

**Supporting Information for:**

**Influence of a Polymer Sunscreen Additive on the Transport and Retention of  
Titanium Dioxide Nanoparticles in Water-Saturated Porous Media**

**Jessica Englehart, Bonnie A. Lyon, Matthew D. Becker<sup>1</sup>, Yonggang Wang, Linda M.**

**Abriola, Kurt D. Pennell\***

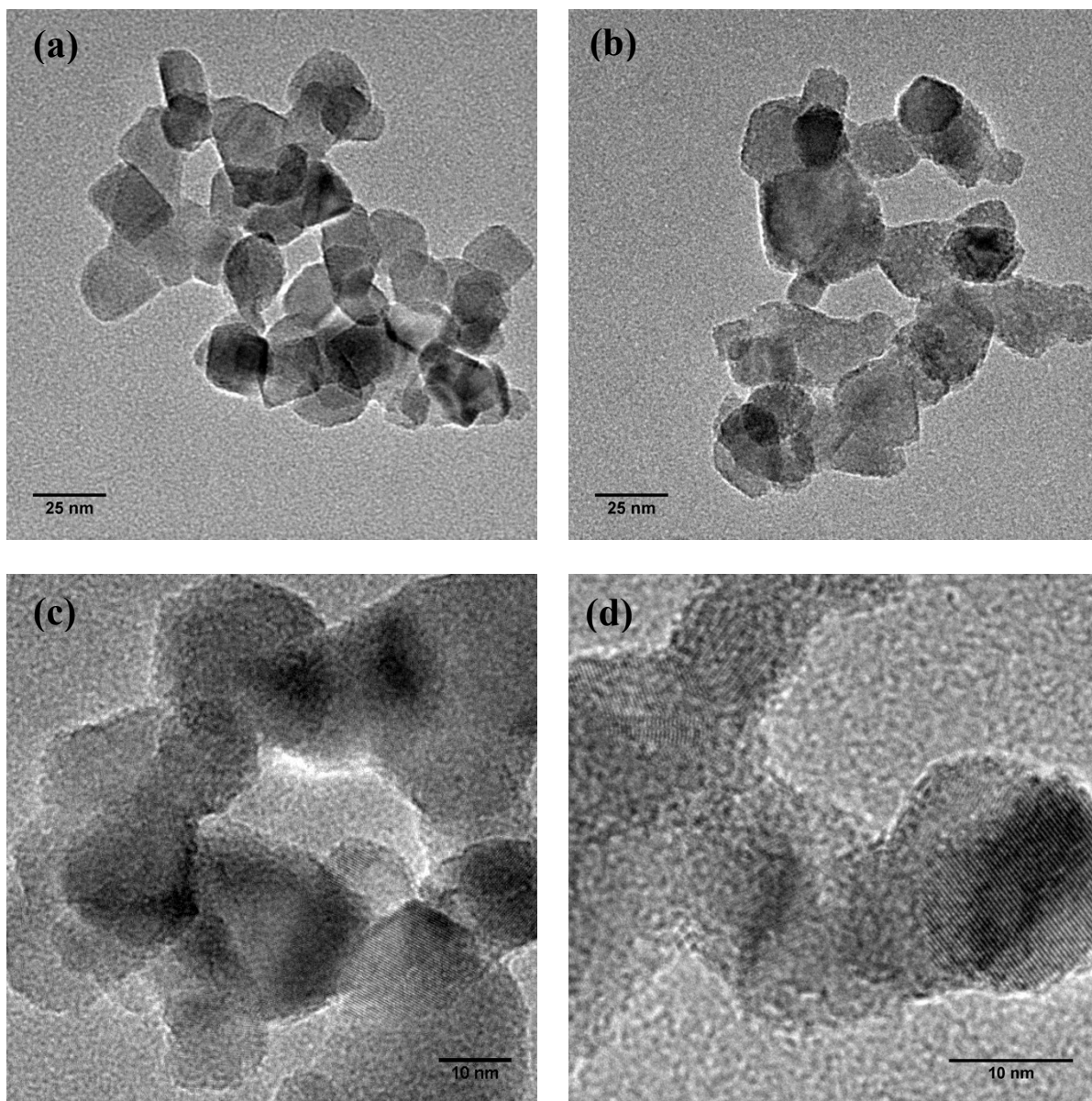
Department of Civil and Environmental Engineering, Tufts University, 200 College Avenue,  
Medford, Massachusetts 02155, USA

\*Corresponding author:

Kurt D. Pennell, PhD, PE, BCEE  
Department of Civil & Environmental Engineering  
Tufts University  
200 College Avenue  
Medford, MA 02155  
Tel: 617-627-3099  
Fax: 617-627-3994  
Email: [kurt.pennell@tufts.edu](mailto:kurt.pennell@tufts.edu)

---

<sup>1</sup> Current address: John and Willie Leone Family Department of Energy and Mineral Engineering and EMS Energy Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA



**Figure S1.** Transmission electron microscope (TEM) images of (a, c) nTiO<sub>2</sub> alone and (b, d) nTiO<sub>2</sub> with 3 mg/L Carbomer. Samples were prepared at pH 7.5 in 1 mM HEPES buffer.

