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Supplementary Material Cover Sheet

Transport of oxytetracycline through saturated porous media: Role of surface

chemical heterogeneity

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S1. Purification of humic acid

The product was purified according to the procedures previously reported in the literature.^[S1] 10 g of HA was added to 1 L of a NaOH solution with pH 10, stirred overnight, and centrifuged to remove undissolved organic and inorganic matter. The supernatant was brought to pH 2 with 1 M HCl, stirred 24 h, and centrifuged at 10000 rpm using a Beckman centrifuge with a JA-20 rotor to precipitate the HA fraction. The precipitate was rinsed with 0.01 M HCl several times to bring the HA into its protonated form, then washed with pure water and filtrated through an ultrafiltration membrane (Millipore, regenerated cellulose, NMWL 10 000) using an Amicon cell. Finally, the sample was shaken with an acid Dowex 50w-X8 resin for a few days to remove all trace metals. The final product was freeze-dried and kept in the dark at 4 °C for future use.

S2. Preparation of montmorillonite-coated sand and goethite-coated sand and humic acid-coated sand

The procedure which coated with montmorillonite was used by the method by Jerez et al.^[S2] First, the montmorillonite particles were treated to remove organic matter with H₂O₂ ^[S3] and iron oxides using citrate-dithionite ^[S4] and were then fractionated to obtain particles $< 2 \mu m$ in hydrodynamic diameter using gravity sedimentation. Then the montmorillonite suspensions were flocculated with 50 mg/L polyacrylamide (PAM). The mixture was then left to settle down, and centrifuged at $100 \times g$ for 5 min. Then, the clay–polymer complex slurry was mixed with silica sand and dried at 100 °C for 24 h. The coated sand was then washed with deionized water and dried again at 100 °C for 24 h. The washing removed all non-attached PAM.

The procedure which coated with goethite was similar to that reported Zhang et al..^[S5] In brief, goethite-coated sand was precipitated onto 500 g of quartz sand by adding 87.5 mL of 0.17 M Fe (NO₃)₃ and 90.0 mL of 0.52 M NaOH in an evaporating dish. The mixture was placed in a drying oven at 105 °C for 72 h. The mixture was stirred periodically to prevent crusting of the salts on the surface. After coating the quartz sand with goethite, the sand was washed in 1.0 mM HCl and 1.0 mM NaOH to remove weakly absorbed iron on the sand surface.

The procedure which coated with HA was based on the methodology described by Jerez and Flury.^[S6] This procedure involved modification of the silica surface with 3-aminopropyltriethoxysilane (APTS) (Aldrich, MI).^[S7] We specifically used the incubation with N-(3-dimethyaminopropyl)-N- ethylcarbodiimide hydrochloride (EDC) at room temperature, and then followed by end-capping of the free amino groups as described in Koopal et al.^[S7] Multilayer-coating is obtained when the APTS reaction is not carried out with a completely anhydrous medium.^[S8] We did not use completely anhydrous conditions during the reactions of APTS with the silica, to obtain as much humic acid coating as possible. This resulted in multilayer humic acid coatings in our samples.^[S6]

Furthermore, the amount of montmorillonite coated on the sand grains (~ 15.7 mg/g) was determined by measuring the mass of detached clay. For PAM, Briefly, montmorillonite was detached by immersing the coated quartz sand in a non-stirred pH 13 solution (adjusted with NaOH) for 24 h.^[S2] The procedure removed the clay coating effectively, as verified by microscopy. The amount of detached clay was quantified by UV/Vis spectrometry at 430 nm.^[S9] The Fe loading of the goethite-coated sand (~1.25 mg/g) was determined by dissolving the iron oxide coating with 65% HNO₃ for 24 h at room temperature, followed by quantification using Atomic Absorption Spectroscopy (AAS, contrAA 700, Analytik Jena).^[S10] The amount of the humic acid in 1 M NaOH followed by quantification with a total organic carbon analyzer from Shimadzu Scientific (Columbia, MD, USA).

