Norfloxacin Sorption and Its Thermodynamics on Surface-modified Carbon Nanotubes

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Supporting Information

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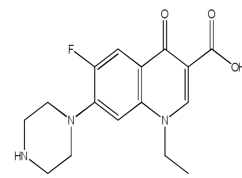
Table S1 NOR properties.

Common name	Abbreviation	Chemical formula	M.W. (g mol^{-1})	Water solubility (mg L^{-1})	pK_a	LogK_{ow}	Molecular structure
Norfloxacin	NOR	$C_{16}H_{18}FN_3O_3$	319.33	161,000[a] (pH 5) 400[a] (pH 7) 910[a] (pH 9)	6.22[a] (pK_{a1}) 8.51[a] (pK_{a2})	-1.7[b] (pH 5) -1.0[b] (pH 7) -1.63[b] (pH 9)	

(a) Ross, D. L.; Riley, C. M. Aqueous Solubilities of Some Variously Substituted Quinolone Antimicrobials. *Int. J. Pharm.* **1990,** *63* (3), 237-250.
(b) Takács-Novák, K.; Józan, M.; Hermecz, I.; Szász, G. Lipophilicity of Antibacterial Fluoroquinolones. *Int. J. Pharm.* **1992,** *79* (2-3), 89-96.

Table S2 Selected properties of carbon nanotubes (CNTs) and activated carbon (AC).

Carbon materials	O% [a]	Content of functional group (wt%)[b]	SSA[d] (m^2 g^{-1})	ID[e] (nm)	OD[f] (nm)	L[g] (μm)	PZC [h]
AC	10.1	--[c]	664	--	--	--	4.8
G-CNTs	<0.1	<0.1	117	3-5	8-15	<50	--
C-CNTs	4.2	2.19	164	3-5	8-15	<50	3.3
H-CNTs	4.1	4.28	228	3-5	8-15	<50	4.0

(a) O% and Oxidized carbon (%) was measured by X-ray photoelectron spectroscopy (XPS).
(b) –COOH content in C-CNTs and –OH content in H-CNTs were measured by XPS and titration.
(c) not available
(d) SSA: special surface area of the CNTs and AC. Brunauer-Emmett-Teller (BET) SSA was determined by N_2 adsorption using Quantachrome Autosorb-1.
(e) ID: inner diameter of the CNTs.
(f) OD: outer diameter of the CNTs.
(g) L: length of the CNTs.
(h) PZC: the point of zero charge of the CNTs and AC. Zeta potential was measured by a Malvern Nano Zetasizer.

Table S3 Thermodynamic index of irreversibility (*TII*) at different temperatures.

sorbent	Temperature (K)	C_0=10 mg L^{-1}	C_0=15 mg L^{-1}	C_0=30 mg L^{-1}	C_0=40 mg L^{-1}
AC	288	0.988	--	0.809	0.797
	298	0.988	0.835	0.688	0.860
	310	0.988	0.934	0.766	0.751
G-CNTs	288	0.692	0.623	0.528	0.512
	298	0.930	0.633	0.440	0.443
	310	0.005	0.008	0.143	0.162
C-CNTs	288	0.881	0.683	0.640	0.619
	298	0.880	0.615	0.361	0.580
	310	0.340	0.333	0.319	0.292
H-CNTs	288	0.969	0.801	0.654	0.664
	298	0.997	0.829	0.586	0.544
	310	0.467	0.382	0.321	0.306

Table S4 Sorption coefficients of NOR on environmental matrices in literature.

Sorbent	log*K* (C_e=0.01C_s) (L kg^{-1})	Reference
Canadian River alluvium	-2.0 - 2.0	Hari, Paruchuri et al., 2005
silica	3.1	Lorphensri, Intravijit et al., 2006
alumina	1.8	
variable charge soils	4.4 - 4.5	Zhang and Dong, 2008
black soil	2.5	
fluvo-aquic soil	2.1	Zoritaa, Mårtensson et al., 2009
red soil	2.5	

Reference

Hari, A. C., Paruchuri, R. A., Sabatini, D. A. and Kibbey, T. C. G. Effects of pH and cationic and nonionic surfactants on the adsorption of pharmaceuticals to a natural aquifer material. *Environ. Sci. Technol.* **2005**, 39(8): 2592-2598.