### DLVO and XDLVO calculations.

The mechanisms leading to particle aggregation in a nano-TiO<sub>2</sub> suspension are commonly described using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The total interaction energy ( $E_{total}$ ) between two particles can be described as the sum of the electrical double-layer repulsion energy ( $E_{edl}$ ) and van der Waals attraction energy ( $E_v$ ).

$$E_{total} = E_{edl} + E_v \quad (S1)$$

The  $E_{total}$  can be calculated for the interaction between two nanoparticles (two spheres) or between a nanoparticle and a sand grain (a sphere and a plane). In the case of a nanoparticle-nanoparticle interaction, the equation for calculating the electrical double-layer repulsion energy ( $E_{edl-NN}$ ) is shown below.<sup>1</sup>

$$E_{edl-NN} = \frac{64\pi n_c k T a}{\kappa^2} \tanh^2 \left( \frac{ze\psi_p}{4kT} \right) e^{(-\kappa D)} \quad (S2)$$

where  $n_c$  is the number of cations in solution,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $a$  is the particle radius,  $\kappa$  is the Debye-Huckel reciprocal length parameter,  $z$  is the charge number,  $e$  is the characteristic charge of an electron,  $\psi_p$  is the surface potential (zeta potential) of the particle, and  $D$  is the distance between the two surfaces. The Debye-Huckel reciprocal length parameter,  $\kappa$ , can be calculated using the following equation:

$$\kappa = \left( \frac{2000e^2 N_A I_C}{\varepsilon_0 \varepsilon_r k T} \right)^{1/2} \quad (S3)$$

where  $\varepsilon_0$  is the permittivity of a vacuum,  $\varepsilon_r$  is the relative dielectric constant of water (78.54),  $N_A$  is Avogadro's number, and  $I_C$  is the ionic strength. The equation for calculating the van der Waals attraction energy between two particles ( $E_{v-NN}$ ) is shown below:

$$E_{v-NN} = \frac{-A_{NN}a}{12D} \left[ 1 - \frac{bD}{\lambda} \ln \left( 1 + \frac{\lambda}{bD} \right) \right] \quad (S4)$$

where  $A_{NN}$  is the Hamaker constant for TiO<sub>2</sub>-water-TiO<sub>2</sub> ( $26 \times 10^{-20}$  J)<sup>2</sup>,  $b$  is a constant with a value of 5.32, and  $\lambda$  is the characteristic wavelength for the interaction (100 nm).<sup>2, 3</sup>

While it is important to understand the attractive or repulsive relationship among a suspension of nanoparticles, the interaction between a nanoparticle and a grain of sand generates a better understanding of nanoparticle transport and retention in a porous medium. A sphere-

plane interaction is used to describe the relationship between a nanoparticle and a grain of sand due to the multiple order of magnitude size difference between these objects (e.g., a 100 nm particle interacting with a 300  $\mu\text{m}$  grain of sand). The larger sand grain is represented by a plane, and the nanoparticle is represented by a sphere. Guzman et al.<sup>4</sup> developed a set of DLVO equations to describe the interaction between a nanoparticle and a grain of sand (Equations S5-S6). This method uses the surface element integration technique described by Bhattacharjee and Elimelech.<sup>5</sup> Equation S5 can be used to calculate the electrical double layer repulsion energy between a nanoparticle and a grain of sand ( $E_{edl-NS}$ ).

$$E_{edl-NS} = \pi \epsilon_0 \epsilon_r \kappa (\psi_p^2 + \psi_s^2) \times \int_0^a \left\{ -\coth \left[ \kappa \left( D + a - a \sqrt{1 - \left( \frac{r}{a} \right)^2} \right) \right] + c \right\} r dr \quad (S5)$$

where  $\psi_s$  is the surface potential of the sand. The van der Waals attraction energy between a nanoparticle and sand grain surface,  $E_{v-NS}$ , can be calculated as:

$$E_{v-NS} = -\frac{A_{NS}}{6} \left[ \frac{a}{D} + \frac{a}{D+2a} + \ln \left( \frac{D}{D+2a} \right) \right] \quad (S6)$$

The Hamaker constant for the silica-water-TiO<sub>2</sub> system ( $A_{NS}$ ) is  $4.5 \times 10^{-20} \text{ J}^2$ . These two values ( $E_{edl}$  and  $E_v$ ) are combined to generate a net energy,  $E_{total}$ , which is then used to generate an interaction energy profile. Negative values indicate a net attractive energy, and net positive values indicate a net repulsive energy. The zeta potential of sand was estimated to be -35 mV and -52 mV at pH 5 and pH 7.5, respectively, based on previously reported values.<sup>6</sup>

