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Extending Applicability of Correlation Equations to Predict Colloidal Retention in Porous Media at Low Fluid Velocity

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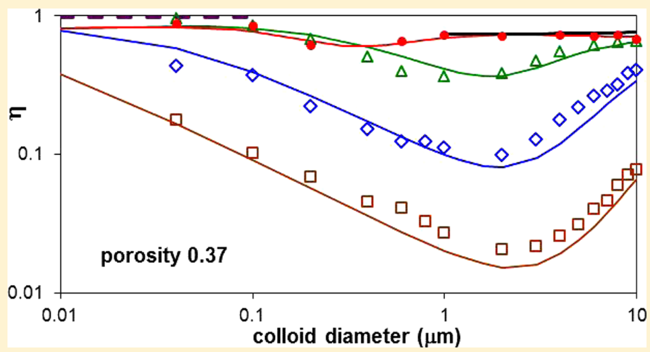
Supporting Information

ABSTRACT: In this work, we analyzed causes for a recently noted shortcoming of filtration models, which is to predict collector efficiencies greater than unity under low fluid velocity conditions. For Eulerian flux approaches, both the underlying mechanistic model and the correlation equation used to export model results may contribute to this error. For particle trajectory approaches, the error results solely from the correlation equation, not from the underlying mechanistic model, making correction a relatively simple endeavor. Whereas a fitted saturation factor was recently used in a correlation equation to try to force collector efficiencies to remain below unity, we herein develop a different saturation factor based on classic mass transfer relationships to extend the applicability of our correlation equation to low fluid velocities.



1. INTRODUCTION

A collection of correlation equations now exist to predict the collector efficiency (η) for colloidal retention in granular porous media under the condition when colloid−collector repulsion is absent (so-called favorable conditions).[1−6] The underlying models for developing these equations typically involved particle trajectory simulation based on force/torque balance[2,5,6] or Eulerian flux analysis via solving the convective diffusive equation[3,4] within representative model geometries. The purpose of these underlying mechanistic models is to predict collector efficiency (η), which is defined as the ratio of the number of colloids retained relative to the number of colloids introduced into the representative unit cell, where the unit cell represents porous media as an isolated sphere,[1] or Happel sphere-in-cell,[2,3,6] or hemispheres-in-cell.[5] By the above definition, the value for η should never exceed unity.

The complexity of the mechanistic models warrants development of correlation equations conditioned to the numerical results, such that researchers can use the correlation equations to obtain close approximations of the mechanistic numerical results without utilizing the mechanistic models. Predictions from correlation equations agree well (within a factor of 2) with experimental results under favorable conditions (lacking colloid−collector repulsion) for a wide range of environmentally relevant parameters, e.g. colloid size (40 nm to 10 μm in diameter), fluid velocity (1×10^{-6} to 1×10^{-3} m/s) and porosity (0.25−0.5).[1,3−6]

However, it was shown that at very low fluid velocity (e.g., below 1×10^{-6} m/s) these correlation equations predict collector efficiencies exceeding unity, especially for large or very small sized colloids.[6−8] Because predictions of η come from correlation equations conditioned to results from mechanistic models, the error in η under low velocity conditions may come from two sources: (1) the correlation equations that approximate the numerical results; specifically, the power law dependence of existing correlation equations for η on Peclet number or gravity number;[6] or (2) the underlying numerical models themselves; specifically, the constant colloid concentration condition conventionally employed on the Happel sphere-in-cell model's outer fluid envelope.[6,7] Nelson and Ginn[6] correctly pointed out some of the problems in applying existing correlation equations at low fluid velocities, but the distinction between the correlation equation predictions versus the underlying mechanistic models as sources of this error warrants clarification. Whereas these authors provided a regressed correlation equation for η (the NG equation) that was intended to correct the error of η above unity,[6] the modified NG equation still predicts η values exceeding unity for certain parametric conditions (e.g., fluid velocity <1×10^{-7} m/s, porosity <0.30, colloid size <50 nm), especially at relatively low porosities, as demonstrated in Figure 1. The goal of this article is to distinguish the above two sources of error in predicting η under low fluid velocity conditions, and to extend the correction offered by Nelson and Ginn.[6]

