Supplementary Material

Nanocomposites of Zirconia@Activated Carbon Derived from Hazelnut Shell for Adsorption of Tetracyclines from Water

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Materials

TC, OTC and CTC were purchased from sigma-aldrich. All other reagents used which were of analytical grade, were obtained from Sinopharm Chemical Reagent Co., Shanghai, China, and used as received. The individual stock solutions were prepared by dissolving 1 g of TC, OTC and CTC (individually) in 1 L of distilled water and the desirable concentrations of the three antibiotics in experimental process were prepared by the dilution of stock solution.

Characterization

The product obtained was characterized by X-ray diffraction using Cu Kα radiation (XRD, Almelo PW-3060, Netherland) from 2θ of 10–90° with 2° scan step, scanning electron microscope (Shimadzu SS 550) equipped with an energy-dispersive X-ray analyzer at 5 keV and a TECNAI G20 transmission electron microscope (TEM, FEI, USA) at 5 keV. The thermogravimetric analysis was obtained by a HCT-2 thermogravimetric analyzer (Beijing Scientific Instrument Factory, China) from 30 to 1000 °C at a heating speed of 10 °C min^{-1} using a 20 mL s^{-1} flow of air atmosphere. The absorption spectra of the nanocomposites were taken at room temperature by a Nicolet 6700 Fourier transmission infrared spectroscopy (FT-IR) in the range of 400-4000 cm^{-1} with a resolution of 1 cm^{-1} using KBr window, and by a Raman spectroscopy (Scientific DXR, Thermo) using a laser wavelength of 514.2nm at c.a. 5mW with a 100x objective. All the pH values were measured by a ST20 pH meter (Ohaus Corporation, USA). The specific surface area was measured by N_2 adsorption-desorption at 77 K (Micromeritics ASAP 2020) using Brunauer–Emmet–Teller (BET) isotherms.

Analysis

Simultaneous determination of OTC, TC and CTC in samples was performed using high-performance liquid chromatography (HPLC) coupled with ultraviolet detection at 355 nm. A Dikma C18 (150×4.6 mm, 5 μm particle size) as the chromatograph column was operated at 35℃. The mixture solution of acetonitrile/0.01mol L^{-1} of oxalic acid solution in a 30:70 (v/v)

ratio were used as mobile phase at a flow rate of 1.0 mL min^{-1}. The injection volume was 20 μL. The details are described in the Supporting Information. Detection limits of TC, OTC and CTC were below 0.004, 0.004 and 0.009 mg L^{-1}, respectively. The quantitation limits of TC, OTC and CTC were 0.04, 0.04 and 0.07 mg L^{-1}, respectively.

Calculation of adsorption capacity

$$q = (C_0 - C_t)\, V/m \qquad \text{(S1)}$$

where q (mg g^{-1}) is the adsorption capacity, C_0 (mg L^{-1}) is the initial concentration of antibiotics, C_t (mg L^{-1}) is the remnant concentration of antibiotics, V (mL) is the volume of solution and m (g) is the mass of sorbents.

Adsorption isotherms

The linearized equations of Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm can be expressed as Eqs. (S1) and (S2), respectively.

$$C_e/q_e = 1/(q_{max}\, b) + C_e/q_{max} \qquad \text{(S2)}$$

$$\log q_e = \log k_F + (1/n) \log C_e \qquad \text{(S3)}$$

$$\ln q_e = \ln q_s - k_{ad}\varepsilon^2 \qquad \text{(S4)}$$

where q_e (mg g^{-1}) is the amount of antibiotics adsorbed per unit mass of sorbents at equilibrium; C_e (mg L^{-1}) is the concentration at equilibrium; q_{max} (mg g^{-1}) is the maximum adsorption at monolayer coverage; b (L mg^{-1}) is the adsorption equilibrium constant; K_F (L g^{-1}) is a Freundlich constant; n is a constant; k_{ad} (mol^2 kJ^{-2}) is the D–R isotherm constant; q_s (mg g^{-1}) is the saturation capacity from D–R isotherm; ε is the Polanyi potential and calculated as follows:

$$\varepsilon = RT \ln (1+1/C_{eq}) \qquad \text{(S5)}$$

where R (8.314 J mol^{-1} K^{-1}) is universal gas constant; T (K) is the absolute temperature. C_{eq} (mol L^{-1}) is the equilibrium concentration of adsorbate.

E (kJ mol^{-1}) is the change of free energy transforming 1 mol of adsorbates from solution to the surfaces and is conducive to the estimation of adsorption reaction type, and is obtained from k_{ad} as follows:

$$E = -(2k_{ad})^{-1/2} \quad \text{(S6)}$$

Kinetic analysis

The pseudo-first-order and pseudo-second-order rate expressions are linearly expressed as:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad \text{(S7)}$$

$$t/q_t = 1/k_2 q_e^{\,2} + t/q_e \quad \text{(S8)}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption. q_e and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and the adsorption amount at time t (min), respectively. k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order equation.

The intraparticle diffusion model is linearly expressed as

$$q_t = k_{pi}\, t^{0.5} + C_{pi} \quad \text{(S9)}$$

Where k_{pi} is the intraparticle diffusion rate constant of stage i (mg g^{-1} min$^{-0.5}$), C_{pi}, the intercept of stage i, gives an idea about the thickness of boundary layer, i.e., the larger of the intercept, the greater of the boundary layer effect.

