[Supplementary material]

Delineating the Role of Surface Grafting Density of Organic Coatings on the Colloidal Stability, Transport, and Sorbent Behavior of Engineered Nanoparticles

Junseok Lee, [a] *Changwoo Kim,* [b] *Daniel Schmucker,* [c] *Seung Soo Steve Lee,* [a] *Shuchi Liao,* [d] *Natalie L. Cápiro,*[e] *Kurt D. Pennell,* [d] *and John D. Fortner*[*a]

[a]Department of Chemical and Environmental Engineering, Yale University, New Haven, CT, 06511 United States

[b]School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea

[c]Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO, 63130 United States

[d]School of Engineering, Brown University, Providence, RI, 02912 United States

[e]Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY, 14853 USA

*To whom correspondence should be addressed:

John D. Fortner: Tel: +1-314-935-9293; Email: john.fortner@yale.edu

Experimental methods

Column experiments. Column experiments were carried out in water saturated columns packed with Ottawa sand (U.S. Silica, Berkeley Springs, WV). The column system consisted of syringe pump (NE-1000, New Era Pump Systems Inc., Farmingdale, NY), fraction collector (FRAC-100, Pharmacia, Sweden), and glass column (Spectra/Chrom, TX) with dimensions of 15 cm in length and 1.5 cm in inner diameter. Prior to use, the Ottawa sand was cleaned thoroughly using 1 N of hydrochloric acid (HCl) for 24 h and subsequently rinsed several times by DI water to remove remaining HCl until achieving pH 7 and dried at 200°C. The cleaned sand was sieved for size distribution and the 30-40 mesh size fraction (d_{50} = 0.5075 mm) of Ottawa sand was used in this study.

For column tests, 1 mM KCl solution was first introduced into the column to completely saturate the sand for 5 pore volume (PV) of column. Following saturation, nonreactive tracer tests were conducted to evaluate hydrodynamic properties of the porous media using 5 PV of 1 mM KBr solution buffered to pH 7 with 0.05 mM of $NaHCO_3$. Prior to NPs injection, the packed column was equilibrated and conditioned with 5 PV of 1 mM KCl solution in a background electrolyte with 0.05 mM of $NaHCO_3$ buffer. The 5 PV of solution containing organic coated Mn_xO_y NPs (1 mg L^{-1} as Mn concentration) with 1 mM of KCl was then introduced to the column for NPs transport experiments. The solutions were introduced into the column at 0.76 m/d of a pore-water velocity, in the range of typical values of real groundwater flow.[1-3] The column was rinsed with 5 PV of 1 mM KCl solution without NPs (NPs-free solutions) at the same flow rate to investigate the release of attached NPs from sand. Column effluent was collected continuously using fraction collector to the tube and analyzed for the manganese concentrations in the samples using ICP-

OES. After each transport experiment, column were sectioned into 5 segments and retained NPs were extracted from the solid phase using 1 N of HCl solution with sonication. The concentration of NPs in each segment was measured by ICP-OES allowing for retention profiles to be described.

Soil batch reactor experiments. Batch reactor experiments were also conducted to evaluate the attachment of NPs to sand media for comparison with column tests. A 5 g of dried Ottawa sand was added to the 10 mL of Mn_xO_y NPs suspensions (1 mg L^{-1} as Mn concentration), prepared in 1 mM of KCl as a background electrolyte buffered to pH 7 with 0.05 mM of $NaHCO_3$.[4] The prepared suspensions were continuously mixed on a rotating rack during 48 h and then let the sand settle for 10 min. The supernatant of solution was collected and the concentration of Mn_xO_y NPs in the supernatant was measured by ICP-OES.

References

1. R. C. Heath, *Basic ground-water hydrology*, US Geological Survey, 1983.
2. G. Grisak, W. Merritt and D. Williams, A fluoride borehole dilution apparatus for groundwater velocity measurements, *Canadian Geotechnical Journal*, 1977, **14**, 554-561.
3. B. M. Patterson, M. D. Annable, E. B. Bekele and A. J. Furness, On-line groundwater velocity probe: Laboratory testing and field evaluation, *Journal of contaminant hydrology*, 2010, **117**, 109-118.
4. N. Solovitch, J. Labille, J. r. m. Rose, P. Chaurand, D. Borschneck, M. R. Wiesner and J.-Y. Bottero, Concurrent aggregation and deposition of TiO2 nanoparticles in a sandy porous media, *Environmental science & technology*, 2010, **44**, 4897-4902.