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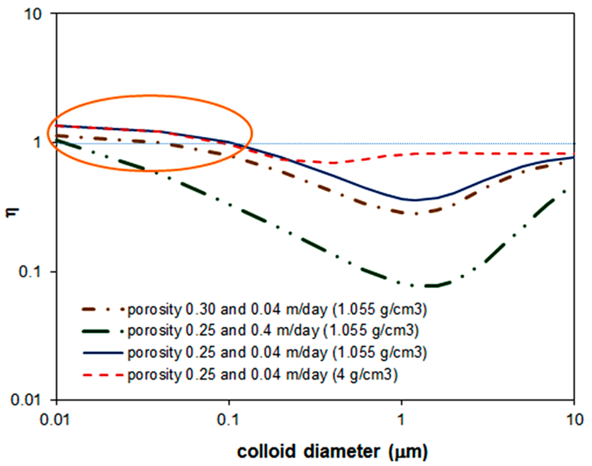

Figure 1. Predicted collector efficiencies from the correlation equation recently proposed by Nelson and Ginn[6] (the NG equation) which are shown to still exceed unity under certain conditions (highlighted with orange oval region) using colloids of two different densities (1.055 and 4 g/cm^3), e.g., fluid velocity <1 × 10^{-7} m/s, porosity <0.30, colloid size <50 nm. The errors of exceeding unity are more pronounced at relatively low porosities (e.g., 0.25).

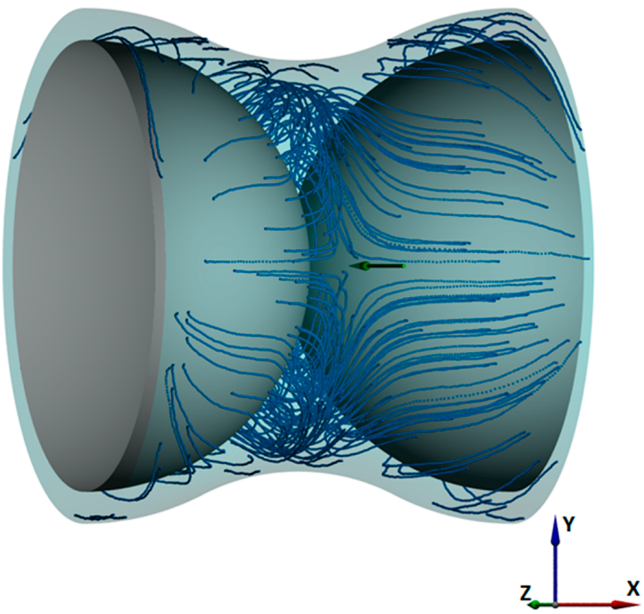

Figure 2. The modified hemispheres-in-cell model geometry, where the outer fluid envelope represents pendular water to match convergence−divergence of fluid trajectories within grain to grain contacts observed in micromodels. The flow direction, as indicated by green arrow, is downward (with gravity) and representative flow streamlines are shown in light blue.

2. METHOD

Modified Hemisphere-in-Cell Model Geometry and Flow Field. The hemisphere-in-cell unit model geometry is herein used, since this model was shown to fall within the range of other existing unit cell predictions for colloid retention under favorable conditions. However, the unit cell flow field was slightly modified relative to that described in Ma et al.[5] Specifically, the outer fluid envelope was modified to express a shape similar to pendular water to match convergence−divergence of fluid trajectories around grain to grain contacts observed in saturated and unsaturated micromodels (Figure 2), which was not captured in the previous flow field (e.g., Ma et al.[9]). The differences in the outer fluid boundaries between our previous and current unit cell models are further illustrated in Figure S1 in the Supporting Information.

Computational meshes for the modified hemisphere model geometry were constructed and fluid flow field within the meshes was obtained by numerically simulating the steady-state Navier−Stokes equation under laminar flow hydrodynamics using the computational fluid dynamics packages STAR-CD and STAR-ccm+ (details on mesh construction and numerical flow field simulation were provided in our previous works[5,10]). The modified outer fluid envelope geometry around grain to grain contact regions (Figure 2) was constructed with fine subsurface prism layers to approximate nontangential stress boundary conditions imposed in classical unit cell such as the Happel Sphere-in-cell.[2,11]

