## SUPPORTING INFORMATION: Effect of Freeze/Thaw on Aggregation and Transport of nano-TiO<sub>2</sub> in Saturated Porous Media

Jeffrey M. Farner\*, Jacopo De Tommaso, Heather Mantel, Rachel S. Cheong, Nathalie Tufenkji

Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada \*Corresponding Author Phone: (514) 398-4494; Fax: (514) 398-6678; E-mail: Jeffrey.farner@mcgill.ca



Figure S1 - Temperature Profiles for 24 h Pretreatments.



**Figure S2 – Column Test Schematic.** 

## XDLVO Calculations for t0 P25 Suspensions at 10 °C

Calculations of particle – collector interactions using extended DLVO (XDLVO) theory were performed using the Micro-and Nanoparticle transport, filtration and clogging Model – Suite (MNMs 2018 version 3.010). In the software package, the double layer interactions were calculated with the Gregory LSA model (1), and the Steric interactions comprehend both osmotic and elastic repulsion. Both contributions were calculated following the Vincent *et al.* 1986 As suggested by Elimelech *et al.*, the Born repulsion was not considered because the presence of the NOM prevents the particles to approach closer than few nanometers.

Values used are given in Table S1, with calculations of potential energy versus separation distance for the  $TiO_2-H_2O-SiO_2$  system shown in Figure S4. Given that our system uses non-spherical particles in a complex media, theoretical calculations should be considered rough estimates only. For example, the overlap in potential energy curves in Figure 1e for 1 and 10 ppm NOM is due to differences in measured DLS size (170 vs 150, respectively) and highlights the imperfection in XDLVO calculations. If the same size particle (e.g. 170 nm) is used, then different potential energy curves are obtained as would be anticipated from measurements of NP breakthrough and calculations of alpha (data not shown). If one looks at MHRW (with an IS of 13mM), calculations of alpha are nearly identical (0.017 and 0.014 for 1 and 10 ppm NOM, respectively) as would be predicted by the XDLVO theory.

Property	Value	Reference
Hamaker collector A11 [J]	8.80E-20	(2)
Hamaker TiO <sub>2</sub> A22 [J]	7.00E-20	(3)
Zeta Sand 0.1 mM [mV]	-35.8	
Zeta Sand 10 mM [mV]	-25.2	(4, 5)
Zeta Sand 100 mM [mV]	-22.2	
Volume fraction Brush layer	0.001	Assumed
		Assumed from
Thickness brush layer [m]	3.00E-09	(6)
Density polymer [kg/m <sup>3</sup> ]	1500	(7)
Volume of polymer molecule [m <sup>3</sup> ]	6.55 e-27	(8)
Average molecular weight [g/mol]	2200	(9)
Average Valence MHRW	1.3	Calculated
Particle size [m]	Table 1	This work
Zeta potential [mV]	Table 1	This work

<b>Fable S1. Values us</b>	ed in MNMs software	for XDLVO calculations.
	,	





Figure S3– BTCs of P25 and CoRI under the same conditions, illustrating that deposition of CoRI is greater than P25 for t0 suspensions.

				Influent Aggregate Size (Diameter, nm)				Apparent $\alpha$
Suspension	IS (mM)	NOM (ppm)	ZP (mV)	Z-average	PDI	Intensity Weighted	<i>C/C</i> <sub>0</sub>	Intensity Weighted
P25, t0	1	0	-29.9 ± 1.5	165	0.19	176	0.99	0.004
CoRI, t0	1	0	-32.9 ± 2.0	934	0.75	355	0.74	0.071
P25, t0	MHRW (13)	10	$-18.8 \pm 0.8$	163	0.18	163	0.97	0.014
CoRI, t0	MHRW (13)	10	-24.2 ± 0.6	1155	0.75	436	0.77	0.079

<b>Fable S2. Summar</b>	y of NP ch	aracterization	for Fi	igure S	S3.



S4 – SEM of various P25 suspensions in 1mM NaCl, illustrating aggregation as a function of NOM concentration and treatment.



Illustration of Eta, Alpha Values as a Function of Size

Figure S5 – Contact and efficiencies for CoRI NPs in 0 ppm NOM, 100 mM NaCl calculated as a function size.

Calculated  $\alpha$  and  $\eta$  values for CoRI NPs in 0 ppm NOM, 100 mM NaCl are shown in Figure S5. Per Tufenkji and Elimelech,  $\eta_0 = \eta_D + \eta_I + \eta_G$  (10). For this sample, the intensity weighted size is 916 nm, while the Z-average size is 2532 nm, yielding very different  $\alpha$  values. Both sizes indicate straining is a factor in the system. This is reflected in the calculated  $\alpha$  value above 1 at 916 nm. The decrease in calculated  $\alpha$  values as particle size increases is a result of gravity beginning to dominate transport, although straining (not represented in  $\eta$  calculations) will also play a role in deposition.

## References

1. Gregory J. Interaction of unequal double layers at constant charge. J Colloid Interf Sci. 1975;51(1):44-51.

2. Tosco T, Bosch J, Meckenstock RU, Sethi R. Transport of ferrihydrite nanoparticles in saturated porous media: role of ionic strength and flow rate. Environ Sci Technol. 2012;46(7):4008-15.

3. Fatisson J, Domingos RF, Wilkinson KJ, Tufenkji N. Deposition of TiO2 nanoparticles onto silica measured using a quartz crystal microbalance with dissipation monitoring. Langmuir. 2009;25(11):6062-9.

4. Redman JA, Walker SL, Elimelech M. Bacterial adhesion and transport in porous media: Role of the secondary energy minimum. Environ Sci Technol. 2004;38(6):1777-85.

5. Kosmulski M, Mączka E, Janusz W, Rosenholm JB. Multiinstrument study of the electrophoretic mobility of quartz. J Colloid Interf Sci. 2002;250(1):99-103.

6. Phenrat T, Song JE, Cisneros CM, Schoenfelder DP, Tilton RD, Lowry GV. Estimating attachment of nano-and submicrometer-particles coated with organic macromolecules in porous media: development of an empirical model. Environ Sci Technol. 2010;44(12):4531-8.

7. Brown P, Leenheer J. Significance of density determination in molecular structures comprising fulvic acid from the Suwannee River. Humic Substances in the

Suwannee River, Georgia: Interactions, Properties, and Proposed Structures. 1989:87-557.

8. Averett RC, Leenheer J, McKnight DM, Thorn K. Humic substances in the Suwannee River, Georgia; interactions, properties, and proposed structures. USGPO; US Geological Survey, Map Distribution; 1994.

9. Chin Y-P, Aiken G, O'Loughlin E. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ Sci Technol. 1994;28(11):1853-8.

10. Tufenkji N, Elimelech M. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. Environ Sci Technol. 2004;38(2):529-36.