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Supplemental Information

A Multi-Constituent Site Blocking Mathematical Model for Simulation of Nanoparticle and Stabilizing Polymer Transport in Saturated Porous Media

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Model Development Supplement

To estimate the grain surface area covered by depositing particles (A_{QD}) the deposited solid phase concentration (S_{QD})can be multiplied by a conversion factor, τ:

$$\tau = N_{Avo} * A_{particle}^{QD} * m_{sand} \tag{S1}$$

where N_{Avo} is Avogadro's Number (6.02 x 10^{23} particles/mol), $A_{particle}^{QD}$ is the area covered by a single QD nanoparticle (m^2/particle) and m_{sand} is the mass of the sand (g) in the corresponding element. This conversion assumes that the area on the sand surface that is occupied by a single quantum dot is equal to the projected area of the spherical quantum dot onto the surface. Similarly for PAA-OA, a conversion factor, ζ, was used to relate polymer adsorption ($S_{PAA\text{-}OA}$) to $A_{PAA\text{-}OA}$:

$$\zeta = \frac{N_{Avo} * A_{molecule}^{PAA} * m_{sand}}{MW^{PAA}} \tag{S2}$$

where MW^{PAA} represents the molecular weight of PAA-OA (g/mol) and $A_{molecule}^{PAA}$ represents the total area occupied by a single molecule of PAA-OA (m^2/molecule). It should be noted that eq S2 is more uncertain than eq S1 because of the difficulty in directly measuring the area occupied by the PAA-OA molecule on the sand surface.[1]

Using τ and ζ to convert S and S_{max} for quantum dots and PAA-OA to their respective areas results in equations 3 and 4:

$$\frac{A_{QD}}{A_{total}} = \frac{\tau * S^{QD}}{\tau * S_{max}^{QD}} = \frac{S^{QD}}{S_{max}^{QD}} \tag{S3}$$

$$\frac{A_{PAA-OA}}{A_{total}} = \frac{\zeta * S^{PAA}}{\zeta * S_{max}^{PAA}} = \frac{S^{PAA}}{S_{max}^{PAA}} \tag{S4}$$

Substituting eqs S1 and S2 into eq 5 in the paper results in the following expression for Ψ.

$$\Psi = 1 - \frac{S^{QD}}{S_{max}^{QD}} - \frac{S^{PAA}}{S_{max}^{PAA}} \tag{S5}$$

Calculation of τ and ζ is predicated on the "one-site" assumption, which postulates that all area available for attachment/adsorption is available for both constituents. Thus, S_{max}^{PAA} can be related to S_{max}^{QD} by:

$$S_{max}^{PAA} = \left(\frac{\tau}{\zeta}\right) * S_{max}^{QD} \tag{S6}$$

To calculate the PAA_OA conversion factor, the area occupied by a single PAA-OA molecule was estimated as 10.70 nm^2. This estimate was obtained by assuming spherical geometry for each acrylic acid monomer ($CH_2{=}CHCO_2H$), calculating the number of monomers from the known molecular weight (~3000 Da), and multiplying the monomer diameter (5.048 Å, estimated from the monomer volume of 67.367 Å^3, predicted using Molinspiration, http://www.molinspiration.com/cgi-bin/properties) by the degree of polymerization to estimate the length of the polymer chain. The width of the polymer chain was estimated as the monomer diameter. A summary of calculated properties for PAA-OA is outlined in Table S1. To calculate the area occupied, it was assumed that the entire polymer chain was lying down on the sand surface, occupying an area encompassed by a rectangle with a length equal to that of the polymer and a width equal to the diameter of a spherical monomer. Complete monolayer coverage values were also estimated for each sand grain mesh size, assuming spherical grains; however it should be noted that these values are conservative estimates, as sand surface topography heterogeneity will create substantially more available surface area than that estimated for a spherical geometry.