Particle Trajectory Analysis. Trajectories of colloids within the hemispheres-in-cell model were simulated based on classical Langevin equation[12]

$$(m + m^*)\frac{du}{dt} = \sum F_i = F_{COLL} + F_D + F_G + F_B \qquad (1)$$

where m is the mass of colloidal particle, m^* is the virtual mass (approximated with the mass of one-half of the fluid displaced by the colloidal particle, which reflects the effect of fluid on a moving particle, and which is to increase the effective mass of the particle), and u is the particle velocity vector. The forces acting on the particle include colloidal forces (F_{COLL}), fluid drag (F_D), gravity (F_G), and Brownian forces (F_B). Since this current work concerned only favorable conditions (lacking colloid−collector repulsion), only van der Waals forces were included in the calculation of colloidal forces. Expressions for these forces were provided in detail in previous works.[5,10]

The coupling of particle trajectory analysis with the computational flow field and numerical simulation procedures was described in detail in previous work.[5,10] Briefly, colloids were introduced randomly to a plane upstream of the collector that was normal to the superficial flow to the collector (Figure 2). All the forces acting on the colloid were integrated according to eq 1 to obtain the velocity of the colloid. Upon resolving the particle velocity vector, the updated particle position was determined from first-order integration ($d\mathbf{x}/dt = u$), where $\mathbf{x}$ is the particle position vector. This process was repeated until the particle was either attached to the collector surfaces (e.g., came within 1 nm colloid−surface separation distances) or exited the system. Simulation parameters and conditions were chosen based on our typical column experimental conditions and are summerized in Table 1. On average, approximately 1000−2000 colloidal trajectories were simulated for each condition to obtain a statistically meaningful and stable value for collector efficiency (η).

3. RESULTS AND DICUSSION

3.1. Testing the Modified Flow Field for Hemispheres-in-Cell Model. Simulated collector efficiencies within the modified hemisphere model (or modified fluid flow field) under favorable conditions were slightly larger than, but in general agreed (within a factor of 2) with, those predicted from the previous version by Ma et al.[5] (e.g., represented by the MFPJ equation), as shown in Figure 3. The slight differences in η between these two model versions reflected the changes in model geometry and resulting fluid flow field. The trajectory simulations in either flow field did not yield η exceeding unity

Table 1. Parameters Used in Lagrangian Trajectory Simulations

parameter	value
collector diameter, d_c	510 μm
particle diameter, d_p	10 nm to 10 μm
porosity, ε	0.25, 0.37[a]
pore water velocity, v_p	0.04, 0.4, 4 m/day
particle density, ρ_p	1055, 4000 kg/m^3
fluid density, ρ_f	998 kg/m^3
fluid viscosity, μ	9.98×10^{-4} kg/(m·s)
Hamaker constant, H	3.84×10^{-21} J
absolute temperature, T	298.2 K

[a]The selected values for porosity bracket the range typical of granular media.

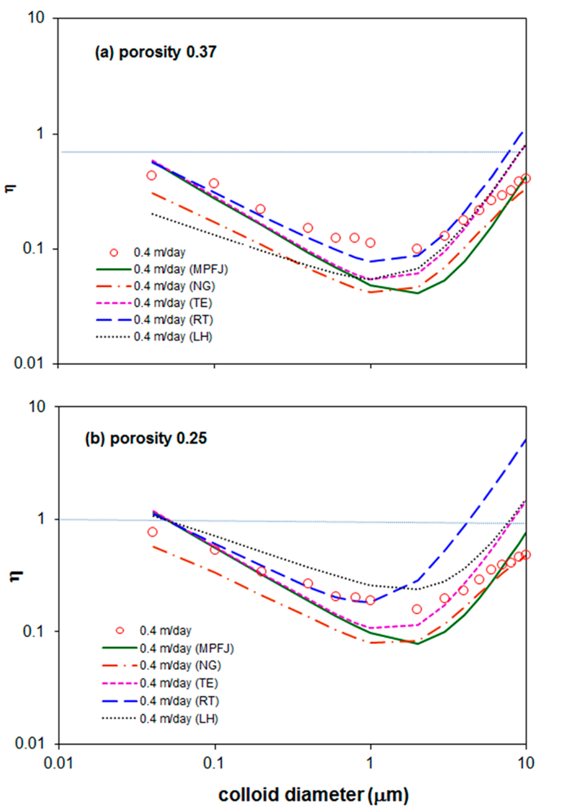

Figure 3. Simulated collector efficiencies (red open circles) from the modified hemispheres-in-cell model shown in Figure 2 under favorable conditions as a function of colloid size at a representative pore water velocity of 0.4 m/day for (a) porosity 0.37 and (b) porosity 0.25. Simulated η values (symbols) were compared to predictions from existing correlation equations (lines), as developed by Rajagopalan and Ties[2] (the RT equation), Tufenkji and Elimelech[3] (the TE equation), Long and Hilpert[4] (the LH equation), Ma et al.[5] (the MPFJ equation), and Nelson and Ginn[6] (the NG equation).