S3. Determination of the ζ -potential of porous media

The zeta potential of sand grains was measured by using a zeta-plus potential analyzer (Zetasizer nano ZS90, Malvern Instruments, UK) at room temperature (25°C) according to the method described in previous studies.^[S11,S12] It should be noted that, the sand grains were too large for direct measurement by the zeta potential analyzer, a few sand grains were crushed into fine powders and then mixed with the appropriate chemistry solution (see Table 1) in an ultrasonic bath for 30 min. Then, the mixture was formed a sufficiently stable suspension that could be used for zeta potential measurement. Note that the zeta potential was calculated from the electrophoretic mobility using the full numerical model by O'Brien and White.^[S13]

S4. Determination of the $\ensuremath{pH_{pzc}}$ of porous media

The pH of zero charge (pH_{pzc}) was measured by the salt addition method. ^[S14, S15] In 6 different beakers, known amounts of porous media were mixed with 100 mL of sodium chloride (0.1 M). A pH value was adjusted for each beaker (from 2 to 12) by adding the necessary amounts of nitric acid or potassium hydroxide. After 24 h of stirring at room temperature, the pH was measured again and plotted as a function of the initial pH. The intersection of this curve with the straight-line pHi = pH corresponds to pH_{pzc}. ^[S16]

S5. Calculation of porosity

The porosity of sand columns was measured gravimetrically. ^[S17, S18] The detailed equation is as follows:

porosity=
$$\frac{V_{\rm c} - V_{\rm s}}{V_{\rm c}} = \frac{V_{\rm c} - \frac{m_{\rm sand}}{\rho_{\rm sand}}}{V_{\rm c}}$$

Where V_c (cm³) is the volume of column, V_s (cm³) is the volume of sand in the column, m_{sand} (g) is the mass of sand in the column and ρ_{sand} (g/cm³) is the real density of sand (2.65 g/cm³). ^[S19, S20]

S6. Transport model

The two-site nonequilibrium transport model was applied in this study to describe antibiotic transport in the porous media.^[S21-S24] The program CXTFIT 2.0 was used to fit the OTC experimental breakthrough curves.^[S25] In this model, two different types of sorption are assumed: kinetic and the equilibrium.^[S26] The model can be explained in Eqs. S1–S7.

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} - \omega (C_1 - C_2)$$
(S1)

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2)$$
(S2)

where parameters without dimensions are as follows:

$$X = \frac{x}{L}$$
(S3)

$$P = \frac{vL}{D}$$
(S4)

$$R = 1 + \frac{\rho_{\rm b}}{\theta} \cdot K_{\rm d} \tag{S5}$$

$$\beta = \frac{\theta + f \rho_{\rm b} K_{\rm d}}{\theta + \rho_{\rm b} K_{\rm d}} \tag{S6}$$

$$\omega = \frac{\alpha(1-\beta)RL}{\nu}$$
(S7)

where C_1 and C_2 (mg/L) are the solute concentrations in sorption sites 1 and 2 respectively, T (d) is the time and L (m) is the column length; X is the vertical spatial coordinate; D (m²/d) is the hydrodynamic dispersion coefficient; P is the Peclet number; ρ_b (g/cm³) and θ (-) are the bulk density of the porous media and porosity of the sand column corrospondingly, K_d (L/kg) is the partition coefficient. β represents the fraction of the instantaneous equilibrium adsorption sites in all the adsorption sites $[^{S27}]$; f(-) is the fraction of Type 1 sites; α (1/d) is the first-order rate coefficient for kinetics at Type 2 sites; and ω is the Damkohler number, indicating the ratio of the reaction rate to the transport rate. $[^{S28}]$ By fitting conservative tracer (Br) curves using the 2.1 code of CXTFIT, the value for dispersion coefficient (*D*) was evaluated (Fig. S2) $[^{S25}]$. We supposed that the OTC's *D* value is the same as that in the column for the bromide (0.425–0.793 m²/d). $[^{S29}]$ By matching the breakthrough curve of the OTC, the value of *R*, ω and β was achieved. The K_d , *f* and α values were determined with equations 6~8.

S7. Montmorillonite, humic acid, or goethite released from the sand grains during OTC transport

In order to verify the role of montmorillonite, humic acid, or goethite colloids in the transport of OTC, an extra experiment was performed using borosilicate glass columns (1.6-cm inner diameter \times 10.3-cm long) packed with ~28 g of various heterogeneous quartz sand. The influents were pumped at a steady fluid velocity of 0.123 cm/min using a syringe pump (KD Scientific, Holliston, MA, USA) in an upflow model. At experiment inception, 25 pore volumes (PV) of DI water was injected into the columns, followed immediately by 20 PV of electrolyte solution (10 mM NaCl) to saturate the columns. Then, ~18 PV 10 mM NaCl solution was pumped into the saturated column. The influent was adjusted to the desired pH level by addition of 0.1 M sodium hydroxide or 0.1 M hydrochloric acid. Effluent samples (~3.5 mL) were continuously collected in every 30 minutes. The concentration of montmorillonite in the effluent was quantified by UV/Vis spectrometry at 430 nm.^[S9] The concentration of Fe was determined by dissolving the iron oxide with 65% HNO₃ for 24 h at room temperature, followed by quantification using Atomic Absorption Spectroscopy (AAS, contrAA 700, Analytik Jena).^[S10] The concentration of humic acid was determined by quantification with a total organic carbon analyzer from Shimadzu Scientific (Columbia, MD, USA). All experiments were performed at least twice.

