Supporting information cover sheet

Manuscript title: ADSORPTION AND DESORPTION OF OXYTETRACYCLINE AND CARBAMAZEPINE BY MULTIWALLED CARBON NANOTUBES

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Kinetics sorption and desorption models

In order to evaluate the kinetic sorption mechanism, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were tested. The linear form of the pseudo-first-order equation is given by:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (1)$$

The linear form of the pseudo-second-order model [1] is given by:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} t \right) \quad (2)$$

The rate constant for intra-particle diffusion (k_{ip}) is given by Weber and Morris [2]:

$$q_t = k_{ip} t^{1/2} + C \quad (3)$$

where q_t are the amounts of compound adsorbed on adsorbent at various time t (mg/g); k_1 is the equilibrium rate constant of pseudo-first order kinetics (min^{-1}) and t is the contact time (min); k_2 is the equilibrium rate constant of the pseudo-second-order kinetics ($\text{g}/(\text{mg h})$); k_{ip} is the intra-particle diffusion rate constant ($\text{mg}/(\text{g min}^{1/2})$) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer.

Desorption kinetics data were fitted to a two-phase first order equation, which consists of rapid and slow desorption fractions [3], using SigmaPlot 10.0 (San Jose, CA):

$$\frac{S_t}{S_0} = F_{rap} \exp(-k_{rap}t) + F_{slow} \exp(-k_{slow}t)$$

where S_t and S_0 are the sediment-sorbed amounts at time t and at the start of the experiment, respectively. F_{rap} and F_{slow} are the rapidly and slowly desorbing fractions, respectively. The rate constants of rapid and slow desorption are designated k_{rap} and k_{slow} (h^{-1}), respectively.

Table S1. Calculated pseudo-second-order adsorption rate constants for OTC and CBZ

Nanotubes	OTC				CBZ			
	q_e	k_2	r^2	t_{80}	q_e	k_2	r^2	t_{80}
MWCNT10	92.59	0.019	1.000	2.3	37.59	0.007	1.000	15.2
MWCNT20	41.15	0.016	1.000	6.1	13.81	0.015	1.000	19.3
MWCNT40	41.32	0.007	0.999	13.8	12.38	0.015	0.999	21.5
MWCNT60	37.45	0.012	1.000	8.9	9.44	0.054	0.999	7.8
MWCNT100	36.36	0.007	1.000	15.7	10.21	0.022	1.000	17.8

q_e is equilibrium solid phase concentration (mg/g). k_2 is the pseudo-second-order rate constant (g/mg·h). t_{80} is equilibration time required to reach 80% of adsorption capacity

Table S2. The monolayer adsorption capacity (Q_m) used in surface coverage calculations

Carbon nanotubes	OTC	CBZ
MWCNT10	814	1004
MWCNT20	287	354
MWCNT40	196	242
MWCNT60	166	205
MWCNT100	132	163

Q_m – is the monolayer adsorption capacity (mmol/kg) calculated by $A_{surf}/(A_m \times N) \times 10^{10}$, where A_{surf} is the MWCNT surface area (m²/g); A_m is the projecting area of a single adsorbate molecule (cm²) estimated by $\pi \times (3MW/(4\pi \times D \times N))^{2/3}$, where N is the Avogadro constant, and MW is the molecular weight (g/mol).

Table S3. Rate constants for rapid (k_{rapid}) and slow (k_{slow}) desorption of OTC and CBZ from multiwalled carbon nanotubes (MWCNT40) along with rapidly (F_{rapid}) and slowly (F_{slow}) desorbing fractions depending on pH of desorption solution

Compound	F_{rapid}	$k_{\text{rapid}} (\text{h}^{-1})$	F_{slow}	$k_{\text{slow}} (\text{h}^{-1})$	r^2
OTC					
pH 5	0.100±0.015	8.2E-02±3.7E-02	0.900±0.014	9.5E-05±1.0E-04	0.973
pH 6	0.050±0.011	5.6E-02±3.2E-02	0.950±0.012	4.0E-04±8.7E-05	0.989
pH 7	0.064±0.015	1.1E-01±6.9E-02	0.936±0.010	2.4E-05±8.2E-05	0.933
pH 8	0.039±0.006	4.0E-02±1.2E-02	0.961±0.006	2.0E-04±4.1E-05	0.997
CBZ					
pH 5	0.484±0.087	5.0E-02±2.0E-02	0.516±0.097	2.1E-03±1.3E-03	0.989
pH 6	0.501±0.123	1.1E-01±7.4E-02	0.499±0.087	1.2E-03±1.4E-03	0.943
pH 7	0.513±0.241	1.9E-01±1.7E-01	0.487±0.094	6.0E-04±1.7E-03	0.847
pH 8	0.788±0.086	4.6E-02±1.2E-02	0.212±0.094	5.6E-5±2.9E-03	0.992

Table S4. Recovery [%] of oxytetracycline (OTC) and carbamazepine (CBZ) from multiwalled carbon nanotubes after methanol extraction.

CNTs	OTC	CBZ
MWCNT10	98.5±2.62	95.8±3.82
MWCNT20	101.1±2.08	98.4±2.29
MWCNT40	97.4±3.46	101.4±1.06
MWCNT60	98.7±1.23	99.5±2.44
MWCNT100	100.4±2.69	96.6±4.91

± solid particles were extracted three times by methanol

Figure S1. Sorption kinetics of oxytetracycline and carbamazepine depending on outer diameter of carbon nanotubes. Initial concentration of pharmaceuticals was 2.5 mg/L

Figure S2. Adsorption isotherms of oxytetracycline on multiwalled carbon nanotubes. The solid lines are the Freundlich (FM), Langmuir (LM) and Polanyi-Manes (PMM) model fitting results, respectively.

Figure S3. Adsorption isotherms of carbamazepine on multiwalled carbon nanotubes. The solid lines are the Freundlich (FM), Langmuir (LM) and Polanyi-Manes (PMM) model fitting results, respectively.

Figure S4. Surface area normalized adsorption isotherms of OTC and CBZ on multiwalled carbon nanotubes

Figure S5. Surface coverage of organic compounds on multi-walled carbon nanotubes with outer diameters. Surface coverage was calculated by dividing the adsorbed amount by monolayer adsorption capacity (Table S4).

Figure S6. TEM images of MWCNT40 before (A) and after (B) ultrasonic treatment

Figure S7. Sorption-desorption hysteresis of OTC on MWCNTs.

Figure S8. Sorption-desorption hysteresis of CBZ on MWCNTs.

Figure S9. Thermodynamic index of irreversibility, TII, for sorption of oxytetracycline (OTC), and carbamazepine (CBZ) on multiwalled carbon nanotubes.

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