Lorphensri, O., Intravijit, J., Sabatini, D. A., Kibbey, T. C. G., Osathaphan, K. and Saiwan, C. Sorption of acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium. *Water Res.* **2006**, 40(7): 1481-1491.

Zhang, J. Q. and Dong, Y. H. Effect of low-molecular-weight organic acids on the adsorption of norfloxacin in typical variable charge soils of China. *J. Hazard. Mater.* **2008**, 151(2-3): 833-839.

Zoritaa, S., Mårtensson, L. and Mathiasson, L. Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden. *Sci. Total Environ.* **2009**, 407(8): 2760-2770.

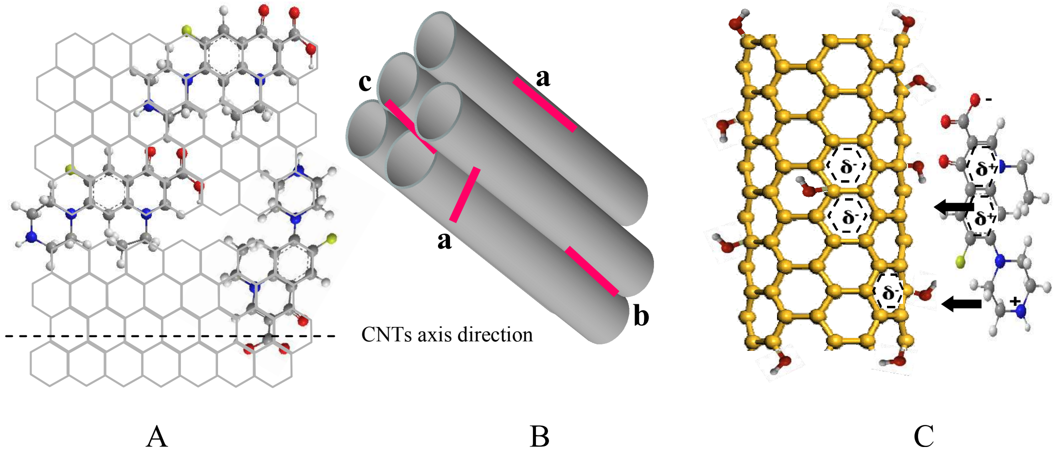


Figure S1. Schematic diagrams for sorption of NOR on CNTs. A: sorption of NOR on CNT surface. B: (a) sorption on the surface area of CNTs; (b) sorption into the groove region; and (c) sorption in interstitial spaces. C: EDA interaction between H-CNTs and NOR.

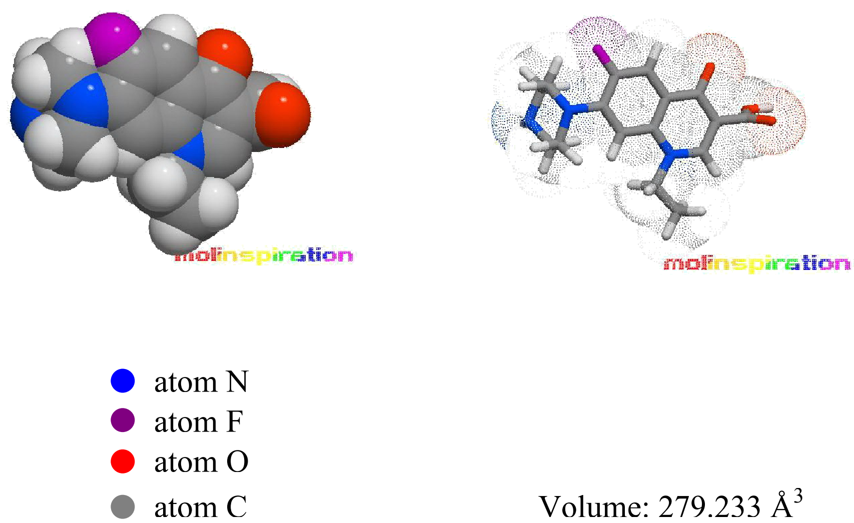


Figure S2. Optimized 3-dimensional structure of NOR. The structure and volume of NOR were modeled by Molinspiration engine v 2009.01 on http://www.molinspiration.com