Table S1. Calculated PAA-OA and QD properties for use in relating nanoparticle retention capacity to polymer adsorption capacity

Property	**Value**	**Units**
Monomer Volume	67.367	Å^3
Monomer Radius (assumed spherical)	2.524	Å
Monomer Area Occupied	2.00E-19	m^2
Monomer Diameter	5.048	Å
Polymer Chain Length	21.203	nm
Polymer area occupied – lying down	10.704	nm^2/#
Polymer area occupied – lying down	1.07E-17	m^2/#
Theoretical complete monolayer coverage (d_c = 0.335 mm)	4.562	ug/g
Theoretical complete monolayer coverage (d_c = 0.165 mm)	10.255	ug/g
Theoretical complete monolayer coverage (d_c = 0.125 mm)	13.619	ug/g
Area Conversion Factor[a] (ζ) - PAA (d_c = 0.335 mm)	2.051E+03	m^2*g-sand/g-PAA
Area Conversion Factor (ζ) - PAA (d_c = 0.165 mm)	1.990E+03	m^2*g-sand/g-PAA
Area Conversion Factor (ζ) - PAA (d_c = 0.125 mm)	1.942E+03	m^2*g-sand/g-PAA
Hydrodynamic Diameter	30	nm
Particle Area occupied	7.069E+02	nm^2
Theoretical Monolayer Coverage (d_c = 0.335 mm)	23.04	pmol/g
Theoretical Monolayer Coverage (d_c = 0.165 mm)	51.79	pmol/g
Theoretical Monolayer Coverage (d_c = 0.125 mm)	68.78	pmol/g
Area Conversion Factor (τ) - QD (d_c = 0.335 mm)	4.064E+07	m^2*g-sand/mol
Area Conversion Factor (τ) - QD (d_c = 0.165 mm)	3.944E+07	m^2*g-sand/mol
Area Conversion Factor (τ) - QD (d_c = 0.125 mm)	3.849E+07	m^2*g-sand/mol

Estimate of the collector efficiency

This study used an empirical correlation to calculate the collector efficiency, developed by Tufenkji and Elimelech:[2]

$$\eta_0 = 2.4A_S^{0.33}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{0.052} + 0.55A_SN_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_v^{0.} \tag{S7}$$

Here, A_s is the Happel correction factor, N_R is the interception number, N_{Pe} is the Peclet number, N_{vdW} is the London-van der Waals attractive forces number, N_A is the attraction number, and N_G is the gravitational number. The three terms in (S7) represent the contributions to collector efficiency by Brownian diffusion, interception, and sedimentation, respectively.

Experimental Methods – For further detail, refer to Wang et al.[3]

The QDs used in this study exhibited a CdSe/CdZnS core/shell structure[4] and a maximum emission wavelength of 582 nm[5]. To render them water soluble, they were coated with an amphiphilic copolymer, polyacrylic acid – octylamine (PAA-OA), with a molecular weight of approximately 3,000 Da [6]. The stock solution contained ca. 4 μM of water soluble QDs (QD-PAA-OA), buffered with 50 mM sodium borate, and stored in the dark. Free residual PAA-OA was removed from solution to non-detectable levels by three rounds of centrifugation at 35,000 rpm for 4 hr each. The column input solution was prepared by diluting the QD stock 400-fold with degassed 3 mM NaCl at pH 7.

Table S2. Column attachment/sorption parameters with 95% confidence intervals, fitted with the multi-constituent site blocking model. Calculated collector and collision efficiencies are also given.

Exp	**QD Attachment Parameters**				**PAA-OA Adsorption Parameters**		
	K_{att} [a]	S_{max}^{QD} [b]	**α** [c]	**η_0** [d]	**K_{ads}** [e]	S_{max}^{PAA} [f]	**$C_{0,PAA}$** [g]
	(1/hr)	**(pmol/g)**	**(n/a)**	**(n/a)**	**(1/hr)**	**(ug/g)**	**(mg/L)**
CS-L	1.41 ± 0.53	6.16± 0.44	0.030	0.505	1058.3 ± 2327000	1.221	2.428
MS-L	2.00 ± 0.50	12.76± 0.55	0.030	0.774	2.50 ± 0.75	2.530	2.330
CS-H*	8.83 ± 2.45	3.00± 0.22	0.101	0.098	77.77 ± 75.46	0.595	2.195
MS-H*	5.50 ± 1.43	7.14± 0.74	0.021	0.146	65.16 ± 120.82	1.415	2.291
MS-HB*	7.50 ± 2.32	7.80± 0.74	0.029	0.146	192.73± 1422.76	1.546	2.230
FS-H*	29.48 ± 4.03	21.16 ± 0.36	0.073	0.174	7328.3 ± 387600	4.193	2.607
FS-HB*	64.29 ± 4.02	21.46 ± 0.15	0.160	0.174	914.97 ± 661.07	4.252	2.607