under any conditions. Simulated collector efficiencies from the modified hemispheres-in-cell model also fell within the approximately factor-of-two range of differences among the other existing correlation equations under favorable conditions, a range which has been well demonstrated to correspond to the range in experimental observations.[1,3−6] We stress here that it is not our intention to claim superiority for any particular correlation equation; rather, the purpose of this paper is to diagnose the causes for η overpredictions (i.e., greater than unity) among existing correlation equations under relatively low fluid velocity conditions, and after briefly establishing the modified hemispheres-in-cell model to be as fit a starting point as any other existing models, to extend the proposed strategy for correcting the errors. Notably for this context (favorable condition), simulations could just as well have been performed using either the hemispheres-in-cell or Happel sphere-in-cell geometries to the same effect.

3.2. Causes of Collector Efficiency Predictions Greater than Unity. Existing correlation equations, including the MPFJ correlation equation derived from the hemispheres-in-cell model[5] and the recently proposed NG correlation equation from the Happel sphere-in-cell model,[6] have been demonstrated to predict η values exceeding unity when fluid velocities were below 1×10^{-6} m/s (e.g., Figure 2 in Nelson and Ginn[6] and Figure 1 above). However, in the case of MPFJ, this error derives from the correlation equation, rather than the underlying mechanistic particle trajectory model, as demonstrated by the fact that η predictions from this model did not exceed unity, as shown for the updated flow field (Figure 4).

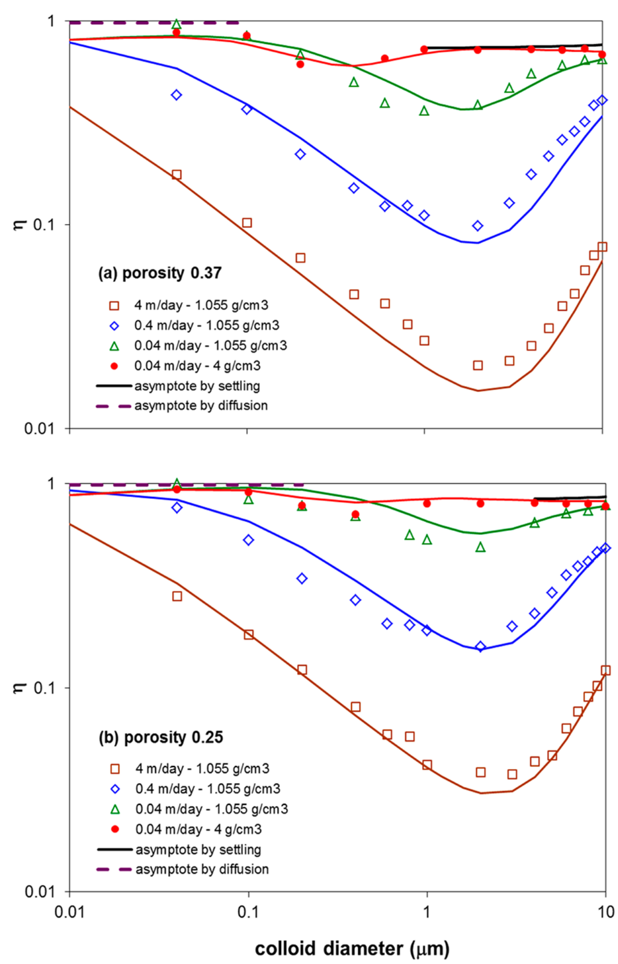

Figure 4. Simulated collector efficiencies (discrete symbols) from particle trajectory model within the modified hemisphere geometry as a function of colloid size under favorable conditions for (a) porosity 0.37 and (b) porosity 0.25. For each porosity, three representative pore water velocity (0.04, 0.4, and 4 m/day) and two particle densities (1.055 and 4 g/cm^3) were simulated. The lines (brown, blue, green, and red) were fitted η values from eq 4. The two asymptotes due solely to diffusion (dashed purple line) or gravitational settling (solid black line) are also shown.

