Supporting information

A new magnetic adsorbent of eggshell-zeolitic imidazolate framework for highly efficient removal of norfloxacin

Chemicals and instrumentation

Norfloxacin (98%), iron oxide (II, III, Fe_3O_4)(99%), dopamine hydrochloride (98%) and tris(hydroxymethyl)aminomethane (denoted as THAM) were purchased from Macklin Company, China. The salts including zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, AR) and 2-methylimidazole (denoted as HMIM, 98%) were purchased from Aladdin company, China. Methonal (gradient grade for liquid chromatography) was purchased from EMD Millipore Corporation, Germany.

For having a better investigation of the functional groups on the surface of the synthesized materials, FTIR analysis was conducted by Fourier Infrared Spectrometer (Rayleigh Company, China) using potassium bromide (KBr) pellet method. Scanning electron microscopy (SEM) was utilized for observation of the general surface morphology of the prepared materials. Transmission electron microscopy (TEM) was characterized on a JEOL JEM-2100 field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo Scientific Escalab 250Xi spectrometer. PXRD analysis was conducted by using Lab-X (XRD-6100, Shimadzu, Japan) to reorganize the crystal structure of materials. Brunauer Emmett-Teller (BET, TriStar II 3020, Micromeritics Company, USA) surface area analysis was exerted to measure both specific surface area and porosity of the synthesized materials through N_2 adsorption/desorption at 77 K. The magnetic property of sample was determined via a vibrating sample magnetometer analysis (VSM). The determination of norfloxacin concentration in solution was detected by double beam UV-Vis spectrophotometer (MAPADA Company, China). Zeta potentials were tested using a Nanotrac wave II (Microtrac, America) instrument at various pH values.

In this study, all batch experiments were performed duplicated. Solution pH was adjusted by dilute acetic acid or dilute NaOH solution. The remaining concentrations of NOR were measured at 273 nm using an UV-vis spectrophotometer, and the

removal efficiency (R%) and the absorption capacity (q (mg/g)) calculated using the fellow equations.

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

Where C_0 (mg/L) and C_t (mg/L) represented the initial concentration of NOR and the concentration of NOR in solution at the fixed time respectively. V (L) was the volume of the solution while m (g) represented the mass of adsorbent.

To learn the NOR adsorption process, the adsorption isotherms as well as kinetics were fully analyzed. FEZ (50 mg) was added into a pH-adjusted NOR solution at different initial concentrations at 298K, 308K, 318K and 328K for 6h. As for the adsorption isotherms studies, the pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)) were utilized to fit to the data obtained from experiments.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where q_e (mg/L) and q_t (mg/L) correspondingly represent the adsorption capacity of NOR at equilibrium and at time t, respectively; k_1 (min^{-1}) was the rate constant for the pseudo-first-order kinetic model while k_2 (g/mg · min) represented the rate constant of the pseudo-second-order kinetic model. As for the study of adsorption isotherms, the Langmuir (Eq. (5)), Freundlich (Eq. (6)) and Temkin (Eq. 7)) [36, 37] models were exerted to fit the data obtained from experiments.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} K_L} \quad (5)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

$$q_e = B \ln A_T + B \ln C_e \quad (7)$$

Where C_e (mg/L) and q_e (mg/g) correspondingly represent the equilibrium solute concentration and equilibrium adsorption capacity. q_{max} (mg/g) is maximum adsorption capacity of the adsorbent. n is an exponential parameter.

B (J/mol) represents the constant related to heat sorption. K_L (mg/L), K_F (mg/g) and A_T (L/g) represent respectively the Langmuir adsorption constant, the Freundlich adsorption equilibrium constant and the Temkin isotherm equilibrium constant.