In addition to the electronic double layer repulsive energy and van der Waals attractive energy of traditional DLVO theory, XDLVO calculations of the total interaction energy ( $E_{total}$ ) include the osmotic and elastic-steric repulsion energies induced by the presence of a polymer layer coating a colloid or nanoparticle. The overlap of the polymer layers for two approaching particles increases the osmotic pressure due to a higher local polymer concentration, which leads to increased repulsion between particles. This is known as the osmotic repulsion energy,  $E_{osm}$ . The second additional force considered in XDLVO is the elastic-steric repulsion energy,  $E_{elas}$ . Compression of the adsorbed polymer layer below the original thickness of the layer leads to a loss of entropy and subsequent elastic repulsion. The values of  $E_{osm-NN}$  and  $E_{elas-NN}$  were



calculated using Equations S7-S8.<sup>7</sup> The values used in XDLVO calculations for this study are listed in Table S1.

$$E_{osm-NN} = 0 \quad \text{for } 2L \leq D \quad (S7)$$

$$E_{osm-NN} = \frac{a4\pi kT}{V_w} \Phi_p^2 \left(\frac{1}{2} - \chi\right) \left(L - \frac{D}{2}\right)^2 \quad \text{for } L \leq D < 2L$$

$$E_{osm-NN} = \frac{a4\pi kT}{V_w} \Phi_p^2 \left(\frac{1}{2} - \chi\right) L^2 \left(\frac{D}{2L} - \frac{1}{4} - \ln\left(\frac{D}{L}\right)\right) \quad \text{for } D < L$$

where  $V_w$  is the volume of the solvent molecule (water in this case),  $\Phi_p$  is the calculated volume fraction of polymer within the brush layer,  $L$  is the thickness of the brush layer (10 nm). The volume fraction of polymer,  $\Phi_p$ , can be estimated using Equation S8:

$$\Phi_p = \frac{3\Gamma_{max}a^2}{\rho_p[(L+a)^3 - a^3]} \quad (S8)$$

In Equation S8,  $\Gamma_{max}$  is the surface excess, which was estimated to be 2 mg/m<sup>2</sup> for this study based on Phenrat et al.,<sup>8</sup> and  $\rho_p$  is the density of the polymer.

$$E_{elas-NN} = 0 \quad \text{for } D > L \quad (S9)$$

$$E_{elas-NN} = \left(\frac{2\pi a kT}{M_w} \Phi_p D^2 \rho_p\right) \left(\frac{D}{L} \ln\left(\frac{D}{L} \left(\frac{3 - \frac{D}{L}}{2}\right)^2\right) - 6 \ln\left(\frac{3 - \frac{D}{L}}{2}\right) + 3\left(1 + \frac{D}{L}\right)^2\right) \quad \text{for } 0 < D \leq L$$

where  $M_w$  is the molecular weight of the polymer (Table S1).

Similar to the nanoparticle-nanoparticle interaction, XDLVO theory can be applied to the nanoparticle-sand surface interaction calculation when Carbomer is present. In this case, the steric interaction energy ( $E_{steric-NS}$ ) is calculated between a polymer-coated nTiO<sub>2</sub> and an uncoated sand grain<sup>9, 10</sup> and summed with the  $E_{edl-NS}$  and  $E_{v-NS}$  values to obtain the total extended interaction energy.

$$E_{steric-NS} = \int_D^L 2\pi a \frac{kT}{s^3} \left(\frac{4L}{5} \left(\left(\frac{L}{D}\right)^{5/4} - 1\right) + \frac{4L}{7} \left(\left(\frac{D}{L}\right)^{7/4} - 1\right)\right) dD \quad \text{for } 0 < D \leq L \quad (S10)$$

$$E_{steric-NS} = 0 \quad \text{for } D > L$$

Where  $s$  is the separation distance between polymer chains on the nanoparticle surface, which was estimated to be 1.1 nm, based on the nanoparticle surface area (e.g.,  $3.1 \times 10^{-14}$  m<sup>2</sup> for a

nanoparticle with radius = 50 nm), polymer molecular weight (1500 g/mol), and polymer surface excess (2 mg/m<sup>2</sup>, equivalent to ~25,000 polymer chains on a 50 nm radius particle).<sup>8</sup>

**Table S1.** Parameters used for XDLVO calculations between two TiO<sub>2</sub> nanoparticles and a TiO<sub>2</sub> nanoparticle and sand grain in the presence of Carbomer.

<b>Variable</b>	<b>Definition</b>	<b>Value</b>	<b>Reference</b>
$L$	Thickness of polymer layer	10 nm	Estimated from DLS data
$\chi$	Flory-Huggins solvency parameter	0.45	Phenrat et al. <sup>8</sup>
$\Gamma_{max}$	Polymer surface excess	2 mg/m <sup>2</sup>	Phenrat et al. <sup>8</sup>
$\rho_p$	Density of polymer	1.4 g/cm <sup>3</sup>	Information from manufacturer
$M_w$	Molecular weight of polymer	1500 g/mol	BF Goodrich <sup>11</sup>
$s$	Separation distance between polymer chains on nanoparticle surface	1.1 nm	Phenrat et al. <sup>8</sup>