The mechanistic particle trajectory models underlying the RT correlation equation[2] and the NG correlation equation[6] are also not expected to yield collector efficiencies exceeding unity. Particle trajectory models in general examine the fate of individual colloids in the model geometry and flow field to determine whether the colloid exits the system or is retained on the collector. There is no mechanism in these models to predict that more colloids will be retained than were introduced to the system. Hence, predictions of η exceeding unity from the RT, MPFJ, and NG correlation equations arise from the correlation equations themselves, rather than the underlying mechanistic trajectory models.

In contrast, the Eulerian flux modeling approach[7] which underlies, for example, the TE correlation equation,[3] may produce η greater than unity. Song and Elimelech[7] concluded that overprediction of η (above unity) at low Peclet number resulted from the constant colloid concentration condition typically prescribed on the Happel sphere-in-cell model's outer fluid envelope when implementing the flux analysis approach. There were two reasons for this conclusion: (1) the constant concentration boundary condition holds only when the diffusion boundary layer is much smaller than the outer fluid envelope thickness as suggested by Ruckenstein,[13] whereas, this assumption is valid only at relatively large Peclet numbers; (2) the concentration on the lower half of the Happel outer boundary should be smaller than the approaching concentration on the upper half due to colloid retention onto the collector surface. Song and Elimelech[7] adopted a modified boundary (so-called Danckwert's condition) that allowed colloids to come only from the upper half of the Happer fluid boundary and demonstrated that the simulation results with this new boundary did not overestimate η at low Peclet numbers.

An additional issue; however, is that whereas collector efficiency is defined as the ratio of retained to introduced colloids, the number of introduced colloids is commonly taken to be the particle flux passing through a given area by *convection*.[3,7,14] Strictly speaking, this approximation for introduced colloids is not correct, since the particle flux passing through an area has three contributions: convection, diffusion, and gravitational settling. In most cases (e.g., for relatively large Peclet numbers), the fluxes due to diffusion and settling are negligible relative to the convective flux. However, for very low velocity, the flux contributions due to diffusion or settling may not be negligible. For instance, in the limiting case of no fluid motion, for small colloids, particle flux across a given area is by diffusion only. If introduced colloids are defined only by convective flux (zero under these conditions), η would approach infinity, which clearly is incorrect. It is likely that this approximation of convective flux contributed to overprediction of η in Song and Elimelech[7] since the diffusive flux would have predominated for their particles (25 nm radius) at the very low fluid velocities they examined. The same issue applies to large, or high density, colloids at low fluid velocity, since particle flux from gravitational settling (as opposed to convection) may predominate under these conditions. Long and Hilpert[4] employed Eulerian flux analysis in their simulations of Brownian colloid transport in packed identical spheres (diffusion-dominated regime). Their model did not employ a constant concentration boundary, nor did it approximate particle flux as being solely convective; therefore, we would not expect their model to produce η exceeding unity, even under low fluid flow conditions.

To summarize (Table 2), among the mechanistic models underlying correlation equations, the particle trajectory models do not yield η exceeding unity. Hence, predictions of superunity η values by correlation equations regressed to particle trajectory models (e.g., RT, MPFJ, and NG) must result from the correlation equations themselves, rather than the underlying mechanistic models. In contrast, Eulerian flux models may produce superunity η values, when a constant concentration boundary condition is employed, and/or when the total particle flux is approximated as the convective flux. Hence prediction of superunity η values by correlation equations regressed to Eulerian flux models (e.g., TE) may arise from both the underlying mechanistic model and the correlation equation used to export the mechanistic model results. Notably, the LH correlation equation borrows its interception and gravitational settling terms directly from the TE correlation equation, making it potentially susceptible to correlation equation errors that we will discuss next.

3.3. Limitations of Existing Correlation Equations. All existing correlation equations for η contain a power law dependence on Peclet number (e.g., $\sim N_{Pe}^{-2/3}$) for the diffusion term.[1−6] It is this term that causes predicted η values to exceed unity at small Peclet numbers ($N_{Pe} = Ud_c/D_{BM}$, where U is the approach fluid velocity, d_c is the collector diameter, and D_{BM} is the Brownian diffusion coefficient, equal to $k_BT/(6\pi\mu a_p)$, where k_B is the Boltzmann constant, T is the absolute temperature, μ is the fluid viscosity, and a_p is the colloid radius). This power law dependence of η on N_{Pe} originated from the power law dependence of the Sherwood number (N_{Sh}) on N_{Pe} derived from mass transfer theory in the single sphere model[15,16] or in the Happel sphere-in-cell model.[13,17] For example, in the Happel model, the Sherwood number, which represents the ratio of convective relative to diffusive mass transport (defined as d_cK_c/D_{BM}, where K_c is the mass transfer coefficient), is related to the Peclet number as:[13,17]

