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Correlation Equation for Predicting Attachment Efficiency (α) of Organic Matter-Colloid Complexes in Unsaturated Porous Media

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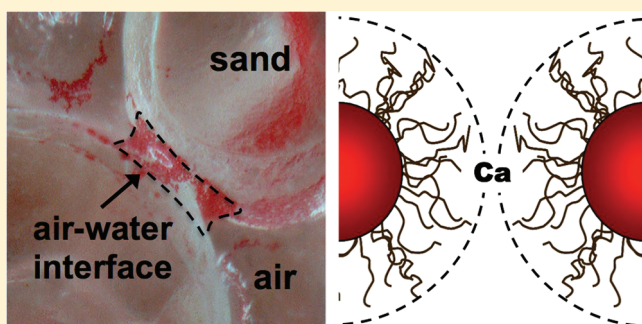
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 Supporting Information

ABSTRACT: Naturally occurring polymers such as organic matter have been known to inhibit aggregation and promote mobility of suspensions in soil environments by imparting steric stability. This increase in mobility can significantly reduce the water filtering capacity of soils, thus jeopardizing a primary function of the vadose zone. Improvements to classic filtration theory have been made to account for the known decrease in attachment efficiency of electrostatically stabilized particles, and more recently, of sterically stabilized particles traveling through simple and saturated porous media. In the absence of an established unsaturated transport expression, and in the absence of applicable theoretical approaches for suspensions with asymmetric and nonideal electrolytes, this study presents an empirical correlation to predict attachment efficiency (α) for electrostatically stabilized suspensions in unsaturated systems in the presence of nonideal electrolytes. We show that existing models fall short in estimating polymer-coated colloid deposition in unsaturated media. This deficiency is expected given that the models were developed for saturated conditions where the mechanisms controlling colloid deposition are significantly different. A new correlation is derived from unsaturated transport data and direct characterization of microspheres coated with natural organic matter over a range of pH and CaCl_2 concentrations. The improvements to existing transport models include the following: adjustment for a restricted liquid-phase in the medium, development of a quantitative term to account for unsaturated transport phenomena, and adjustments in the relative contribution of steric stability parameters based on direct measurements of the adsorbed polymer layer characteristics. Differences in model formulation for correlations designed for saturated systems and the newly proposed correlation for unsaturated systems are discussed, and the performance of the new model against a comprehensive set of experimental observations is evaluated.



INTRODUCTION

Predictive models of the fate and transport of microparticles and nanoparticulate material or ‘nanoenabled’ products in aqueous environments are of great interest because of the growing concern regarding the threat that some particles pose on environmental and public health.¹ Recurrent outbreaks of waterborne diseases from colloidal groundwater contaminants (e.g., *Giardia*, *E. coli* O157:H7, *Cryptosporidium* oocysts, *Cryptosporidium parvum*, and toxic disinfection byproducts)^{2,3} and the growing incorporation of underinvestigated engineered nanoparticles into consumer products (e.g., nano silver, TiO_2 , and nanotubes)^{4–6} has motivated investigations to improve predictive models for the transport and fate of particulate matter that enters the environment via deliberate or inadvertent pathways.

A large body of research has been conducted to understand the fundamental processes that drive colloid and nanoparticle

transport and fate in porous media. However, the majority of this information applies to saturated conditions. A solid and a liquid phase make up saturated porous media systems, where particles can be retained at solid-water interfaces and at grain-to-grain contacts.^{7,8} In unsaturated porous media, an air phase exists, where particles can be retained at air–water^{9,10} and at air–water–solid interfaces^{11–15} in addition to the active sites in saturated systems.

It is well accepted that the enhanced mobility of colloidal particles is often achieved by addition of anionic surface coatings. Such coatings are often engineered to improve the stability of

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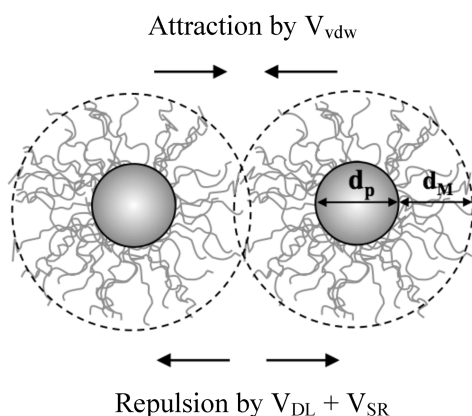


Figure 1. Schematic representation of the forces acting on two electrosterically stabilized organic matter-colloid complexes. The particles are represented by the spheres of diameter d_p ; adsorbed organic matter are the strands extending from the surface of the particle, which make up the stabilizing shell of thickness d_M ; and the Debye-length is represented by the dashed line. Interacting forces include the following: van der Waals attraction (V_{vdw}), double layer repulsion (V_{DL}), and steric repulsion (V_{ES}) (modified from Phenrat et al.¹⁶).