### Transport modeling equations.

The three mechanisms that are generally thought to contribute to the single-collector contact efficiency ( $\eta_0$ ) are Brownian diffusion ( $\eta_D$ ), interception ( $\eta_I$ ), and gravitational sedimentation ( $\eta_G$ ). These mechanisms are summed to generate the single-collector contact efficiency.<sup>12</sup> Correlations for each value ( $\eta_D$ ,  $\eta_I$ , and  $\eta_G$ ) were developed by Tufenkji and Elimelech:<sup>13</sup>

$$\eta_0 = \eta_D + \eta_I + \eta_G \quad (\text{S11})$$

$$\eta_D = 2.4A_S^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{0.052} \quad (\text{S12})$$

$$\eta_I = 0.55A_SN_R^{1.675}N_{RA}^{-0.125} \quad (\text{S13})$$

$$\eta_G = 0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{0.053} \quad (\text{S14})$$

where

$$A_S = \frac{2(1 - \gamma^5)}{2 - 3\gamma + 3\gamma^5 - 2\gamma^6} \quad (\text{S15})$$

$$\gamma = (1 - n)^{1/3} \quad (\text{S16})$$

$$N_R = \frac{d_p}{d_{50}} \quad (\text{S17})$$

$$N_{Pe} = \frac{v_p d_{50}}{D_H} \quad (\text{S18})$$

$$N_{vdW} = \frac{A_{NS}}{kT} \quad (\text{S19})$$

$$N_{RA} = \frac{A_{NS}}{12\pi\mu a^2 v_p} \quad (\text{S20})$$

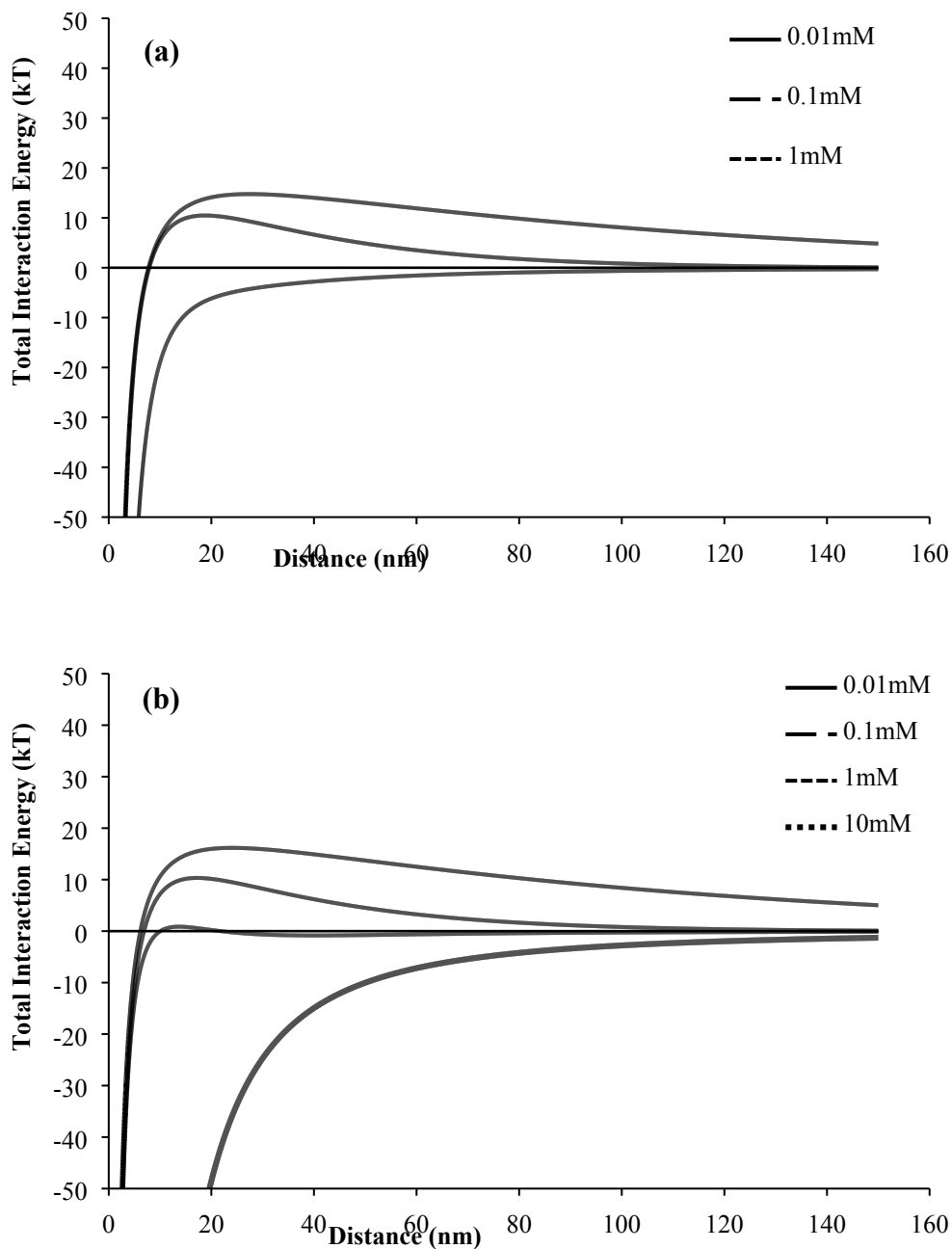
$$N_G = \frac{2a^2(\rho_p - \rho_w)g}{9\mu v_p} \quad (\text{S21})$$