$$N_{sh} = A_s^{1/3} N_{Pe}^{1/3}, \text{ when } N_{Pe} > 70 \tag{2}$$

where $A_s = 2(1-\gamma^5)/(2-3\gamma+3\gamma^5-2\gamma^6)$, with $\gamma = (1-\varepsilon)^{1/3}$, where ε is the porosity. The power law dependence of the diffusion term in η on N_{Pe} (i.e., $\eta \propto N_{Pe}^{-2/3}$) can then be derived from eq 2, as described in detail by Tien (pp 124–125).[14] However, earlier studies[16−18] stated that eq 2 (or in general, $N_{sh} \propto N_{Pe}^{1/3}$) was valid only when $N_{Pe} > 70$, and $N_{Pe} < 10\,000$. At very low Peclet number, the Sherwood number becomes *independent* of N_{Pe}, approaching an asymptotic value that is dependent upon porosity;[16,17] the porosity-dependent asympotes for N_{sh} for the limiting case of no fluid flow will be shown below shortly.

Since the power law relationship $\eta \propto N_{Pe}^{-2/3}$ in existing correlation equations was derived based on eq 2, the underlying condition $N_{Pe} > 70$ should also apply to these equations. Notably, the low fluid velocity conditions examined by Nelson and Ginn[6] that resulted in superunity η values corresponded to $N_{Pe} < 70$. Nelson and Ginn[6] correctly pointed out the problem in applying existing correlation equations at low fluid velocities. However, their correction was done by maintaining the same power law dependence ($\eta \propto N_{Pe}^{-2/3}$) for the diffusion term, but moderating η with the following fitted saturation expressions for diffusion and gravitation, respectively: $((N_{Pe})/(N_{Pe} + 16))^{0.75}$ and $((N_{Gi})/(N_{Gi} + 0.9))$, where $N_{Gi} = 1/(N_G + 1)$, N_G is the gravity number ($= 2a_p^2(\rho_p - \rho_f)g/(9\mu U)$, ρ_p and ρ_f are colloid and fluid density, respectively; g is the acceleration due to gravity). As illustrated in Figure 1, this correction still

Table 2. Basic Features about Prior Correlation Equations and Models for Colloidal Filtration

		Rajagopalan and Tien[2]	Tufenkji and Elimelech[3]	Long and Hilpert[4]	Ma et al.[5]	Nelson and Ginn[6]
porous media model		Happel sphere-in-cell	Happel sphere-in-cell	randomly packed uniform spheres	Hemispheres-in-cell	Happel sphere-in-cell
simulation method		Lagrangian	Eulerian	Eulerian	Lagrangian	Lagrangian
correlation equation acronym		RT	TE	LH	MPFJ	NG
causes for predicting η > 1	mechanistic model problem?	no	possibly	no	no	no
	correlation equation problem?	yes	yes	yes	yes	yes
other features		numerical solution for interception and sedimentation, superimposed with analytical solution for diffusion	numerical solution for diffusion, interception and sedimentation	numerical solution for diffusion only, used solution from the TE equation for interception and sedimentation	numerical solution for diffusion, interception and sedimentation	numerical solution for diffusion, interception and sedimentation
range of Peclet number for which correlation equation is valid		70–10 000	70–10 000	70–10 000	70–10 000	conceptually 70– 10 000, may apply to as low as 20

leads the NG correlation equation[6] to predict η values exceeding unity for certain parametric conditions as listed in their Table 2 (e.g., fluid velocity <5 × 10^{-7} m/s, porosity <0.30, colloid size <50 nm), demonstrating that it is very difficult to obtain a functional correlation equation for all conditions.

3.4. Constraining Power Law Dependence Using Mass Transfer Theory to Predict η. Developing a correlation equation applicable to convective and nonconvective conditions for a range of porous media porosities is difficult. Fortunately asympotes corresponding to limiting conditions can be obtained as follows from mass transfer theory. Under the limiting condition of no fluid flow, η can be derived assuming particle fluxes solely due to diffusion, or gravitational settling. When diffusion is the only mechanism for colloid mass transfer (e.g., for very small size colloids), η equals unity under the steady state condition.[19] At this limit, following the analysis for an isolated sphere (Sherwood et al.,[19] p 215), the Sherwood number for the Happel model can be derived as follows (see Supporting Information for detailed derivation):

$$N_{sh} = \frac{2}{1-\gamma} = \frac{2}{1-(1-\varepsilon)^{(1/3)}} \tag{3}$$

Equation 3 is applicable for the steady-state mass transfer to collectors under no-flow conditions. Theoretical values for N_{sh} from eq 3 were corroborated by the numerical results from Pfeffer and Happel[17] for a porosity range of 0.4−1.0, where porosity = 1.0 refers to the case of an isolated spherical collector.