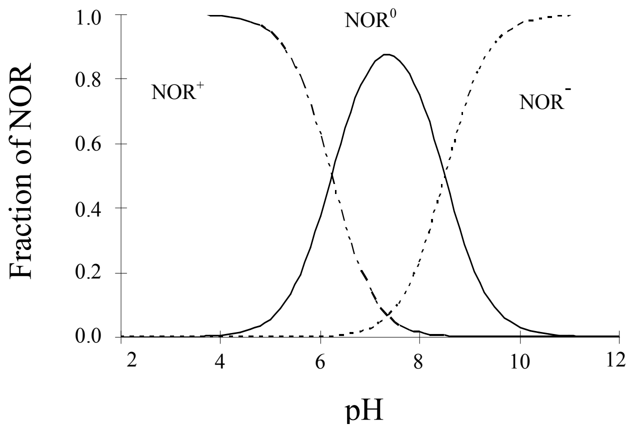


Figure S3. NOR solution speciation. The figure was calculated from NOR pKa values.

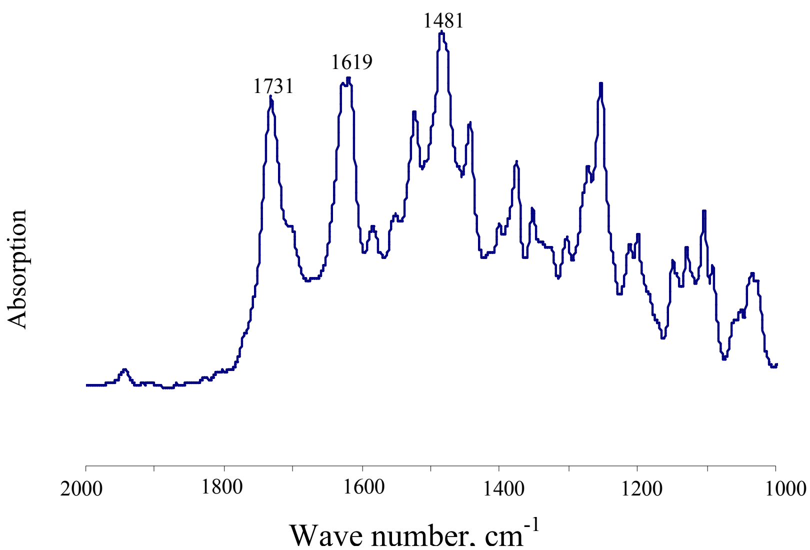


Figure S4. DRIFT spectrum of NOR.

