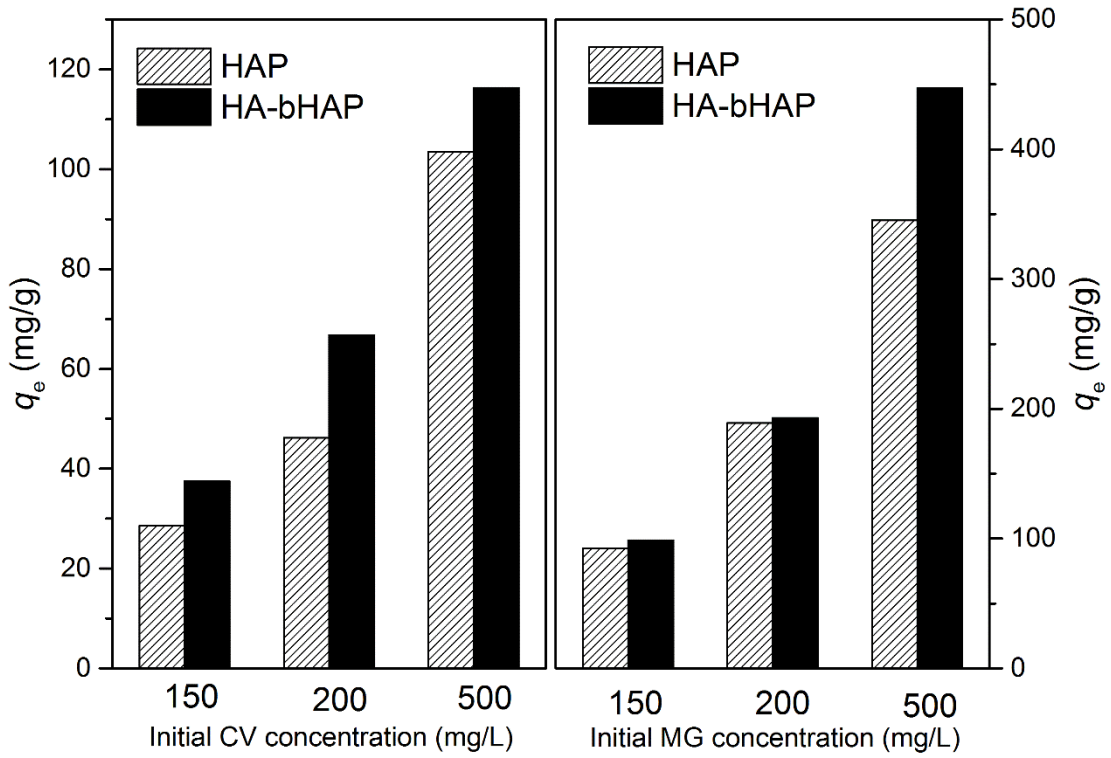

Figure S2. Comparison of crystal violet (CV) and malachite green (MG) adsorption onto bHAP and HA-bHAP. (Adsorption conditions: adsorbent dosage = 1.0 g/L, initial pH 7.0, and temperature = 298 K).

References

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