Under the condition where gravitational settling is solely responsible for colloid mass transfer (e.g., for colloids of large size or high density), η is entirely dictated by the location of introduction, such that interception is guaranteed if the colloid vertical trajectory is within one colloid radius outside of the projected collector surface. For the Happel model, this yields

$$\eta = \frac{\pi(a_c + a_p)^2}{\pi b^2} = (1-\varepsilon)^{2/3}(1+N_R)^2 \tag{4}$$

where b is the radius of the outer fluid envelope, and N_R equals a_p/a_c, where a_c is the collector radius. It follows that eq 4 is valid when the colloid size is not greater than the thickness of the outer fluid shell (i.e., $a_p \leq b - a_c$) and under conditions when gravitational settling is solely responsible for colloid mass transfer.

The above two limiting cases for mass transfer yield two asymptotes that constrain η under low fluid velocity conditions, provided that convective particle flux is negligible relative to the diffusion or settling fluxes. Following the analysis by Tien (pp 124−125)[14] and using the above limiting relationship for diffusion (i.e., eq 3), a new diffusion term for the correlation equation was derived using a definition for the introduced particle flux that includes both convection and diffusion (see Supporting Information for detailed derivation). The gravitational term for the correlation equation developed by Nelson and Ginn[6] produced results similar to the limiting case in eq 4, as illustrated in Figure 4, and was therefore retained. The final correlation equation thus obtained based on regression to mechanistic simulation results from the modified hemispheres-in-cell model under favorable conditions is

$$\eta \cong \gamma^2\left[\frac{8 + 4(1-\gamma)A_s^{1/3}N_{Pe}^{1/3}}{8 + (1-\gamma)N_{Pe}^{0.97}}N_{Lo}^{0.015}N_{Gi}^{0.8}N_R^{0.028} + A_s N_R^{15/8}N_{Lo}^{1/8} + 0.7N_R^{-0.05}N_G\frac{N_{Gi}}{N_{Gi}+0.9}\right] \quad (5)$$

where $N_{Lo} = H/(9\pi\mu a_p^2 U)$; H is the Hamaker constant. Predictions from eq 5 (Figure 4) agree with simulated η values from the underlying trajectory model for a large range of fluid velocity (0.04−4 m/day), colloid size (40 nm to 10 μm diameter), and porosity (0.25−0.37). Compared to all prior correlation equations (Table 2), eq 5 extends the applicable range in Peclet number to 0−10 000 (the upper limit is constrained by laminar flow regime).

Although eq 5 avoids superunity η values at low fluid velocities (or low Peclet numbers), we suggest that this equation should be used in conjunction with the above-mentioned asympotes to predict η, as illustrated in Figure 4. Discontinuities may exist between the predictions from eq 5 and the asymptotes under particular conditions (e.g., especially at very high porosity). Notably, the crossing of the predicted trends at 0.04 and 0.4 m/day (Figure 4b) for very small colloid sizes is an artifact solely from eq 5, not from the mechanistic model simulations.

4. IMPLICATIONS

An important consideration for employing correlation equations under conditions where η approaches unity (e.g., at very low fluid velocities) is the retention of almost all colloids in the unit collector. Under these conditions, colloid−colloid interactions likely become a predominant control on colloid retention, regardless of whether they are unfavorable (possibly leading to blocking), or favorable (possibly yielding ripening). Essentially, the "clean bed" assumption is violated when η approaches unity. Hence, the low fluid velocity condition represented by correlation equations may be largely hypothetical, since blocking and/or ripening, which probably will exist in experimental systems, are not represented in these equations.

In summary, while eq 5 above represents an improvement for predicting η under a wider variety of fluid velocities than represented by previous correlation equations, we do not consider it a major improvement, but rather a useful clarification. In fact, all existing correlation equations basically agree (within a factor of 2) except for conditions of unusual porosity,[10] or very low fluid velocity,[6] with the latter being a largely hypothetical application due to expected violation of clean bed conditions. Furthermore, all existing correlation equations (to date) succeed only under favorable conditions; so our next goal will be developing correlation equations that may be applicable under unfavorable experimental conditions (colloid−collector repulsion present).

