Amino functional SBA-15 assisted NU-1000 for rapid and efficient adsorption of tetracycline antibiotics

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Part 1. Experimental section

1.1 Chemicals

SBA-15 was purchased from Nanjing XFNANO Materials Technology Co. (China), 1,3,6,8-Tetra(4-carboxyphenyl) pyrene (H_4TBAPy) and zirconium (IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) were purchased from Aladdin Industrial Co. Ltd. Tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), aclacinomycin (ACL), penicillin (PEG), streptomycin sulfate (STR), sulfachlorpyridazine (SCP), sulfamethoxypyridazine (SMP), sulfamerazine (SMR) were purchased from Sigma-Aldrich. All of the other chemicals were purchased from commercial suppliers and utilized without purifying.

1.2 Characterizations

Scanning electron microscopy (SEM) images were taken by Cezch Republic Tescan mira. Transmission electron microscopy (TEM) was measured by Japan JEM-2100F. Powder X-ray diffraction (PXRD) and small-angle X-ray diffraction (SXRD) were scanned on a Japan Smartlab 9X Advance X-ray diffractometer. Thermogravimetric analysis (TGA) was carried out by America Perkin-Elmer STA8000. The N_2 sorption isotherms were obtained by an America Micrometrics ASAP 2460 surface area analyzer. Fourier transform infrared (FT-IR) spectra were recorded on an America Perkin-Elmer Spectrum 100. The X-ray photoelectron

spectroscopy (XPS) was measured using America Thermo Scientific K-Alpha. Ultraviolet-visible spectroscopy (UV–Vis) was performed using Shanghai UV-1901 spectrometer. The zeta potential was measured by ZEN 3600 Malvern Zetasizer Nano analyzer.

Part 2. Tables

Table S1. Kinetic model parameters for the adsorption of TC on SBA-15@NU-1000

Models	Parameters	TC	OTC	CTC
Pseudo-first-order model	Q_e (mg·g^{-1})	83.1 ± 1.0	82.6 ± 0.8	87.3 ± 0.5
	k_1 (min^{-1})	1.105 ± 0.129	0.882 ± 0.073	1.636 ± 0.119
	R^2	0.9502	0.96919	0.98812
Pseudo-second-order model	Q_e (mg·g^{-1})	84.9 ± 0.4	84.4 ± 0.1	88.4 ± 0.2
	k_2 (mg·g^{-1}·min^{-1})	0.0274 ± 0.0021	0.0218 ± 0.0004	0.0601 ± 0.0043
	R^2	0.9924	0.9994	0.9967
Elovich model	α	6.381E6 ± 1.798	1.717E8 ± 4.153	4.119E12 ± 2.719
	β	0.308 ± 0.036	0.266 ± 0.032	0.531 ± 0.078
	R^2	0.9744	0.9649	0.9869
Weber-Morris model	k_{i1}	8.81 ± 0.23	15.83 ± 1.29	9.81 ± 0.56
	C_{i1}	55.66 ± 1.36	41.93 ± 2.24	64.13 ± 0.98
	R^2	0.9971	0.9776	0.9848
	k_{i2}	0.08 ± 0.01	0.24 ± 0.07	0.09 ± 0.03
	C_{i2}	83.92 ± 2.71	81.04 ± 0.79	87.29 ± 0.34
	R^2	0.9966	0.9734	0.9819

Table S2. Isotherm parameters for the adsorption of TC on SBA-15@NU-1000

Models	Parameters	TC	OTC	CTC
Langmuir isotherm	Q_m ($mg \cdot g^{-1}$)	281.3 ± 30.5	357.0 ± 11.9	497.1 ± 42.0
	b ($L \cdot mg^{-1}$)	0.130 ± 0.05	0.079 ± 0.008	0.215 ± 0.059
	R^2	0.9278	0.9706	0.9311
Freundlich isotherm	K_f ($mg^{1-1/n} \cdot L^{-1/n} \cdot g^{-1}$)	60.8 ± 6.9	59.1 ± 5.8	142.2 ± 3.9
	n	2.60 ± 0.25	2.45 ± 0.17	2.94 ± 0.08
	R^2	0.9735	0.9798	0.9964
Sips isotherm	Q_m ($mg \cdot g^{-1}$)	424.2 ± 33.7	450.7 ± 26.9	526.3 ± 51.8
	b_s ($mg^{-1/n} \cdot L^{-1/n}$)	0.103 ± 0.018	0.042 ± 0.007	0.148 ± 0.063
	n	0.44 ± 0.12	0.75 ± 0.04	0.37 ± 0.06
	R^2	0.9682	0.9987	0.9962
Temkin isotherm	a_T ($L \cdot g^{-1}$)	2621 ± 407	1047 ± 134	2023 ± 312
	b_T ($kJ \cdot mol^{-1}$)	0.049 ± 0.006	0.071 ± 0.003	0.061 ± 0.009
	R^2	0.9323	0.9871	0.8631