In the above equations,  $N_R$  is the aspect ratio (particle diameter to sand grain diameter),  $N_{Pe}$  is the Peclet number (ratio of advective to dispersive transport),  $N_{vdW}$  characterizes the ratio of van der Waals attractive energy to thermal energy,  $N_{RA}$  is the influence of van der Waals forces and fluid

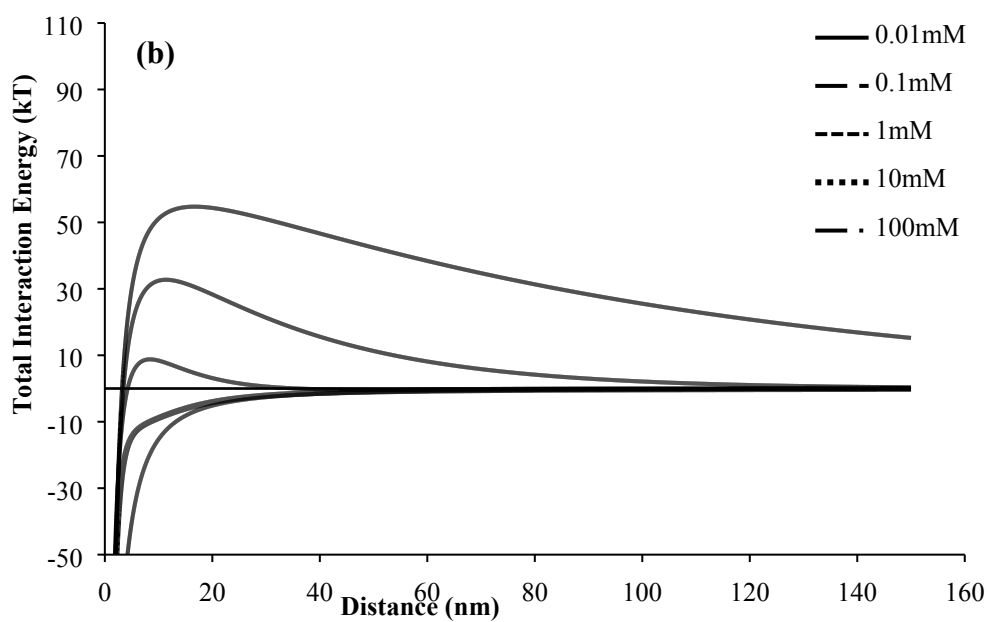
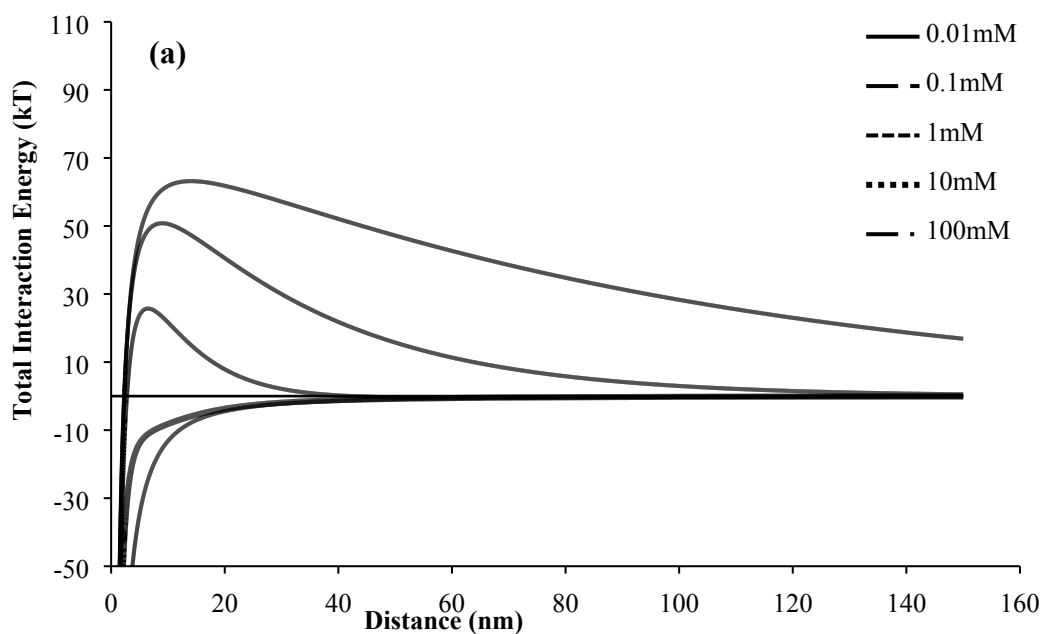
velocity on particle deposition due to interception, and  $N_G$  represents the ratio of Stokes' particle settling velocity to the pore water velocity of the fluid.