[a] - Fitted QD attachment rate; [b] - Fitted QD Retention Capacity; [c] – Attachment efficiency calculated from filtration theory (eq 8); [d] – Calculated collector efficiency[2]; [e] - Fitted PAA-OA adsorption rate; [f] - PAA-OA adsorption capacity, which is equivalent to S_{max}^{QD} in solid phase surface area; [g] - calculated injection concentration of residual aqueous PAA-OA. B indicates duplication. [3]

Sensitivity Analysis Supplement

Values of the optimization function for the CS-H experiment's model fit are presented here to further explore the calculated model confidence intervals and the lack of model sensitivity to the k_{ads} model parameter. For the figures presented here, the optimization function presented in the manuscript (sum of the squared residuals) was calculated over a range of k_{att} and k_{ads} values, holding the fitted value of S_{max}^{QD} (3.00 pmol/g) constant. Here, it is evident that the fitted values of 8.83 and 77.7 correspond to the global minimum, validating the optimization function used for model fitting. This analysis demonstrates the lack of sensitivity to the k_{ads} parameter that was also seen in fitted parameter confidence intervals and the sensitivity analysis in the manuscript. In the contour plot in Figure S3, for the k_{att} parameter, the minimum of the objective function lies within a small range of about 6.5 to 11.5 1/hr, with the minimum occurring at k_{att}=8.83 1/hr. This observation is consistent with the fitted parameter and calculated confidence intervals. Much less sensitivity is observed along the k_{ads} axis. Here, values remain close to the objective function minimum from about $10^{1.1}$ to the end of the domain tested. This result is consistent with the calculated confidence intervals for this experiment in that the model is much more sensitive to k_{att} than k_{ads}. Similar results were observed for other experiments, with the optimization function being relatively insensitive to k_{ads} in all cases. The only experiment with a small k_{ads} confidence interval (80-100S) occurred because this experiment demonstrated the smallest upward slope near the inlet in the QD retention profile.