Part 3. Figures

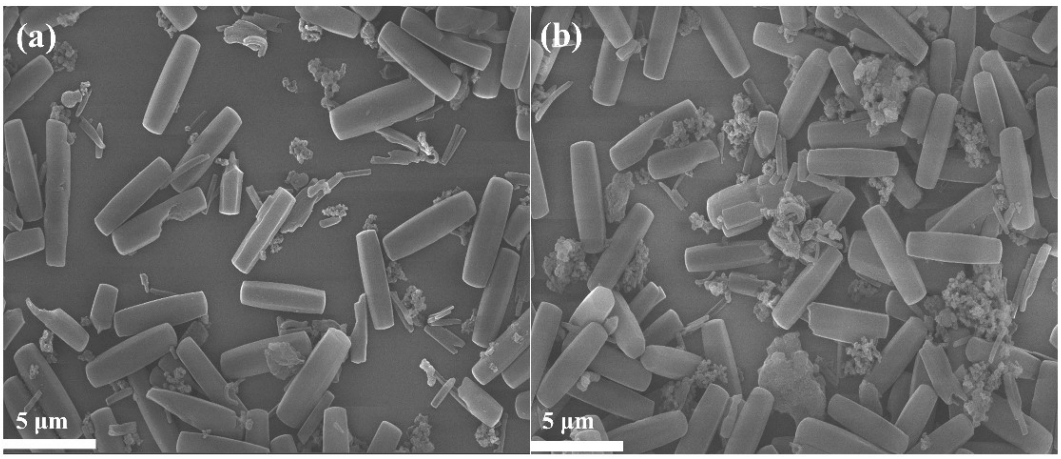

Fig. S1 SEM images showing the physical mixture of SBA-15 and NU-1000.

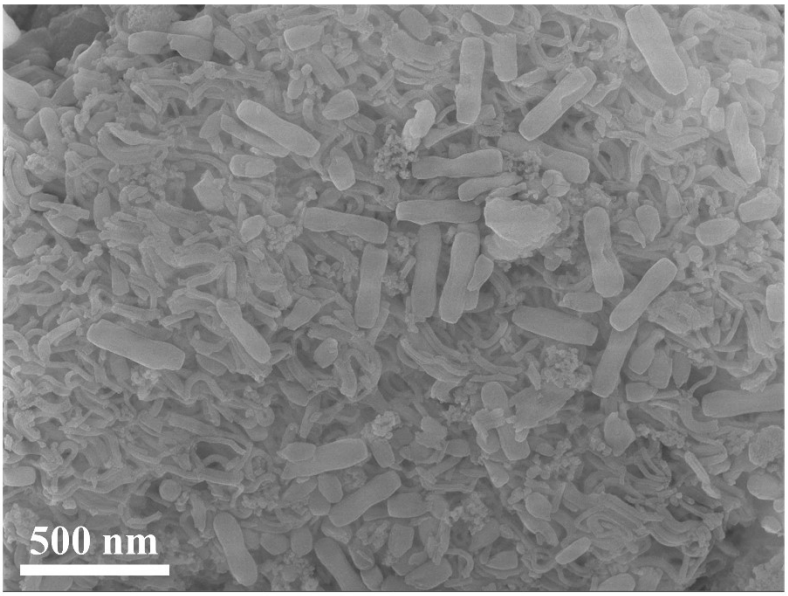

Fig. S2 SEM image of 0.25-SBA-15@NU-1000.