Thermodynamic analysis

Thermodynamic parameters such as standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) at equilibrium at different temperatures can be calculated from the constant (b, L mol^{-1}) of Langmuir isotherm equation as the following equations:

$$\Delta G^{o} = -RT \ln b \quad \text{(S10)}$$

In order to use b in the thermodynamic calculations, the value of b expressed in L mg^{-1} in Langmuir isotherm equation can be multiplied by 1000 to convert the units in L g^{-1}, and then multiplied by the molecular weight of the antibiotics, to transform b in L mol^{-1}.

ΔH° and ΔS° were obtained from Eq.S10.

$$ln\, b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad \text{(S11)}$$

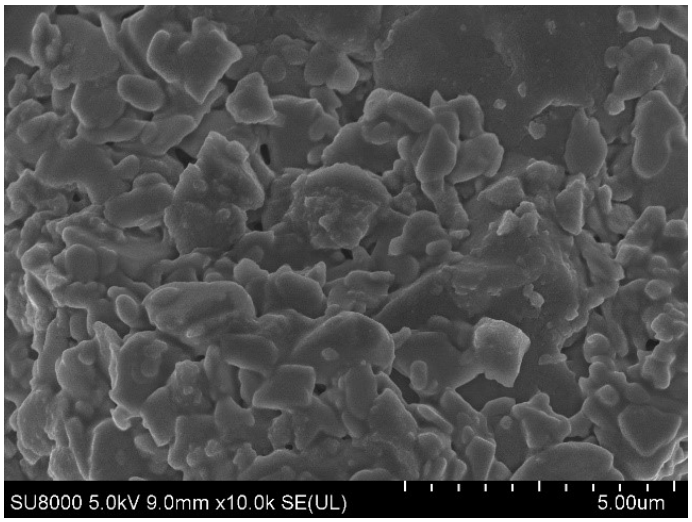

Figure S1 SEM image of the AC.

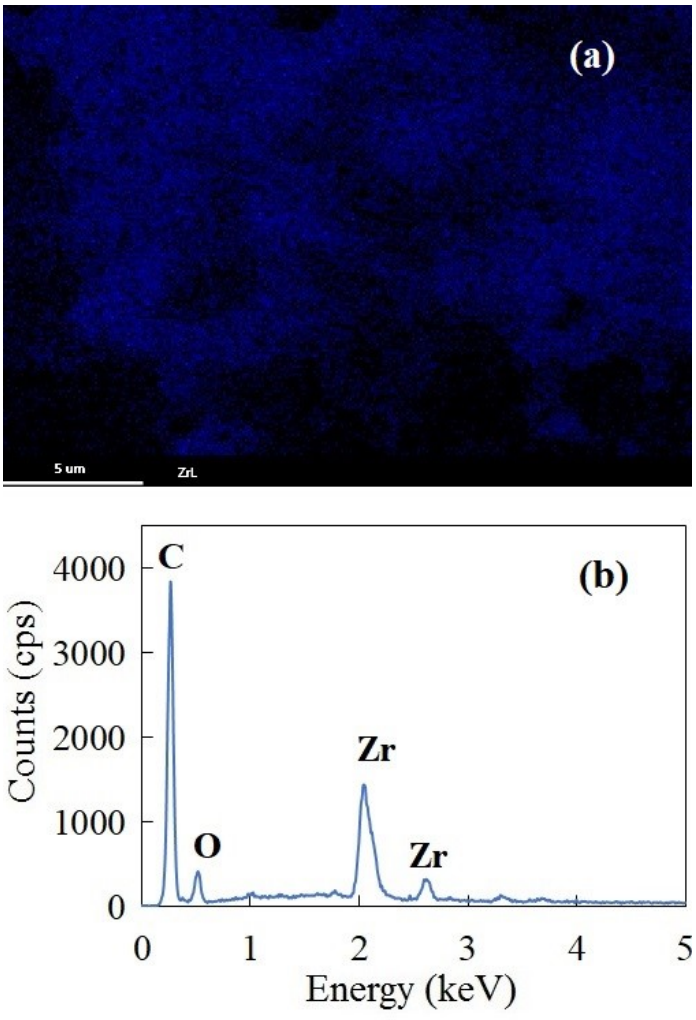

Figure S2 EDS spectra of the ZrO_2@AC.

Table S1 Physic-chemical parameters of the culture wastewater

Measured parameters	Culture wastewater
Conductivity (μs cm^{-1}) [a]	2997
Salinity (ppt) [a]	1.5
Oxidation-reduction potential (mV) [a]	487
Total dissolved solids (mg L^{-1}) [a]	1243
Dissolved organic carbon (mg C L^{-1}) [b]	32.2±2.9
Chemical oxygen demand (mg L^{-1}) [c]	789.6±55.7
pH	8.7±0.1
TC (mg L^{-1})	N.D.[d]
OTC (mg L^{-1})	N.D.
CTC (mg L^{-1})	2.3

[a] Conductivity, salinity, oxidation-reduction potential and total dissolved solids were measured by pen conductivity meter (ST10C-B), pen salinity meter (ST20S), pen ORP meter (ST10R) and pen TDS meter (ST10T-B), respectively (Ohaus, Canada).

[b] Dissolved organic carbon was measured using a TOC analyzer (Dohrmanne DC-190, GE, USA).

[c] Chemical oxygen demand was measured by potassium dichromate method.

[d] N.D. means not detected.