## References

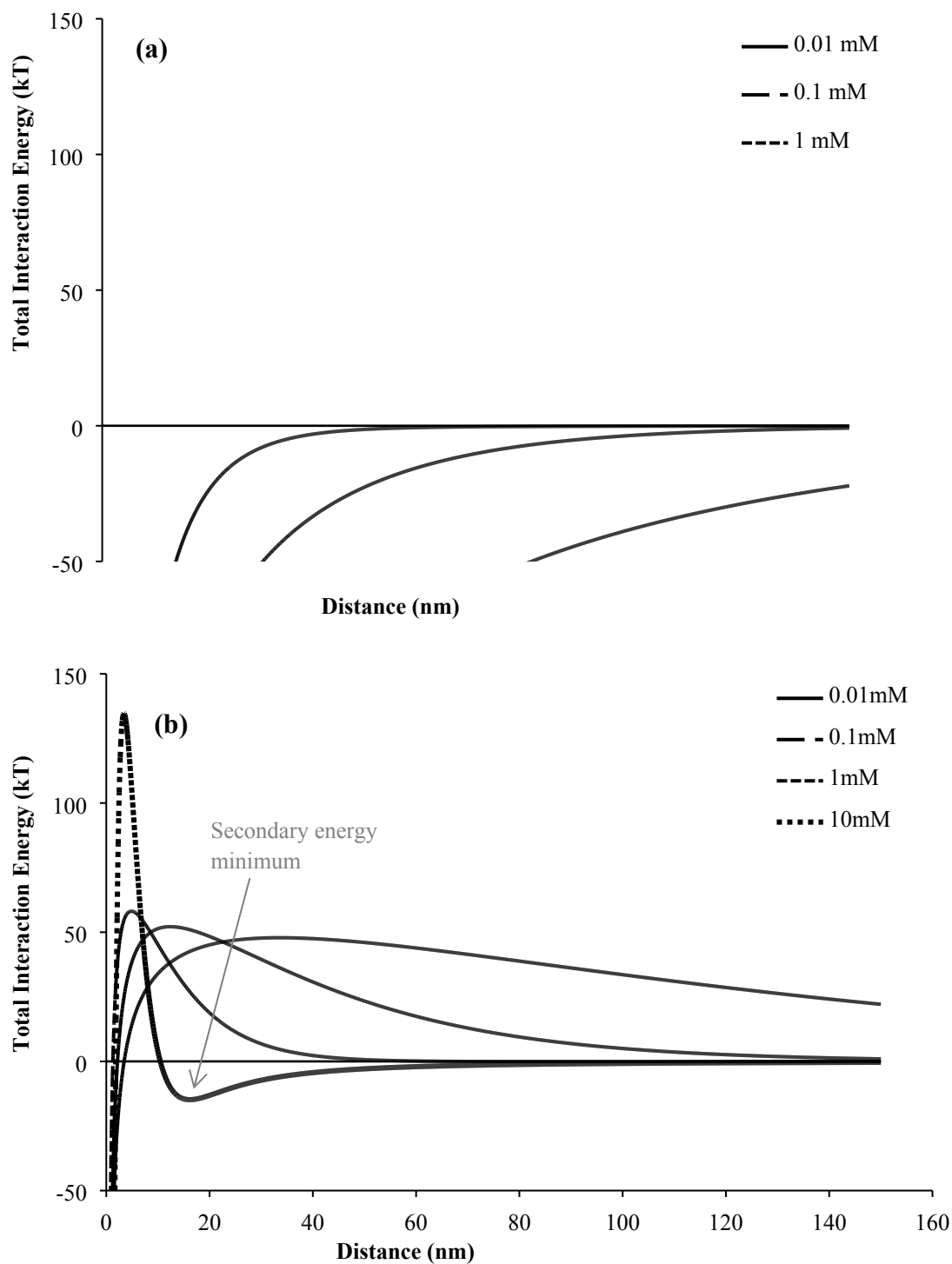
1. J. Gregory, *J. Colloid Interf. Sci.*, 1975, **51**, 44-51.
2. G. Chen, X. Liu and C. Su, *Langmuir*, 2011, **27**, 5393-5402.
3. Y. Wang, Y. Li and K. D. Pennell, *Environ. Toxicol. Chem.*, 2008, **27**, 1860-1867.
4. K. A. Dunphy Guzman, M. P. Finnegan and J. F. Banfield, *Environ. Sci. Technol.*, 2006, **40**, 7688-7693.
5. S. Bhattacharjee and M. Elimelech, *J. Colloid Interf. Sci.*, 1997, **193**, 273-285.
6. A. Kaya and Y. Yukselen, *Canadian Geotechnical Journal*, 2005, **42**, 1280-1289.
7. G. Fritz, V. Schädler, N. Willenbacher and N. J. Wagner, *Langmuir*, 2002, **18**, 6381-6390.
8. T. Phenrat, N. Saleh, K. Sirk, H.-J. Kim, R. Tilton and G. Lowry, *J. Nanopart. Res.*, 2008, **10**, 795-814.
9. T. L. Byrd and J. Y. Walz, *Environ. Sci. Technol.*, 2005, **39**, 9574-9582.
10. A. R. Petosa, D. P. Jaisi, I. R. Quevedo, M. Elimelech and N. Tufenkji, *Environ. Sci. Technol.*, 2010, **44**, 6532-6549.
11. B. Goodrich, *BF Goodrich Company Technical Literature: Carbopol Resin Handbook*, 1991.
12. K. M. Yao, M. M. Habibian and C. R. Omelia, *Environ. Sci. Technol.*, 1971, **5**, 1105-1112.
13. N. Tufenkji and M. Elimelech, *Environ. Sci. Technol.*, 2004, **38**, 529-536.