Molecular formula	Chemical structure	Molecular weight (g/mol)	Solubility (g/L) ^a	$\log K_{ow}^{b}$	$pk_a{}^b$
C ₂₂ H ₂₄ N ₂ O ₉	H ₃ C CH ₃ H ₃ C CH ₃ OH NH OH OH O OH O NH ₂	496.47	0.062	-0 .90	$pK_{a1}=3.22$ $pK_{a2}=7.46$ $pK_{a3}=8.94$

 Table S1. Selected properties of OTC.

^a Derived from Daghrir and Drogui.^[S30]

^b Derived from Rivera-Utrilla et al.^[S31]

Column No.	porous media ^{<i>a</i>}	Electrolyte solution	pН	ζ potential of sand (mV)
1	MMT-coated sand	10 mM NaCl	7.0	$\textbf{-62.9}\pm0.8$
2	Quartz sand	10 mM NaCl	7.0	$\textbf{-50.3}\pm3.0$
3	HA-coated sand	10 mM NaCl	7.0	$\textbf{-53.0}\pm0.6$
4	Goe-coated sand	10 mM NaCl	7.0	$\textbf{-40.0} \pm 0.9$
5	MMT-coated sand	0.5 mM CaCl ₂	5.0	-52.7 ± 1.7
6	Quartz sand	0.5 mM CaCl ₂	5.0	$\textbf{-42.3}\pm0.5$
7	HA-coated sand	0.5 mM CaCl ₂	5.0	$\textbf{-45.5}\pm0.9$
8	Goe-coated sand	0.5 mM CaCl ₂	5.0	-36.2 ± 1.0
9	MMT-coated sand	10 mM NaCl	5.0	-55.2 ± 2.5
10	Quartz sand	10 mM NaCl	5.0	-45.3 ± 1.8
11	HA-coated sand	10 mM NaCl	5.0	$\textbf{-50.5} \pm 1.6$
12	Goe-coated sand	10 mM NaCl	5.0	-35.8 ± 2.1
13	MMT-coated sand	10 mM NaCl	9.0	-67.2 ± 1.5
14	Quartz sand	10 mM NaCl	9.0	-56.1 ± 1.3
15	HA-coated sand	10 mM NaCl	9.0	-59.7 ± 2.1
16	Goe-coated sand	10 mM NaCl	9.0	$\textbf{-52.1}\pm0.3$

Table S2 ζ -potentials of sand grains under different conditions.