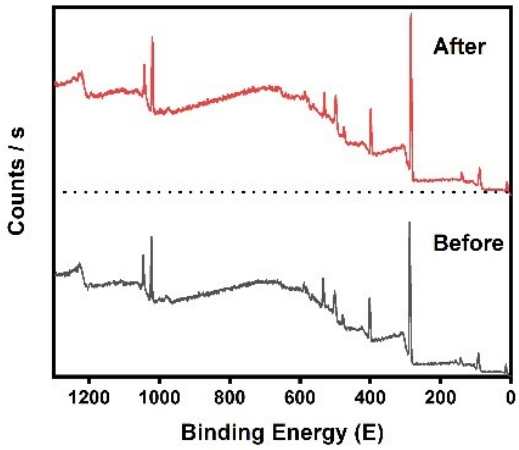

Figure S1. XPS analysis for the FEZ before and after adsorption.

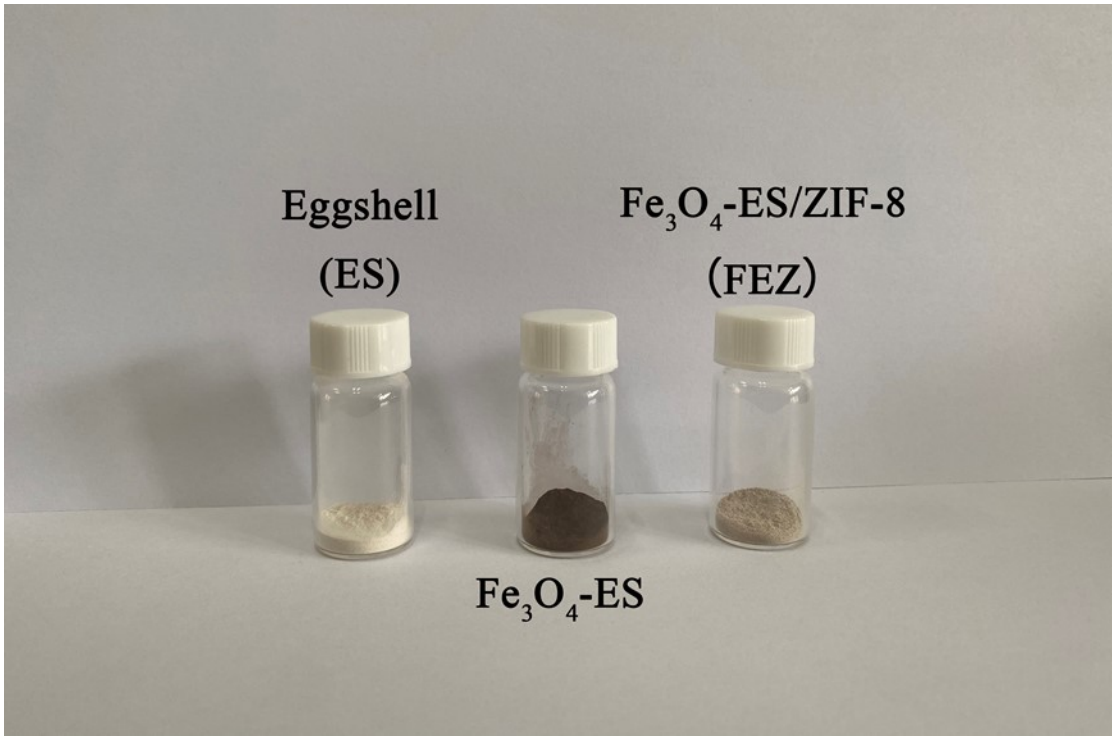

Figure S2. The colour change of the preparation of eggshell (ES), Fe_3O_4-ES and Fe_3O_4-ES/ZIF-8 (FEZ).