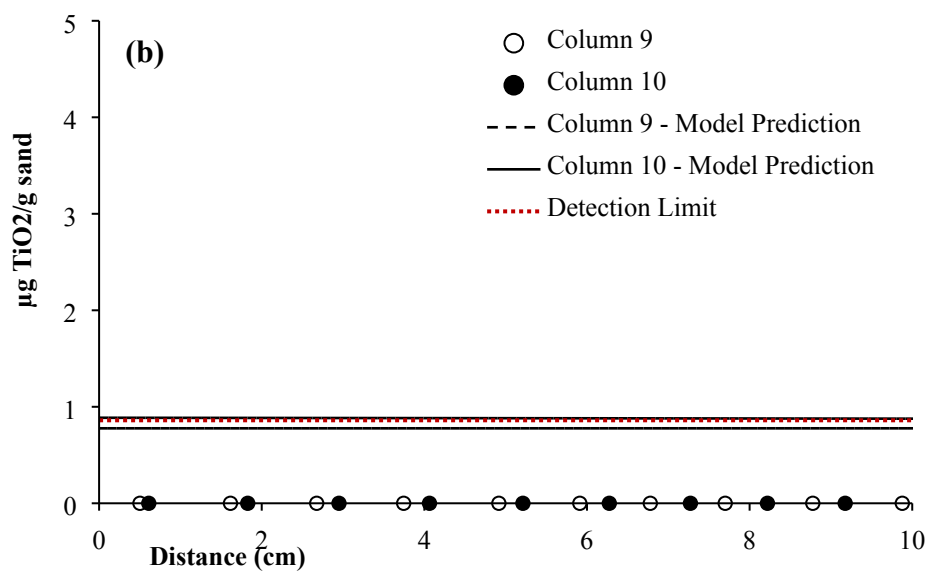
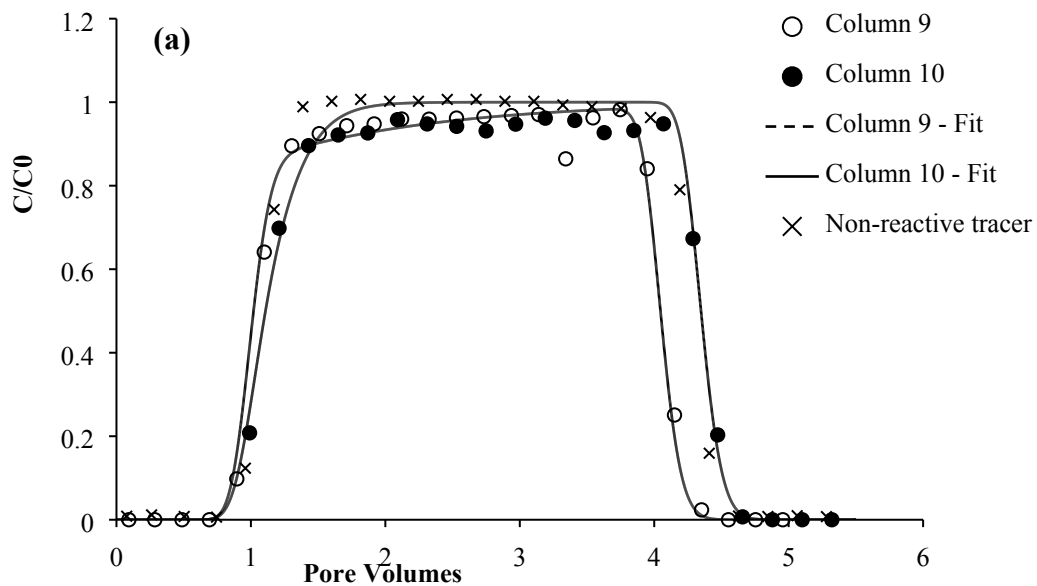
**Figure S2.** DLVO interaction profiles for two nTiO<sub>2</sub> particles without Carbomer stabilizing agent at (a) pH 5 and (b) pH 7.5. At pH 5 and  $\geq 0.005$  M NaCl, nTiO<sub>2</sub> suspensions became unstable, resulting in sedimentation of larger nanoparticle aggregates and unstable size and zeta potential readings.