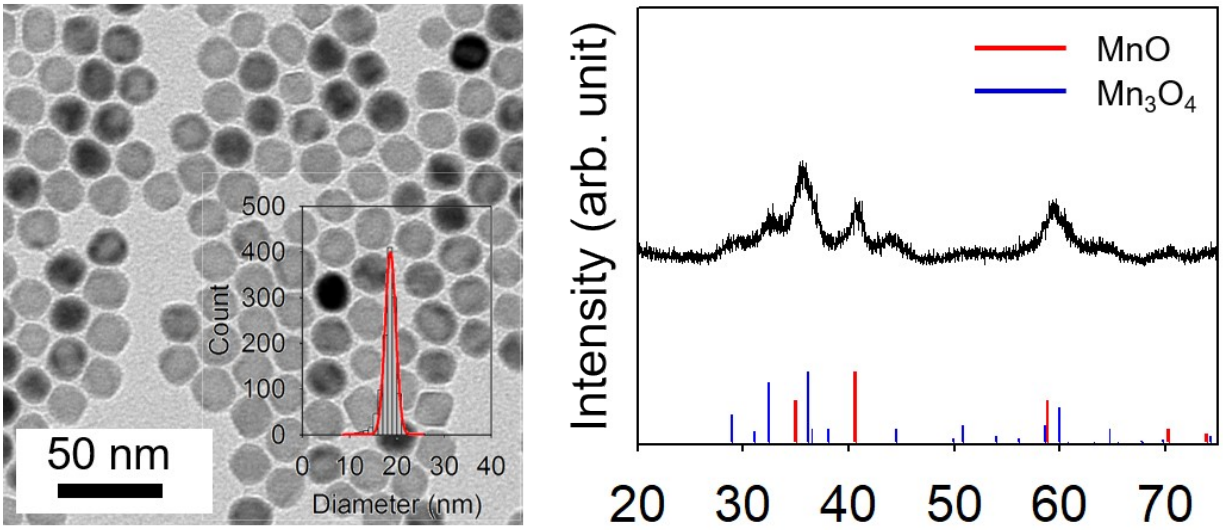


Fig. S1. Highly monodisperse manganese oxide nanoparticles (Mn_xO_y NPs) were precisely synthesized via manganese oleate (precursor) decomposition in the presence of oleic acid at 320°C. As measured by TEM, the sizes and size distributions of resulting synthesized Mn_xO_y NPs were 18.4 ± 1.5 nm. XRD patterns were matched with MnO (JCPDS Card # 07-0230) and Mn_3O_4 (JCPDS Card # 24-0734); the synthesized NPs were well known as MnO core with Mn_3O_4 shell structure.

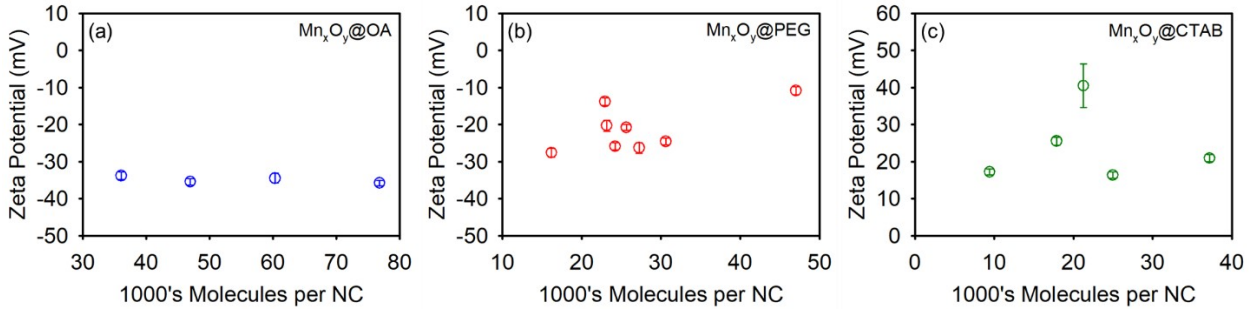
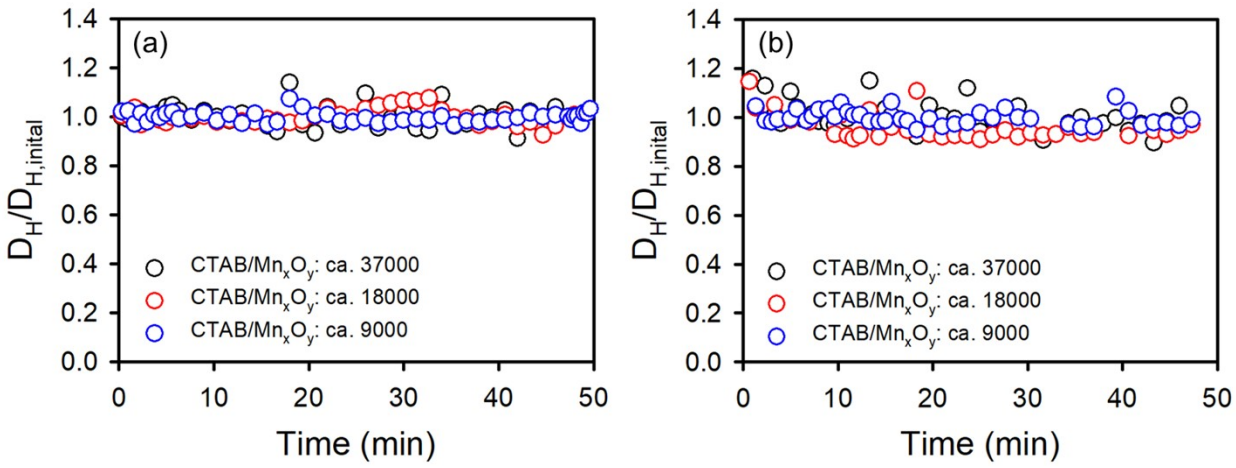