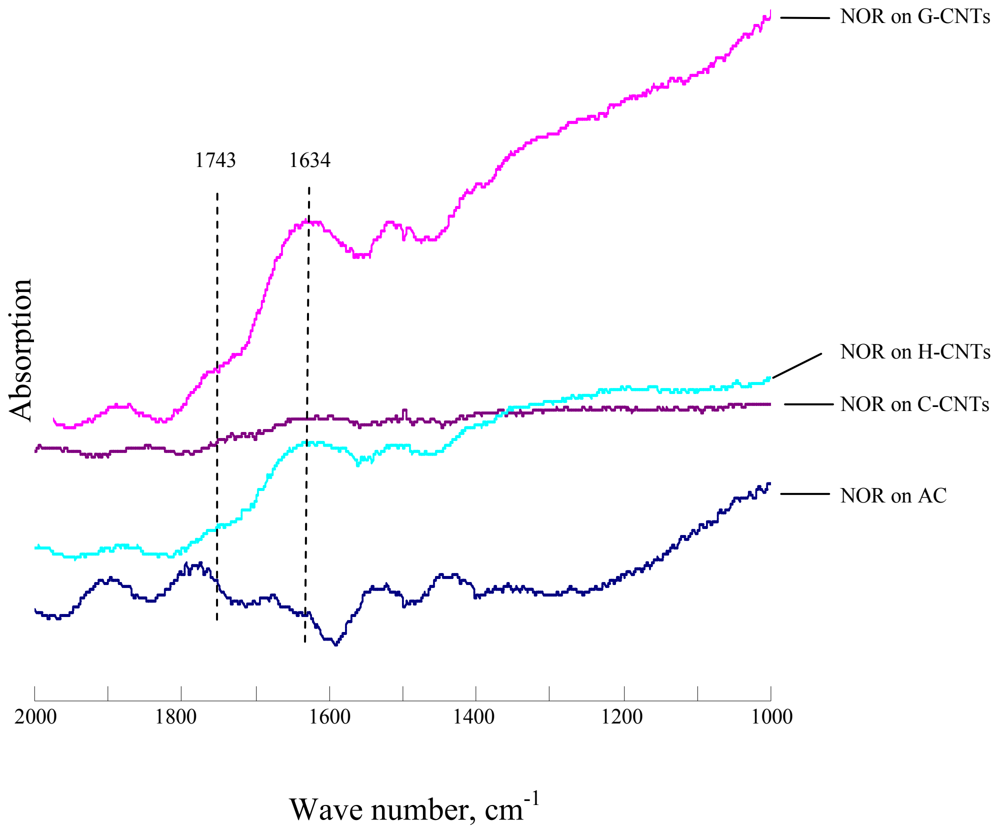


Figure S5. DRIFT spectra of adsorbed NOR on CNTs and AC.