**Figure S3.** DLVO interaction profiles for two nTiO<sub>2</sub> particles in the presence of 3 mg/L Carbomer at (a) pH 5 and (b) pH 7.5.

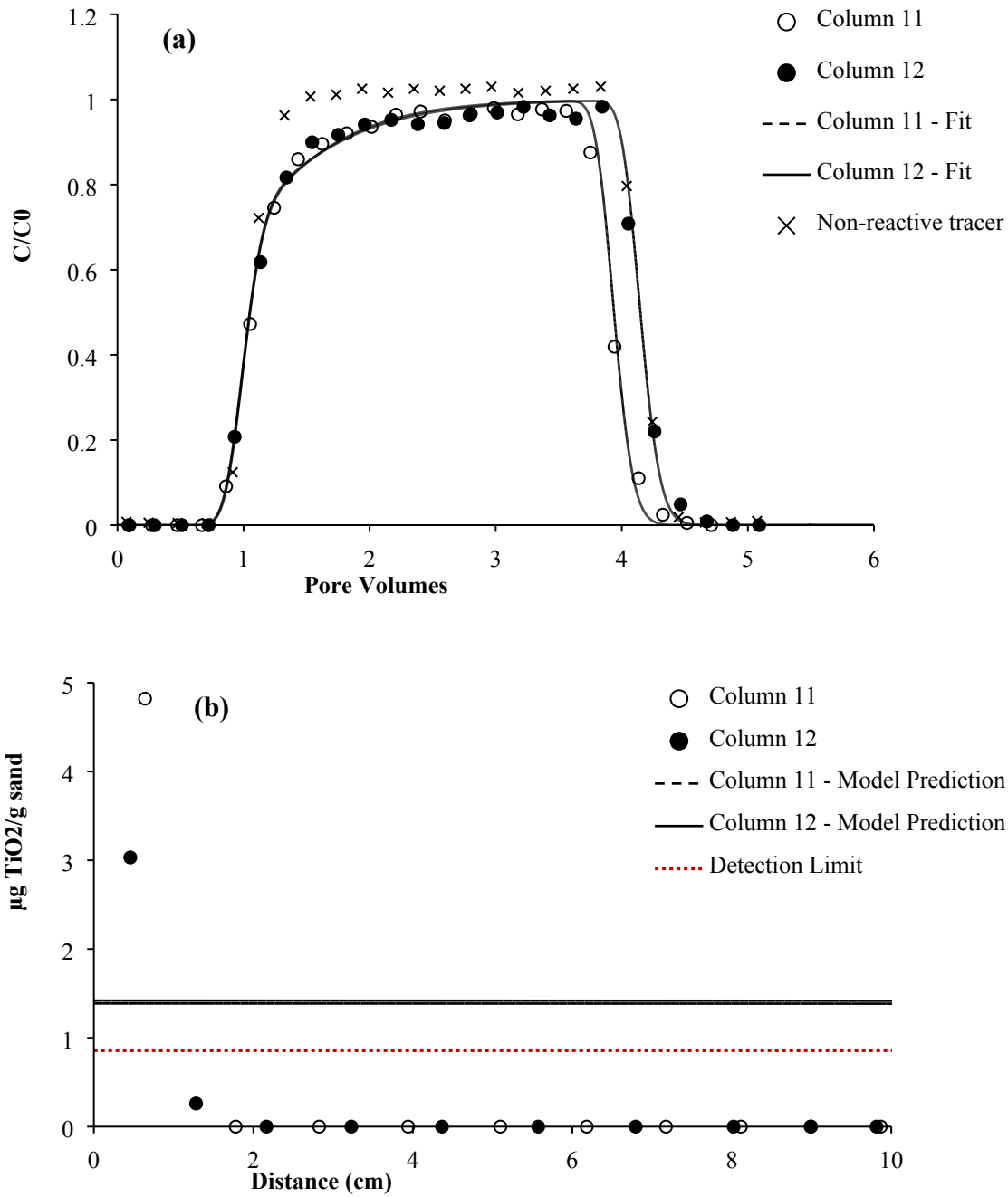


**Figure S4.** DLVO interaction profiles for nTiO<sub>2</sub> and a quartz surface (i.e., sand grain) without Carbomer at (a) pH 5 and (b) pH 7.5. At pH 5 and  $\geq 0.005$  M NaCl, nTiO<sub>2</sub> suspensions became unstable, resulting in sedimentation of larger nanoparticle aggregates and unstable size and zeta potential readings.



**Figure S5.** Comparison of experimentally measured and simulated (a) effluent breakthrough curves and (b) solid phase retention profiles with 3 mg/L Carbomer and 3 mM NaCl at pH 5.2 in Federal Fine (30-140 mesh) Ottawa sand (duplicate columns).





**Figure S6.** Comparison of experimentally measured and simulated (a) effluent breakthrough curves and (b) solid phase retention profiles with 3 mg/L Carbomer and 3 mM NaCl at pH 7.7 in Federal Fine (30-140 mesh) Ottawa sand (duplicate columns).