Fig S2. Zeta potential of the surface functionalized manganese oxide nanoparticles (Mn_xO_y NPs) with different surface grafting densities at pH 7.0 ± 0.2; (a)Mn_xO_y@OA, (b)Mn_xO_y@PEG, and (c)Mn_xO_y@CTAB.



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75 Fig. S3. Aggregation profile of Mn_xO_y@CTAB NPs with various surface grafting densities.
76 Aggregation experiments were performed in the presence of (a) 2000 mM of NaCl and (b) 1000
77 mM of $CaCl_2$ concentrations at pH 7.0 ±0.2.

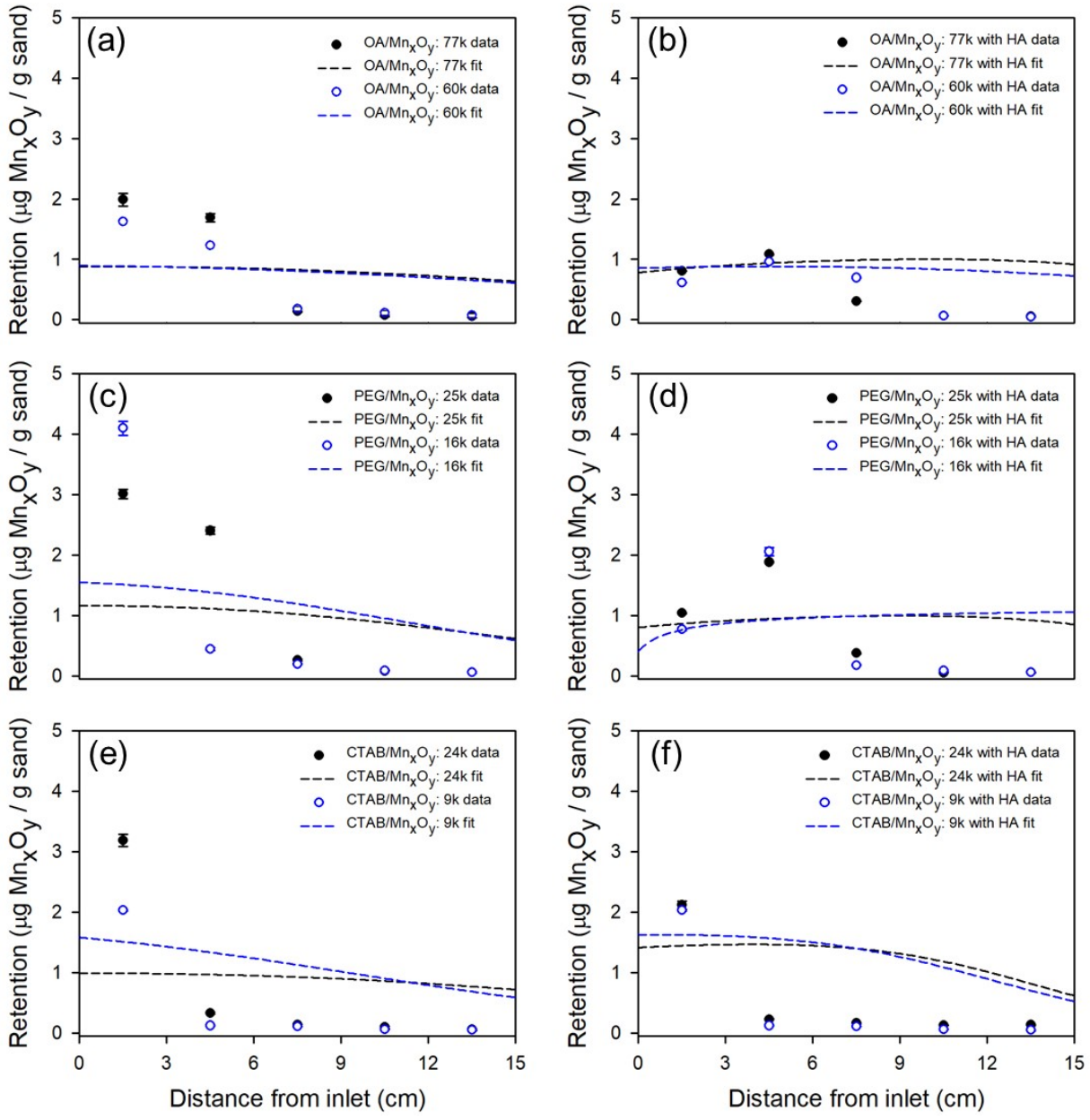

Fig. S4. Experimental and fitted retention profiles of Mn_xO_y NPs with different grafting densities in water saturated column packed with 30-40 mesh Ottawa sand in the absence and presence of HA; (a-b) Mn_xO_y@OA, (c-d) Mn_xO_y@PEG, and (e-f) Mn_xO_y@CTAB. All column experiments were performed at 0.76 m/d of a pore-water velocity and pH 7.0 ± 0.2.

Table S1. Relative concentration (C/C_0) obtained by batch reactor experiments with respect to the surface grafting density of organic coatings. All experiments were conducted at pH 7.0 ± 0.2.

