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 balance2,5,6 or Eulerian flux analysis via solving the convective diffusive equation3,4 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).1,3–5

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 Ginn6 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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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.)5. The differences in the outer fluid boundaries in 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 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 works5,10). 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 equation12

\[(m + m^*) \frac{dx}{dt} = \sum F_i = F_{\text{COLL}} + F_D + F_C + F_B\]  

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 \(x\) is the particle velocity vector. The forces acting on the particle include colloidal forces \(F_{\text{COLL}}\), 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 \((dx/dt = u)\), where \(x\) 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 summarized 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 (\(\eta\)).

3. RESULTS AND DISCUSSION

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 \(\eta\) 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 \(\eta\) exceeding unity.
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

3.2. Causes of Collector Efficiency Predictions Greater than Unity. Existing correlation equations, including the MPFJ correlation equation derived from the hemispheres-in-cell model5 and the recently proposed NG correlation equation from the Happel sphere-in-cell model,6 have been demonstrated to predict \( \eta \) values exceeding unity when fluid velocities were below \( 1 \times 10^{-6} \) m/s (e.g., Figure 2 in Nelson and Ginn6 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 \( \eta \) predictions from this model did not exceed unity, as shown for the updated flow field (Figure 4).
The mechanistic particle trajectory models underlying the RT correlation equation\(^7\) 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 \( \eta \) 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,\(^8\) may produce \( \eta \) greater than unity. Song and Elimelech\(^7\) concluded that overprediction of \( \eta \) (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,\(^9\) 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 Danckwerts’ condition) that allowed colloids to come only from the upper half of the Happel fluid boundary and demonstrated that the simulation results with this new boundary did not overestimate \( \eta \) 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), \( \eta \) would approach infinity, which clearly is incorrect. It is likely that this approximation of convective flux contributed to overprediction of \( \eta \) 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\(^5\) 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 \( \eta \) 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 \( \eta \) exceeding unity. Hence, predictions of superunity \( \eta \) 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 \( \eta \) 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 \( \eta \) 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 \( \eta \) 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 \( \eta \) values to exceed unity at small Peclet numbers \((N_{Pe} = Ud/D_{BBM})\), where \( U \) is the approach fluid velocity, \( d \) is the collector diameter, and \( D_{BBM} \) is the Brownian diffusion coefficient, equal to \( k_B T/(6\pi a_r \eta) \), where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \mu \) is the fluid viscosity, and \( a_r \) is the colloid radius). This power law dependence of \( \eta \) 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 \( dK_e/D_{BBM} \)) where \( K_e \) is the mass transfer coefficient, is related to the Peclet number as:\(^13,17\)

\[
N_{Sh} = A_1^{1/3}N_{Pe}^{1/3}, \quad \text{when } N_{Pe} > 70
\]  
(2)

where \( A_1 = 2(1 - \gamma)/(2 - 3\gamma + 3\gamma^2 - 2\gamma^3) \), with \( \gamma = (1 - \epsilon)^{1/3} \), where \( \epsilon \) is the porosity. The power law dependence of the diffusion term in \( \eta \) 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 asymptotes 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\(^8\) that resulted in superunity \( \eta \) 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 \( \eta \) with the following fitted saturation expressions for diffusion and gravitation, respectively: \( (N_{Di}/(N_{Di} + 16)^{0.75} \) and \( (N_{Di}/(N_{Di} + 0.9)) \), where \( N_{Di} = 1/(N_{Ci} + 1) \), \( N_{Ci} \) is the gravity number \((= 2a_r^2(\rho_p - \rho_f)g/(9\mu U)) \), \( \rho_p \) and \( \rho_f \) 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

<table>
<thead>
<tr>
<th>Correlation Equation</th>
<th>Rajagopalan and Tien</th>
<th>Tufenkji and Elimelech</th>
<th>Long and Hilpert</th>
<th>Ma et al.</th>
<th>Nelson and Ginn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous media model</td>
<td>Happel sphere-in-cell</td>
<td>Happel sphere-in-cell</td>
<td>randomly packed uniform spheres</td>
<td>Hemispheres-in-cell</td>
<td>Happel sphere-in-cell</td>
</tr>
<tr>
<td>Simulation method</td>
<td>Lagrangian</td>
<td>Eulerian</td>
<td>Eulerian</td>
<td>Lagrangian</td>
<td>Lagrangian</td>
</tr>
<tr>
<td>Correlation equation acronym</td>
<td>RT</td>
<td>TE</td>
<td>LH</td>
<td>MPFJ</td>
<td>NG</td>
</tr>
<tr>
<td>Predicting ( \eta ) &gt; 1 cases for</td>
<td>no</td>
<td>possibly</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Mechanistic reasoning?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Other features</td>
<td>numerical solution for interception and sedimentation, superimposed with analytical solution for diffusion</td>
<td>numerical solution for diffusion, interception and sedimentation</td>
<td>numerical solution for diffusion only, used solution from the TE equation for interception and sedimentation</td>
<td>numerical solution for diffusion, interception and sedimentation</td>
<td>numerical solution for diffusion, interception and sedimentation</td>
</tr>
</tbody>
</table>
| 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