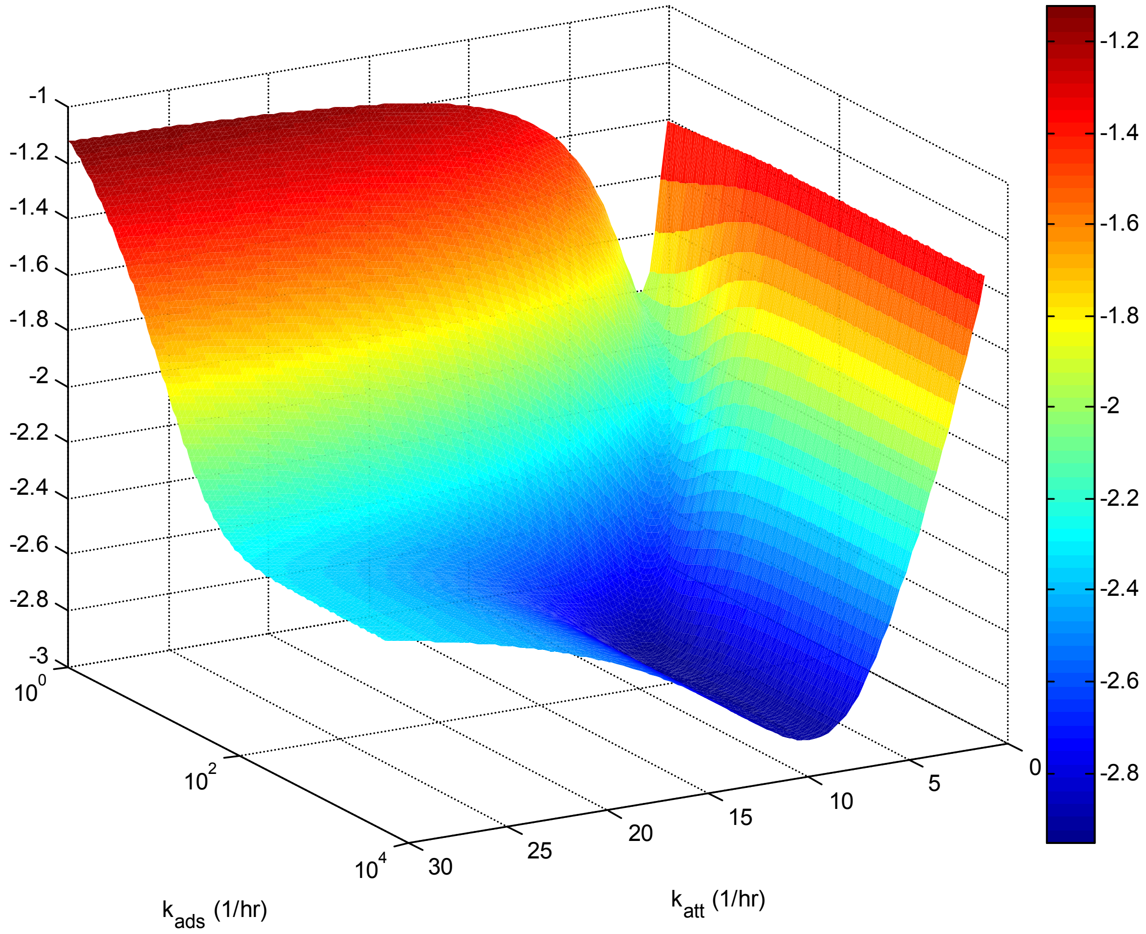

Figure S1. Surface plot of the common logarithm of the values of the optimization function with variable k_{ads} and k_{att} for the 40-50F Experiment. The minimum of k_{att}=8.83 1/hr and k_{ads}=77.8 1/hr is evident, as is the much greater sensitivity of the function to k_{att} than k_{ads}.