Surface Stabilizer	Grafting density	Relative Concentration (C/C_0)
OA	77000	0.761 ± 0.01
	60000	0.624 ± 0.01
PEG	25000	0.567 ± 0.01
	16000	0.517 ± 0.01
CTAB	24000	1.088 ± 0.01
	9000	0.851 ± 0.01

Table S2. Fitted parameters obtained from NP BTC data using MFT model.

Column identifier	k_{att} (h^{-1})	k_{det} (h^{-1})	S_{max} (μg/g sand)
OA/Mn_xO_y:77k	1.386 ± 0.23	0.016 ± 0.01	1.495 ± 0.26
OA/Mn_xO_y:60k	1.200 ± 0.12	0.015 ± 0.01	1.556 ± 0.32
OA/Mn_xO_y:77k with HA	3.068 ± 0.85	0.027 ± 0.01	1.500 ± 0.16
OA/Mn_xO_y:60k with HA	1.545 ± 0.31	0.019 ± 0.01	1.494 ± 0.24
PEG/Mn_xO_y:25k	1.795 ± 0.29	0.016 ± 0.01	1.970 ± 0.44
PEG/Mn_xO_y:16k	1.820 ± 0.25	0.012 ± 0.00	2.488 ± 0.59
PEG/Mn_xO_y:25k with HA	3.361 ± 1.00	0.024 ± 0.01	1.455 ± 0.18
PEG/Mn_xO_y:16k with HA	30.125 ± 21.49	0.050 ± 0.02	1.230 ± 0.03
CTAB/Mn_xO_y:24k	1.452 ± 0.22	0.011 ± 0.01	1.410 ± 0.16
CTAB/Mn_xO_y:9k	1.426 ± 0.14	0.007 ± 0.00	2.425 ± 0.46
CTAB/Mn_xO_y:24kwith HA	3.317 ± 0.85	0.014 ± 0.01	2.005 ± 0.39
CTAB/Mn_xO_y:9k with HA	2.841 ± 0.55	0.010 ± 0.00	2.160 ± 0.41

Values after '±' indicates 95% confidence limits of fitted parameters.