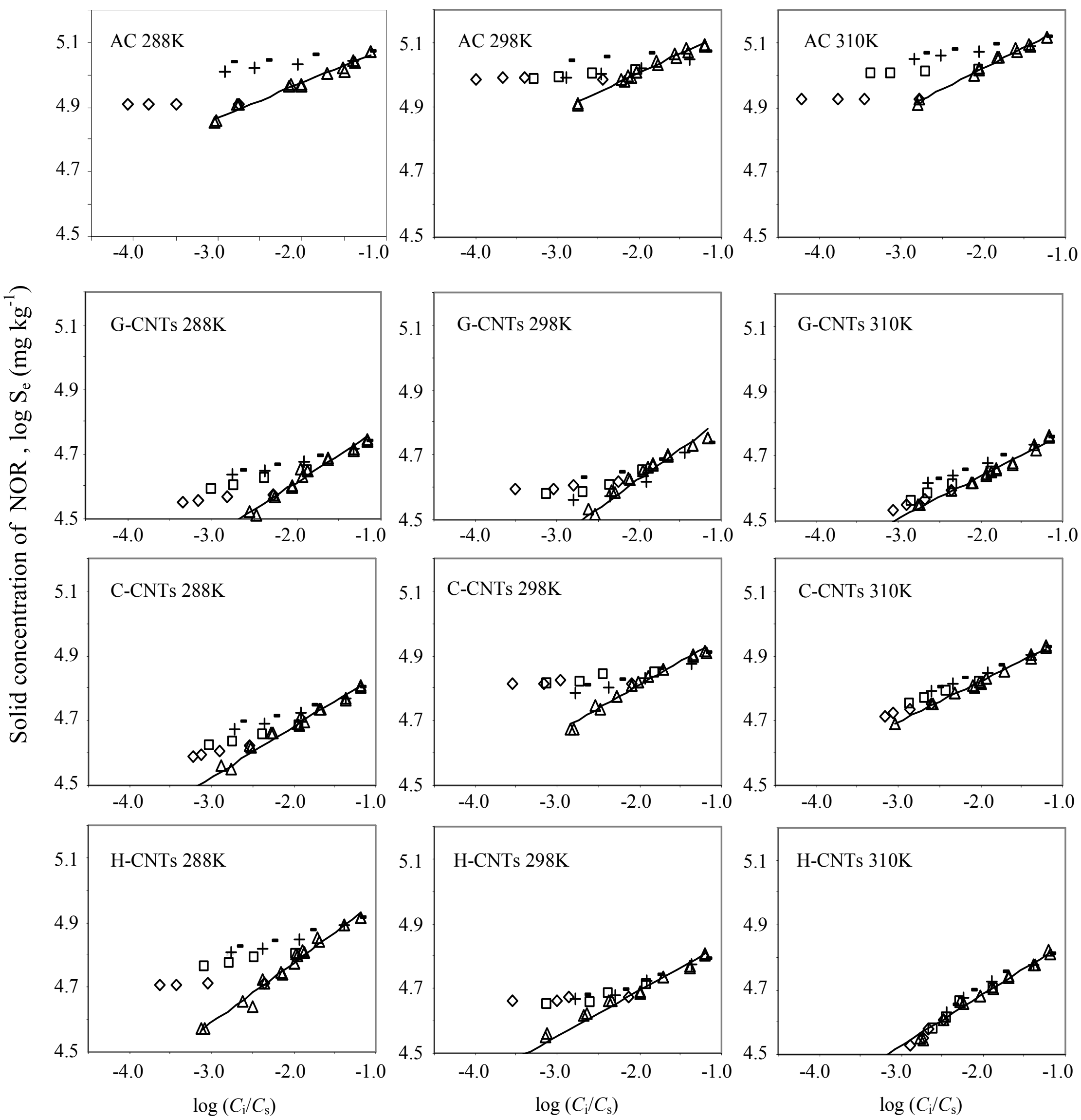


Figure S6. Desorption isotherms of NOR from CNTs and AC at 288K, 298K, and 310K. The solid lines are the original adsorption isotherms. The successive series of desorption from a single sorption point use the same symbol. Different symbols stand for different original NOR concentrations (C_0). C_0 = 10 mg L^{-1} (◊), C_0 = 15 mg L^{-1} (□), C_0 =30 mg L^{-1} (+), and C_0 = 40 mg L^{-1} (-), respectively.

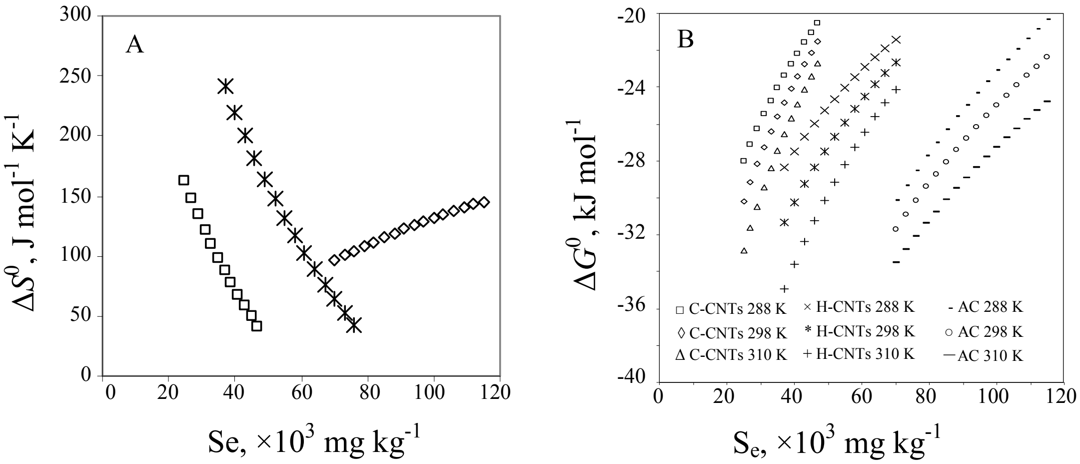


Figure S7. A: Plots of standard entropy change (ΔS^0) of NOR sorption on different sorbents. B: Plots of sorption standard Gibbs free energy change (ΔG^0) of NOR sorption on different sorbents at different temperatures. Symbols in Plots A and B stand for AC (◊), C-CNTs (□), and H-CNTs (∗), respectively.