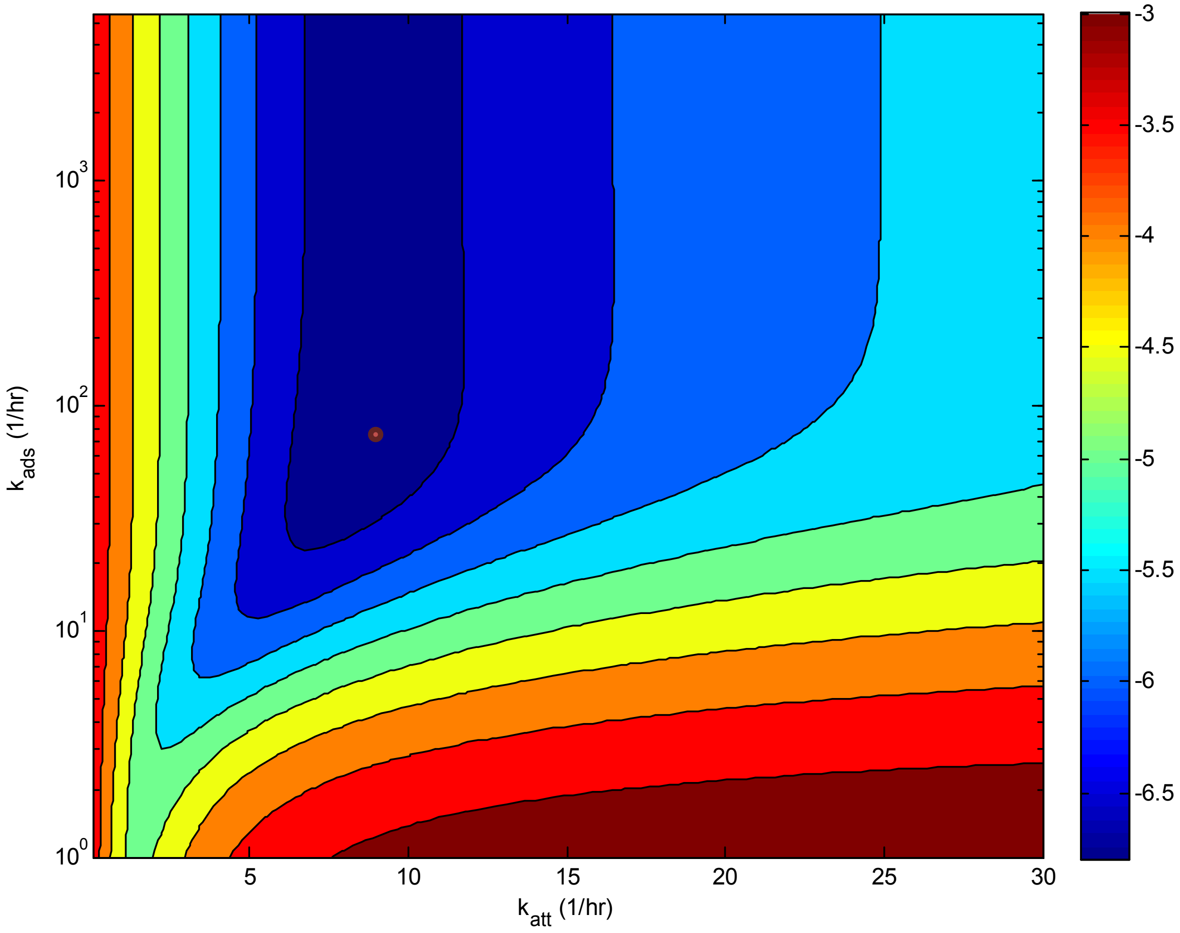

Figure S2. Contour plot of values of the natural logarithm of the optimization function for the 40-50F experiment. The minimum of k_{att}=8.83 ± 2.45 and k_{ads}=77.8 ± 75.5 is indicated by the red dot. The difference in sensitivity of the function to katt versus kads is evident from the long trough from k_{ads} from $10^{1.1}$ to the extent of the domain ($10^{3.5}$).

Coupled Retention/Adsorption Capacity. Model sensitivity to changes in available area for attachment and adsorption was also explored by fixing k_{att}= 20 1/hr and k_{ads} = 100 1/hr, and varying S_{max}^{NP} between 1 and 20 ug/g-sand (Figure S3) to explore the effect over the full range of fitted values. Here, it was assumed that 100% of an adsorbed macromolecule's surface area "lying down" occupies the sand surface. This value was chosen because it will lead to the highest amount of quantum dot breakthrough by minimizing the area available for attachment (maximizing the area occupied by adsorbed stabilizing agent). As expected, increasing available area for nanoparticle retention and stabilizing agent adsorption resulted in more retention. Another interesting result was the increasing slope in nanoparticle retention near the inlet. This result suggests that both rate and capacity control the increasing retention behavior of nanoparticles.