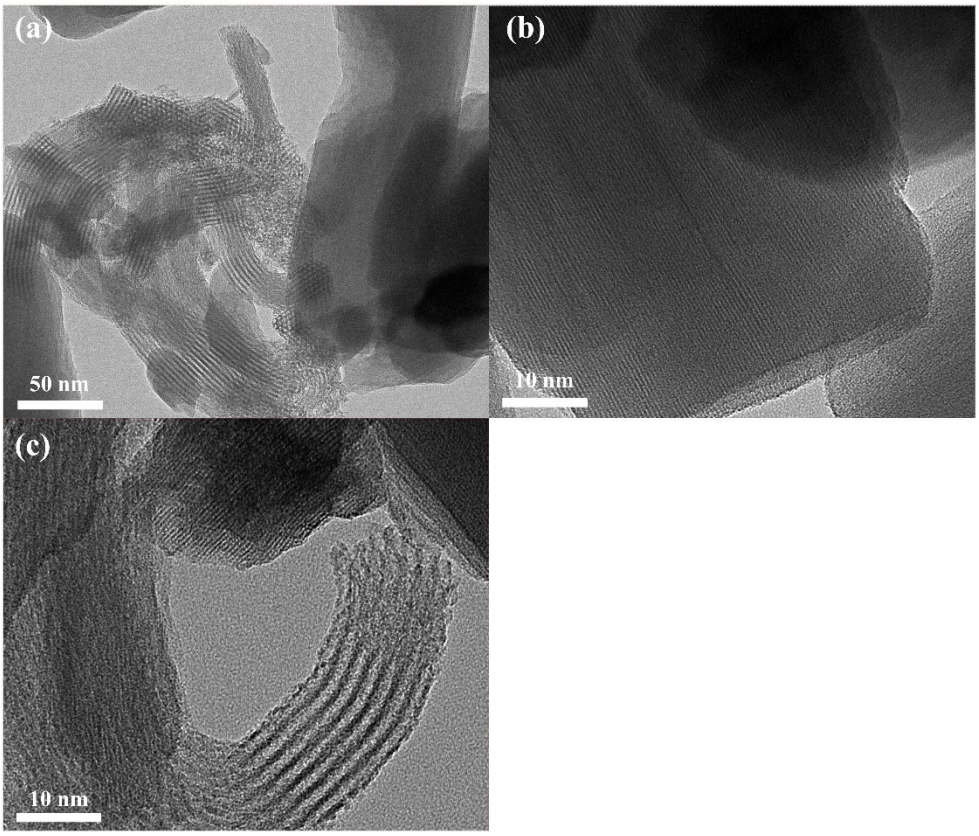

Fig. S3 High-resolution TEM images of 0.2-SBA-15@NU-1000.

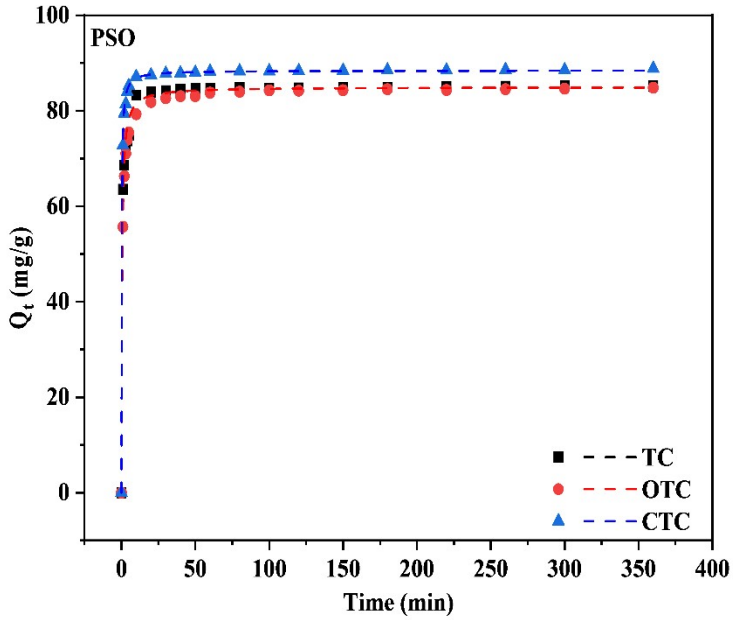

Fig. S4 Adsorption kinetics of TCs on SBA-15@NU-1000 fitted by nonlinear PSO model.