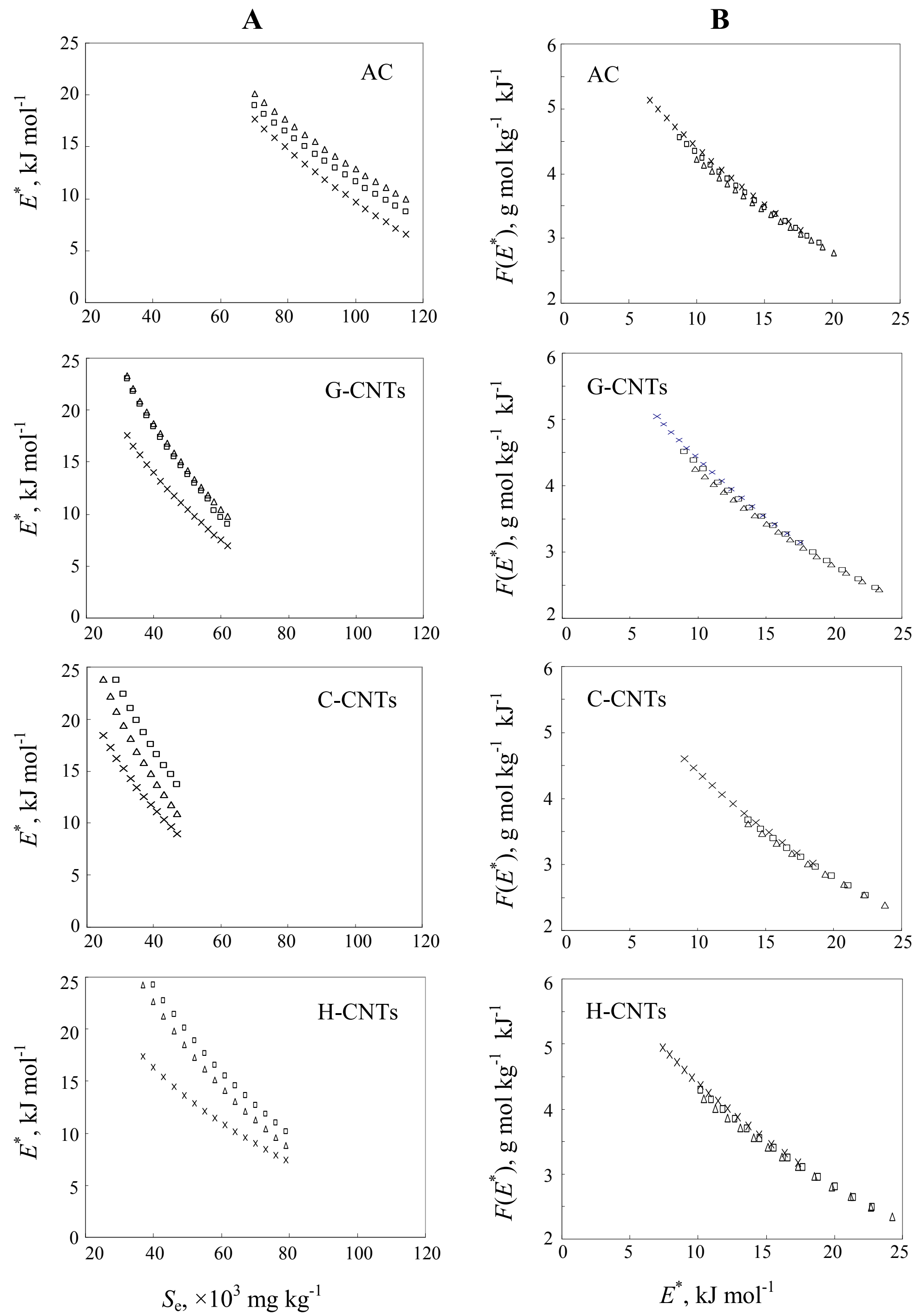


Figure S8. A: Dependence of sorption site energy on the different sorbate loading. B: Site energy distribution of NOR sorption. Symbols are 288 K (×), 298 K (□), and 310 K (Δ), respectively.