Column No.	porous media ^a	electrolyte solution		Parameters of two-site nonequilibrium transport model						
			pH -	R (-)	β(-)	ω (-)	<i>f</i> (-)	α (1/d)	$K_{\rm d}$ (L/kg)	r^2
1	MMT-coated sand	10 mM NaCl	7.0	9.9 ± 0.5	0.585 ± 0.015	0.601 ± 0.015	0.538 ± 0.023	2.52 ± 0.23	2.75 ± 0.32	0.998
2	Quartz sand	10 mM NaCl	7.0	13.2 ± 1.7	0.562 ± 0.023	1.042 ± 0.072	0.526 ± 0.017	3.08 ± 0.15	3.75 ± 0.45	0.996
3	HA-coated sand	10 mM NaCl	7.0	21.0 ± 0.5	0.451 ± 0.026	2.743 ± 0.115	0.423 ± 0.010	4.07 ± 0.21	6.15 ± 1.12	0.997
4	Goe-coated sand	10 mM NaCl	7.0	106.3 ± 3.8	0.071 ± 0.009	5.259 ± 0.232	0.062 ± 0.008	8.02 ± 0.39	32.9 ± 3.37	0.968
5	MMT-coated sand	0.5 mM CaCl ₂	5.0	21.7 ± 1.5	0.515 ± 0.015	1.388 ± 0.079	0.487 ± 0.037	1.78 ± 0.10	5.35 ± 2.15	0.996
6	Quartz sand	0.5 mM CaCl ₂	5.0	23.7 ± 1.2	0.439 ± 0.036	1.561 ± 0.098	0.411 ± 0.085	2.32 ± 0.25	6.22 ± 1.74	0.993
7	HA-coated sand	0.5 mM CaCl ₂	5.0	26.0 ± 2.2	0.377 ± 0.022	2.575 ± 0.101	0.351 ± 0.113	5.73 ± 0.76	7.66 ± 2.69	0.999
8	Goe-coated sand	0.5 mM CaCl ₂	5.0	115.1 ± 3.1	0.051 ± 0.023	6.676 ± 0.231	0.043 ± 0.005	9.99 ± 1.26	36.2 ± 3.97	0.953
9	MMT-coated sand	10 mM NaCl	5.0	20.3 ± 1.2	0.587 ± 0.035	1.076 ± 0.023	0.666 ± 0.036	2.02 ± 0.11	5.93 ± 1.01	0.996
10	Quartz sand	10 mM NaCl	5.0	20.9 ± 0.7	0.536 ± 0.016	1.213 ± 0.027	0.612 ± 0.089	2.15 ± 0.09	6.03 ± 0.97	0.995
11	HA-coated sand	10 mM NaCl	5.0	24.1 ± 2.1	0.472 ± 0.019	3.192 ± 0.035	0.449 ± 0.033	4.31 ± 0.22	7.01 ± 0.16	0.998
12	Goe-coated sand	10 mM NaCl	5.0	113.2 ± 3.7	0.096 ± 0.012	6.624 ± 0.136	0.087 ± 0.010	10.11 ± 1.45	34.6 ± 2.36	0.952
13	MMT-coated sand	10 mM NaCl	9.0	8.7 ± 0.5	0.767 ± 0.010	0.436 ± 0.029	0.736 ± 0.068	0.90 ± 0.08	2.35 ± 0.76	0.977
14	Quartz sand	10 mM NaCl	9.0	9.1 ± 0.6	0.632 ± 0.039	0.574 ± 0.035	0.696 ± 0.103	2.93 ± 0.36	2.93 ± 1.08	0.997
15	HA-coated sand	10 mM NaCl	9.0	12.9 ± 1.2	0.589 ± 0.033	3.064 ± 0.027	0.554 ± 0.081	3.71 ± 0.43	3.68 ± 1.39	0.993
16	Goe-coated sand	10 mM NaCl	9.0	96.7 ± 2.5	0.088 ± 0.007	4.645 ± 0.239	0.087 ± 0.011	7.85 ± 1.69	29.3 ± 2.25	0.971

Table S3. Fitted parameters of two-site nonequilibrium transport model from breakthrough results of column experiments.

^{*a*} HA coated-sand, Goe coated-sand, and MMT coated-sand represent humic acid-coated sand, goethite coated sand, and montmorillonite-coated sand, respectively.

(a) MMT-coated sand



(b) sand



(c) HA-sand











Si Ka1



C Ka1_2



Fe Ka1

Fig. S1. Elemental mapping of (a) MMT-coated sand, (b) Quartz sand, (c) HA-coated sand, and (d) Goe-coated sand.



Fig. S2. Calibration curve as absorbance at the wavelength of 360 nm vs. concentration of OTC in solution.



Fig. S3. Representative breakthrough curve of conservative tracer (Br⁻). The line was plotted by fitting the breakthrough data with the one-dimensional steady-state advection-dispersion equation.



Fig. S4. pH-dependent speciation of the whole OTC molecular and the functional groups, respectively.

(b) sand

(b) Goe-coated sand



Fig. S5. Scanning electron microscope (SEM) images of (a) quartz sand and (b) Goecoated sand. The inset of images show characteristic micro-structures of porous media.



Fig. S6. Montmorillonite, humic acid, or goethite released from the sand grains during OTC transport at pH 7.0 (at a fixed ionic strength, 10 mM NaCl).



Fig. S7. Fitted parameters of two-site nonequilibrium transport model from breakthrough results of column experiments: (a) the fraction of Type 1 sites; (b) the fraction of instantaneous retardation to the total retardation; and (c) the coefficient of partitioning between the equilibrium and nonequilibrium phases; (d) the first-order rate for kinetics at Type 2 sites; (e) The distribution coefficients of OTC between porous media and water.



Fig. S8. Transport of OTC through saturated porous media with different surface chemical heterogeneities at (a) pH 5.0 (columns 9–12, Table 1) and (b) 9.0 (columns 13–16, Table 1) at a fixed ionic strength (10 mM NaCl). Solid lines are plotted by curve-fitting experimental data with the two-site nonequilibrium transport model.



Fig. S9. Transport of OTC in saturated (a) MMT-coated sand, (b) Quartz sand, (c) HA-coated sand, and (d) Goe-coated sand columns in the presence of 0.3 mM Na+ and 0.1 mM Ca^{2+} at pH 5.0. Solid lines are plotted by curve-fitting experimental data with the two-site nonequilibrium transport model.

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