Supporting Information

Adsorption and reduction transformation behaviors of Cr(VI) on mesoporous polydopamine/titanium dioxide composite nanospheres

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Preparation of mesoporous TiO₂.

Mesoporous TiO₂ materials were obtained by a traditional method. The weight of 2.88 g (0.012 mol) of titanium sulfate and 5.76 g (0.096 mol) urea were added into 150 ml pure water and stirred mildly at room temperature. After the reagents were dissolved completely, 1.212 g (0.000096 mol) of amphiphilic triblock copolymer F127 was put into the pellucid solution with vigorous stirring. The mixed solution was stirred for 30 min, and transferred into autoclave with fluoroethylene liner to react at 110 °C for 24 h. After cooling down to room temperature, the mixture was centrifuged, and then the prepared materials were dried overnight, and designed as pure mesoporous TiO₂.

Carbonization of PDA/TiO₂-0.5.

The pre-prepared claret materials using titanium sulfate as the titanium precursor were heated in the mixed gases of 90 % Ar and 10 % H_2 at a rate of 1 °C/min from 20 °C to 260 °C and maintained at the temperature for 1 h, then heated up to 550 °C at a rate of 1 °C/min and maintained 2 h.

Adsorption isotherm models:

Langmuir isotherm model:

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_{\rm max}K_{\rm I}} + \frac{C_{\rm e}}{Q_{\rm max}}$$

Freundlich isotherm model:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_f$$

Tempkin model:

$$Q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$$

Dubinin-Radushkevich model:

$$\ln Q_e = \ln Q_{\max} - k\varepsilon^2, \quad \varepsilon = RT \ln(1 + \frac{1}{C_e}), \quad E = (2k)^{-\frac{1}{2}}$$

where C_e (mg/L) is the equilibrium concentration of Cr (VI) in the solution, Q_e (mg/g) is the equilibrium adsorption ability. Q_{max} (mg/g) is the the maximum adsorption ability of the adsorbent, K_1 (L/mg) is a constant, C_o (mg/L) is the initial concentration of Cr (VI) solution, K_f (mg^{1-n.}L/g) is a content relate to adsorption capacity, and n is the uniformity coefficient that can be utilized to indicate the heterogeneity of adsorbent. R (8.3145 J/mol/K) is molar gas constant. T (K) is kelvin temperature. b_T is a constant that was associated with adsorption energy. k (mol²/KJ²) is a constant and ε is adsorption potential. E (KJ/mol) is mean free adsorption energy.

Adsorption kinetic models:

Pseudo-first-order kinetic model:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

Pseudo-Second-order kinetic model:

$$\frac{\mathrm{t}}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Elovich model:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

Webber-Morris model:

$$Q_t = k_{wm} t^{\frac{1}{2}} + C$$

Bangham model:

$$\ln Q_t = \ln k_B + \frac{1}{m} \ln t$$

where $Q_e (mg/g)$ is the equilibrium adsorption capacity, Q_t is the adsorption capacity at time t, and k_1 , k_2 , $k_{wm} (mg/g/min^{1/2})$ and k_B are the rate constant of models, respectively. α (g/mg/min) and β (g/mg) are initial absorbing rate and desorption constant, severally. Thermodynamic equations:

$$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$$
$$\ln K_{c} = -\frac{\Delta H^{0}}{RT} + \frac{\Delta S^{0}}{R}$$
$$K_{c} = \frac{Q_{e}}{C_{e}}$$

where K_c is the equilibrium constant, Q_e and C_e are the equilibrium adsorption capacity and equilibrium concentration, severally.



Fig. S1. The FT-IR spectra of pure PDA.







Fig. S2. The SEM (a), TEM (b and c) and EDS (d) images of PDA/TiO₂-0.5.



Fig. S3. The removal capacities of PDA/TiO₂-(0.25, 0.5, 1.0, 1.5) with different contact time.



Fig. S4. The removal capacity of PDA/TiO₂-0.5 with different Cr (VI) concentration and contact.



Fig. S5. The removal efficiency and capacity of TiO₂ and PDA/TiO₂- 0.5 at 24 h, 200 mg/l, 1.5 pH.



Fig. S6. Adsorption kinetics of Cr(VI) on mesoporous PDA/TiO₂-0.5: (a) Pseudo-first-order kinetic, (b) Pseudo-second-order kinetic, (c) Elovich, (d) Webber-Morris, and (e) Bangham



Fig. S7. Adsorption isotherms of Cr(VI) on mesoporous PDA/TiO₂-0.5: (a) Langmuir isotherm,

(b) Freundlich isotherm, (c) Tempkin, (d) D-R



Fig. S8. The CV pattern of PDA/TiO₂-0.5.



Fig. S9. The removal efficiency of carbonizing PDA/TiO₂-0.5 for Cr (VI)