■ ASSOCIATED CONTENT

Supporting Information

Mass transfer theory-based relationships and changes to the hemisphere-in-cell flow field. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Yao, K.-M.; Habibian, M. T.; O'Melia, C. R. Water and waste water filtration: Concepts and applications. *Environ. Sci. Technol.* **1971**, *5* (11), 1105−1112, DOI: 10.1021/es60058a005.

(2) Rajagopalan, R.; Tien, C. Trajectory analysis of deep-bed filtration with the sphere-in-cell porous media model. *AIChE J.* **1976**, *22* (3), 523−533.

(3) Tufenkji, N.; Elimelech, M. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ. Sci. Technol.* **2004**, *38* (2), 529−536, DOI: 10.1021/es034049r.

(4) Long, W.; Hilpert, M. A correlation for the collector efficiency of Brownian particles in clean-bed filtration in sphere packings by a Lattice-Boltzmann method. *Environ. Sci. Technol.* **2009**, *43* (12), 4419−4424, DOI: 10.1021/es8024275.

(5) Ma, H.; Pedel, J.; Fife, P.; Johnson, W. P. Hemispheres-in-cell geometry to predict colloid deposition in porous media. *Environ. Sci. Technol.* **2009**, *43* (22), 8573−8579, DOI: 10.1021/es901242b. (correction: *Environ. Sci. Technol.* **2010**, *44* (11), 4383).

(6) Nelson, K. E.; Ginn, T. R. New collector efficiency equation for colloid filtration in both natural and engineered flow conditions. *Water Resour. Res.* **2011**, *47* (5), W05543 DOI: 10.1029/2010WR009587.

(7) Song, L.; Elimelech, M. Deposition of Brownian particles in porous media: Modified boundary conditions for the Sphere-in-cell model. *J. Colloid Interface Sci.* **1992**, *153* (1), 294−297.

(8) Keller, A. A.; Auset, M. A review of visualization techniques of biocolloid transport processes at the pore scale under saturated and unsaturated conditions. *Adv. Water Resour.* **2007**, *30* (6−7), 1392−1407, DOI: 10.1016/j.advwatres.2006.05.013.

(9) Ma, H.; Pazmino, E.; Johnson, W. P. Surface heterogeneity on hemispheres-in-cell model yields all experimentally-observed non-straining colloid retention mechanisms in porous media in the presence of energy barriers. *Langmuir* **2011**, *27* (24), 14982−14994, DOI: 10.1021/la203587j.

(10) Ma, H.; Johnson, W. P. Colloid retention in porous media of various porosities: Predictions by the hemispheres-in-cell model. *Langmuir* **2010**, *26* (3), 1680−1687, DOI: 10.1021/la902657v. (correction: *Langmuir* **2010**, *26* (9), 6864).

(11) Happel, J. Visous Flow in Multiparticle Systems: Slow Motion of Fluids Relative to Beds of Spherical Particles. *AIChE J.* **1958**, *4* (2), 197−201.

(12) Ermak, D. L.; McCammon, J. A. Brownian dynamics with hydrodynamic interactions. *J. Chem. Phys.* **1978**, *69* (4), 1352−60.

(13) Ruckenstein, E. On mass transfer in the continuous phase from spherical bubbles or drops. *Chem. Eng. Sci.* **1964**, *19* (2), 131−146.

(14) Tien, C. *Granular Filtration of Aerosols and Hydrosols*, 1st ed.; Butterworth-Heinemann: Stoneham, MA, 1989.

(15) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962.

(16) Brian, P. L. T.; Hales, H. B. Effects of transpiration and changing diameter on heat and mass transfer to spheres. *AIChE J.* **1969**, *15* (3), 419−25.
(17) Pfeffer, R.; Happel, J. An analytical study of heat and mass transfer in multiparticle systems at low Reynolds numbers. *AIChE J.* **1964**, *10* (5), 605−611.
(18) Cookson, J. T. Removal of submicron particles in packed beds. *Environ. Sci. Technol.* **1970**, *4* (2), 128−134.
(19) Sherwood, T. K.; Pigford, R. L.; Wilke, C. R. *Mass Transfer*; McGraw-Hill Kogakusha, Ltd.: Tokyo, 1975.