Supplementary Material

Adsorptive removal of ciprofloxacin by chitosan modified Fe pretreatment biochar composite from aqueous solution

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1.1 Characterization methods

XPS (Escalab 250Xi) was used to analyze the surface composition of the produced samples, and the results were fitted using "XPS peak" software. The Brunauer–Emmett–Teller (BET) surface areas of the samples were determined using N_2 adsorption on a Micromeritics ASAP2420 instrument, and the plot of the pore-diameter distribution was determined by using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. The micromorphological characteristics of samples were characterized using a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 5.0 kV. The X-ray

diffraction (XRD) patterns of samples were obtained using a Rigaku D/max-IIIB X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) generated at 40 kV and 20 mA. Functional groups in the compounds were analyzed by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet IS10). The Nano Series (Malvern, UK) Zeta Sizer Nano-ZS system was used to detect zeta potentials at a temperature of 25℃.

1.2 The information of models

The adsorption capacities of CS-FBC at time t (q_t) and at adsorption equilibrium (q_e) were calculated according to the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 and C_e represent the initial and equilibrium time concentrations of CIP (mg/L), respectively. C_t represents the concentration at time t (mg/L), V is the volume of the solutions (L), and m is the mass of the adsorbent (g).

1.3 Adsorption kinetics

To further understand the adsorption capacity and the underlying adsorption mechanism, adsorption kinetic models are usually selected. The primary focus of adsorption kinetics investigation is the rate of time-dependent adsorption of adsorbent onto adsorbate. The most common adsorption kinetic models include: pseudo-first-order kinetic model, pseudo-second-order kinetic model, intraparticle diffusion model (Weber and Morris), and Elovich kinetic model. The adsorption process of CIP by CS-FBC is studied by two kinetic models, the formula is as follows:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e is the amount of CIP (mg/g) at equilibrium time and q_t is the amount of CIP

(mg/g) at a certain time t (min), k_1 is the pseudo-first-order rate constant (min^{-1}) and k_2 is the pseudo-second-order rate constant (g/(mg×min)).

1.4 Adsorption isotherm

The adsorption of CIP by CS-FBC at various temperatures was investigated, and the Langmuir and Freundlich isotherm models were usually used to analyze the adsorption process. The Langmuir adsorption model, which assumes that the adsorption sites are entirely independent and homogenous, is a monolayer adsorption model. The nonlinear and linear expressions of the Langmuir isothermal adsorption model are as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{5}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \tag{6}$$

Unlike the Langmuir model, the Freundlich adsorption isotherm model is an empirical equation with no prior assumptions. These are its linear and nonlinear expressions, respectively, are as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{7}$$

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \tag{8}$$

where q_{max} (mg/g) is the theoretical maximum adsorption capacity, b (L/mg) is the Langmuir constant related to the adsorption energy, and K_F $(mg/g)(L/mg)^{1/n}$ and n are the Freundlich constants.

1.5 Adsorption thermodynamic

Temperature is another important factor affecting the efficiency of adsorbents. The adsorption of CS-FBC on CIP in solution was studied at 15℃, 25 ℃ and 35 ℃. By computing the standard enthalpy change (ΔH°), the standard entropy change (ΔS°),

and the standard free energy variation (ΔG°) to represent the adsorption thermodynamics, the feasibility of the adsorption process was examined. The expressions of the equations are as follows:

$$lnK_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

$$\Delta G^\circ = -RTlnK_C \quad (10)$$

where R is the molar constant of the gas with a value of 8.3145 (J/(mol×k)), T is the absolute temperature (k), and K_C is the standard thermodynamic equilibrium constant (L/mg).