3.4. Constraining Power Law Dependence Using Mass Transfer Theory to Predict \( \eta \) Values for Colloidal Particles

Equation 3 is applicable for the steady-state mass transfer to collectors under no-flow conditions. Theoretical results for \( \eta \) values from eq 3 were correlated by the numerical results from Nelson and Ginn for a porosity range of 0.4–0.6. Pfieffer and Happel\(^{17}\) for a porosity range of 0.4–0.6, where the correlation \( \eta = \frac{N_a - N_b}{N_b - N_a} \), and under conditions of the outer spherical collector surface. Eq 4 holds when the collector radius is not greater than the thickness of the outer fluid shell (i.e., \( \delta_s = \sqrt{\pi b \delta}N_a \)).

Where \( b \) is the radius of the outer fluid envelope, and \( N_a \) equals \( \delta_s / \delta \), where \( \delta \) is the collector radius. It follows that eq 4 is valid when the fluid colloid is not greater (under conditions of the outer fluid envelope) than the outer fluid shell. The above two limiting cases for mass transfer yield two asymptotes that constrain \( \eta \) under low fluid velocity conditions as illustrated in Figure 4, and was therefore retained. The final expression for the correlation \( \eta = \frac{N_a - N_b}{N_b - N_a} \), and under conditions of gravitational settling, is solely responsible for \( \eta \) and \( \delta_s / \delta \).

Under the condition where gravitational settling is responsible for \( \delta \), where the location of \( \delta \) is entirely dictated by the location of the collector. \( \delta \) is the collector radius. It follows that eq 4 is valid when gravitational settling is not greater than the thickness of the outer fluid shell (i.e., \( \delta_s = \sqrt{\pi b \delta}N_a \)).

\[ N_a = \frac{1}{1 - \frac{2}{\left(1 - \frac{1}{\delta_s / \delta}\right)^{1/3}}} \]

Equation 3 and Equation 4. Equation 3 is applicable for the steady-state mass transfer to collectors under no-flow conditions. Theoretical results for \( \eta \) values from eq 3 were correlated by the numerical results from Nelson and Ginn for a porosity range of 0.4–0.6. Pfieffer and Happel\(^{17}\) for a porosity range of 0.4–0.6, \( N_a \) are the correlation \( \eta = \frac{N_a - N_b}{N_b - N_a} \), and under conditions of the outer spherical collector surface. Eq 4 holds when the collector radius is not greater than the thickness of the outer fluid shell (i.e., \( \delta_s = \sqrt{\pi b \delta}N_a \)).

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\[ N_a = \frac{1}{1 - \frac{2}{\left(1 - \frac{1}{\delta_s / \delta}\right)^{1/3}}} \]
\[
\eta \approx \gamma \left[ \frac{8 + 4(1-\gamma)A_{\lambda}^{1/3}N_{E_0}^{1/3} - N_{O_{L_0}}N_{G_i}N_{G_i}^{0.028}}{8 + (1-\gamma)N_{E_0}^{0.57}N_{G_i}N_{G_i}^{0.8}N_{E_0}^{0.039}} + A_{\lambda}N_{G_i}^{1.58}N_{O_{L_0}}^{1.3} \cdot 0.7 N_{E_0}^{0.53}N_{G_i}N_{G_i}^{0.9} \right]
\]

where \( N_{E_0} = H/(9\pi\mu a^2 U) \); \( H \) is the Hamaker constant. Predictions from eq 5 (Figure 4) agree with simulated \( \eta \) values from the underlying trajectory model for a large range of fluid velocity (0.04–4 m/day), colloid size (40 nm to 10 \( \mu \)m 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 \( \eta \) values at low fluid velocities (or low Peclet numbers), we suggest that this equation should be used in conjunction with the above-mentioned asymptotes to predict \( \eta \), 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 \( \eta \) 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 \( \eta \) 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 \( \eta \) 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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