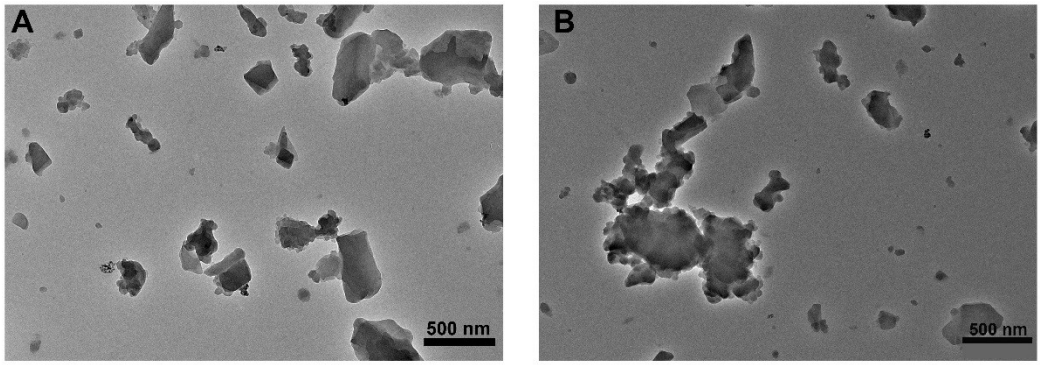

Figure S3. TEM images for Fe_3O_4-ES (A) and Fe_3O_4-ES/ZIF-8 (FEZ) (B).

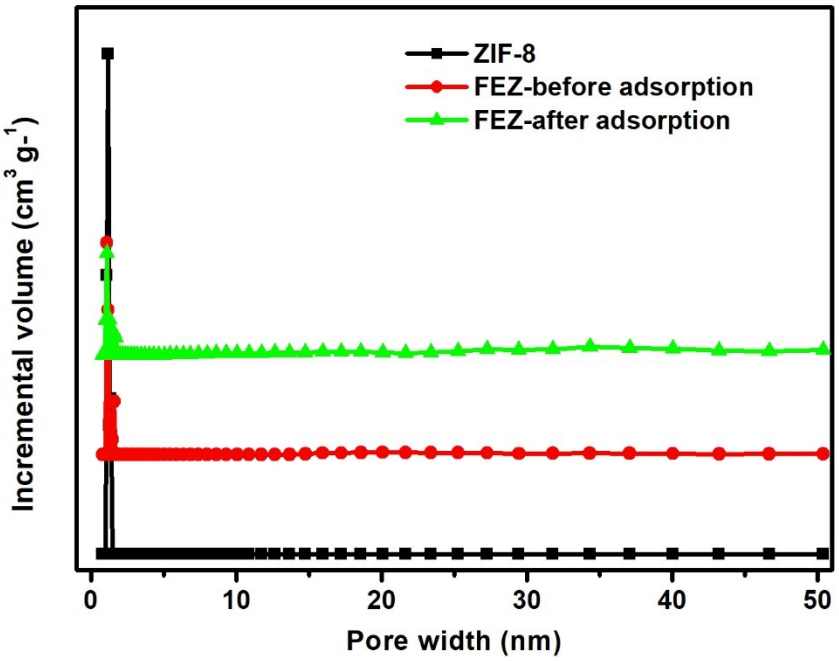

Fig. S4 the corresponding pore size distribution curves of ZIF-8, FEZ-before adsorption and FEZ-after adsorption.

Table S1. The Zeta potential of the FEZ in the NOR solution with different pH value.

The pH value of the NOR solution	Zeta potential of the FEZ
4	+31.2
5	+25.7
6	+20.8

Table S2. Textural properties of the samples.

Sample	S_{BET}[a] $m^2\ g^{-1}$	Pore width (nm)	V_{total}[b] $cm^3\ g^{-1}$	V_{micro}[c] $cm^3\ g^{-1}$
ZIF-8	1785	1.18	0.53	0.53
FEZ-before adsorption	865	1.09	0.23	0.22
FEZ-after adsorption	298	1.27	0.18	0.11

[a] S_{BET} was calculated in the partial pressure (P/P_0) range of 0.05 to 0.20 which gives the best linearity; [b] Total pore volume at relative pressure $P/P_0 = 0.98$; [c] Cumulative micropore volume with diameter ≤ 2 nm.