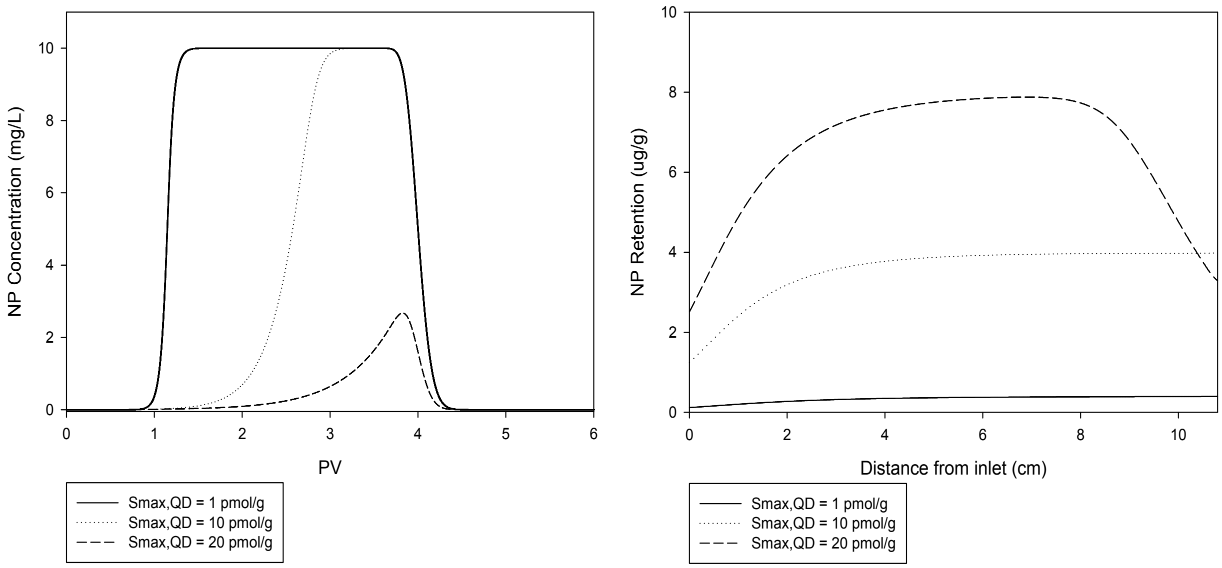

Figure S3. Nanoparticle transport and retention sensitivity to changes in total retention capacity

Large Scale (10m) Column Simulations. In an effort to understand the importance of model assumptions (selection of a conceptual model) at larger scales, two 1D simulations of 10 meter long sand columns were performed using the CS-H experiment as the base case (See Tables 1 and 2 for parameters, Figure S4). These results suggest that although the inlet effects will only be apparent in a very small portion of the column, the estimated S_{max}^{QD} value will strongly affect the fractions of eluted and retained mass. This simple example highlights the importance of choosing the most appropriate mathematical model to analyze bench-scale systems. Using inaccurate conceptual models or model parameters, such as those acquired using an MFT-based analysis, could result in amplification of errors in larger scale model implementation.

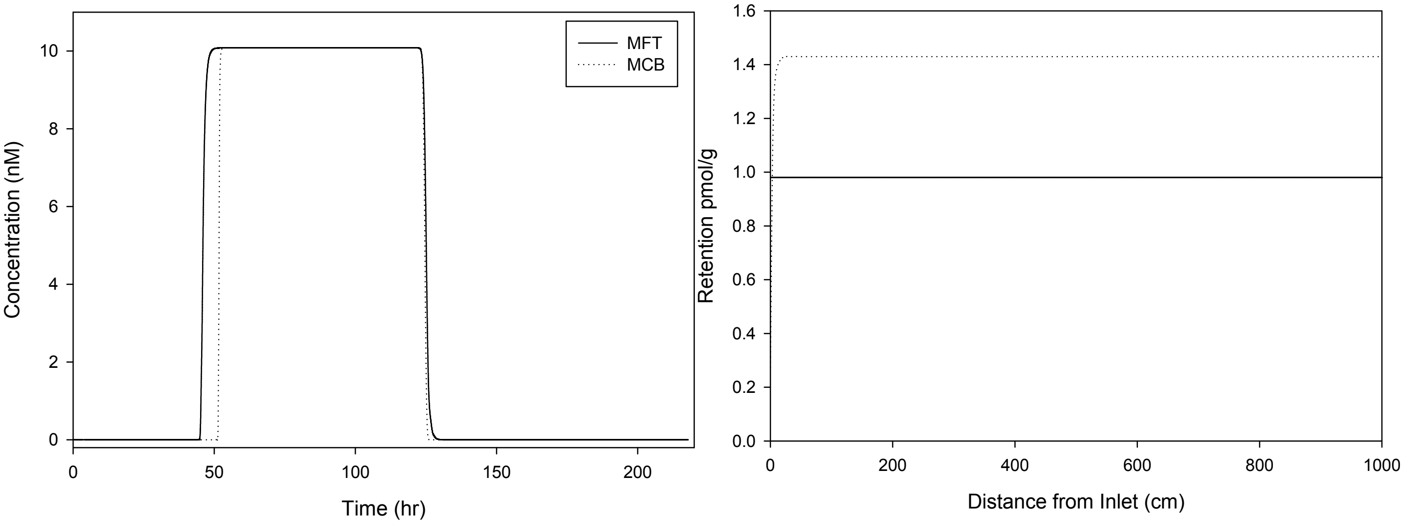

Figure S4. Modified Filtration Theory – fit to BTC Only (MFT) and Multi-Constituent Site Blocking (MCB) Model prediction for a 10-meter long 40-50 mesh (dc=0.335 mm) clean Ottawa sand column. Here, the MFT Model predicts that 15.0% of the 57.6 nmol injected will be retained, compared to 21.8% for the MCB Model.

References

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