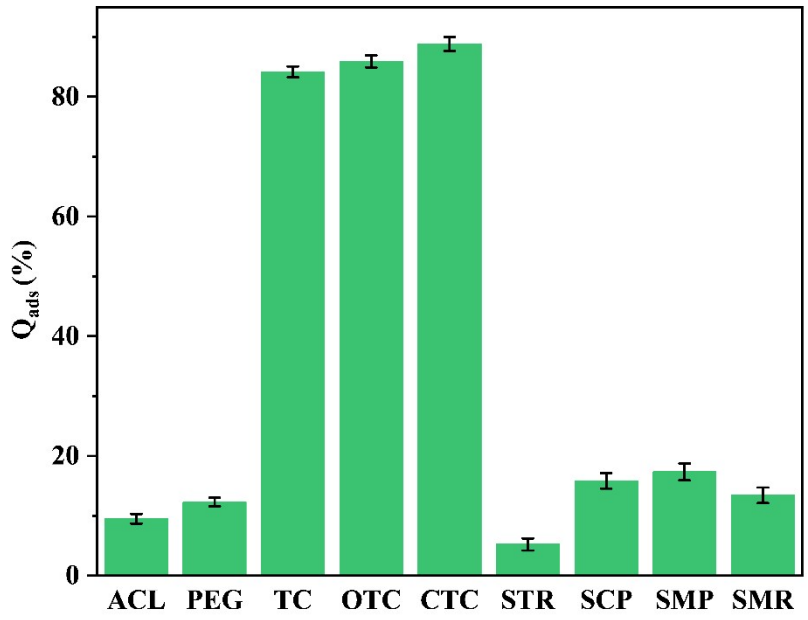

Fig. S5 Removal efficiency (Q_{ads} (%)) of SBA-15@NU-1000 toward various antibiotics (5 mg of SBA-15@NU-1000, 40 mg/L of the investigated antibiotics).

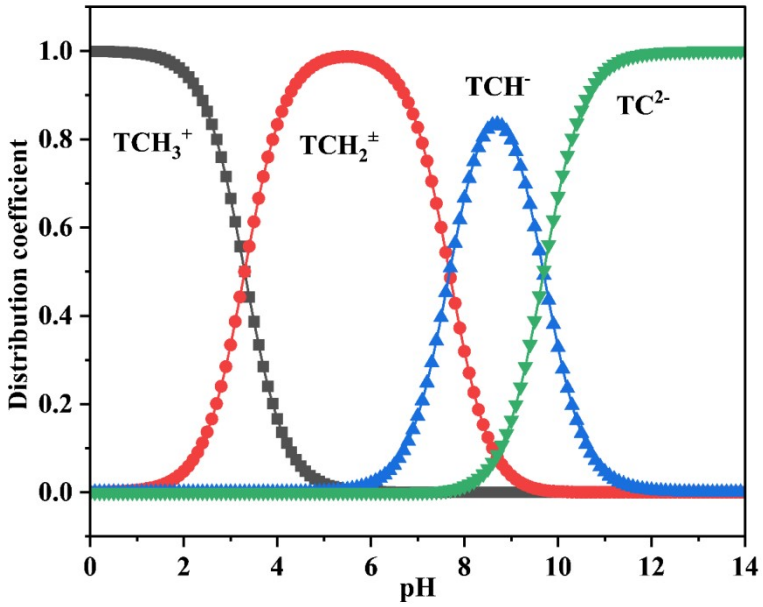

Fig. S6 Distribution plotting curve of TC at different pH.

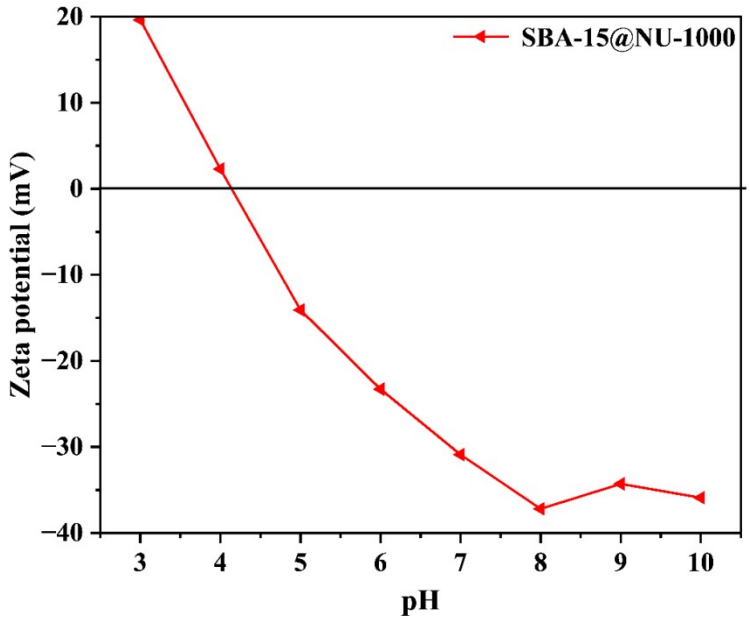

Fig. S7 Zeta potential values of SBA-15@NU-1000 at different pH.