suspensions,^{16,17} although attention has been growing with respect to the similar role that adsorbed natural organic matter (NOM) can play when particles enter soil environments. The consensus from studies concerned with the effect of NOM on colloid transport is that colloid stability and mobility is increased in the presence of NOM via a combination of changes in particle surface potential and through development of a “brush-like” molecular layer on the particle’s surface.^{15,18–20} The electrostatic and steric stability acquired by suspensions coated with highly charged macromolecules such as NOM is schematically illustrated in Figure 1. In this schematic, classic colloid interactions (van der Waals (V_{vdw}) and double layer potentials (V_{DL})) as well as electrosteric component (V_{SR}) are presumed to be the driving forces that maintain the stability of polymer-coated particle suspensions, even in solution compositions thought to favor retention/aggregation. The steric component is necessary to account for experimental observations of polymer-coated colloids exhibiting attachment efficiencies lower than 1 at ionic strengths where the electric double layer is nearly completely screened.²¹

In previous work,¹⁵ we investigated the effect of adsorbed NOM macromolecules on colloid transport through unsaturated porous media under a broad range of solution compositions and determined through direct measurements the dimensions of the adsorbed polymer layer depicted in Figure 1. This research demonstrated that NOM rich environments generally result in colloid suspensions that are stabilized by electrosteric forces. However, a threshold exists where polymer-coated colloids transition between exhibiting soft and rigid properties. I.e., when the stabilizing polymer coating shell density becomes exceedingly high, then the particle can lose steric-related stability and return to the case where the electrostatic double layer provides the sole type of repulsive force. Additionally, pore-scale visualization revealed that retention of organic matter-coated colloids in unsaturated media occurs primarily at the air–water interface, which is a unique component of unsaturated systems.

Available semiempirical correlations for attachment efficiencies, such as those proposed by Elimelech²² and Bai and Tien²³ sensibly capture deposition trends for electrostatically repulsive

surface interactions. More recently Phenrat et al.¹⁸ proposed a semiempirical model that includes a dimensionless parameter for an additional steric repulsion to more closely predict the even lower attachment efficiency of polymer-coated particles (i.e., soft particles). Phenrat et al.’s semiempirical correlation was based on polymeric characteristics estimated from Ohshima’s soft particle theory,²⁴ which calculates the thickness of the adsorbed polymeric layer from electrophoretic mobility. A limitation to this approach is that it is only applicable for suspensions in symmetric and indifferent electrolyte solutions (e.g., NaCl and KCl). Even with direct measurements of polymer layer thickness, the existing attachment efficiency models are valid only for fully water saturated porous systems.

The research presented in this study adapted an existing saturated system model for attachment efficiency of electrosterically stabilized particles (derived by Phenrat et al.¹⁸) to develop a new correlation that would capture attachment efficiencies of NOM-coated colloids moving through unsaturated media. As shown below, the correlation from Bai and Tien²³ does not predict differences in attachment, while the correlation from Phenrat et al.¹⁸ underestimates attachment efficiency by 72%, indicating that the correlations developed for saturated systems cannot be transferred directly to predict transport in unsaturated media without modification. In light of the limitations of the available attachment efficiency correlations, we developed a method to account for the differences in fate and transport processes in unsaturated systems, such as the previously observed retention of organic matter-coated colloids at the air–water interface.¹⁵ Experimental observations of polymer-coated colloid transport in unsaturated media and direct characterization of humic acid- and fulvic acid-coated colloids in the presence of CaCl_2 were used to derive the new empirical correlation. A set of particle and porous media properties is identified that can be deterministically evaluated and used to apply the new model.

■ BACKGROUND

Colloid filtration theory (CFT) estimates the fate of particles moving through a porous medium from the filter’s attachment (i.e., collision) efficiency (α), which represents the probability that an approaching particle will become attached to the collector upon coming into contact with it.²⁵ Column experiments in clean-beds are commonly used to empirically determine α for a given set of physicochemical conditions. CFT has been developed for predictions of particle transport in saturated porous media, and an equivalent expression for unsaturated conditions has not yet been established. The experimental attachment efficiency for unsaturated transport experiments is therefore calculated here using the CFT-based relationship derived by Saiers and Lenhart,²⁶ as it accommodates the effect of lower pore water availability in unsaturated systems, viz

$$\alpha_{\text{exp}} = k_d \frac{2d_c}{3u_s} \frac{nS_w}{(1 - nS_w)\eta_o} \quad (1)$$

Here, k_d is the deposition rate coefficient representing the sum of all participating sinks and can be obtained from breakthrough curve fitting with a one-dimensional advection dispersion equation and first order attachment kinetics. d_c is the mean collector diameter, u_s is the pore water velocity, n is the bed porosity, S_w is the ratio of volumetric moisture content to porosity, and η_o is the single-collector contact efficiency, which can be calculated from the relationship proposed by Tufenkji and Elimelech.²⁷ In order

Table 1. Summary of Dimensionless Parameters Governing Attachment Efficiency^a (from Phenrat et al.¹⁸)

parameter	definition	
N_{LO}	$\frac{4A}{9\pi\mu d_p^2 u_s}$	London number
N_{EI}	$\frac{\varepsilon\varepsilon_o(\zeta_p^2 + \zeta_g^2)}{3\pi\mu u_s d_p}$	first electrokinetic parameter
N_{E2}	$\frac{2\zeta_g \zeta_p}{(\zeta_p^2 + \zeta_g^2)}$	second electrokinetic parameter
N_{DL}	κd_p	double-layer force parameter
N_{LEK}	$\frac{d_p d_M^2 u_s \Gamma N_a \rho_p}{\mu M_w}$	layer-electrokinetic parameter

^a A is the Hamaker constant, μ is the fluid viscosity, d_p is the particle diameter, u_s is the superficial velocity, ε is the relative permittivity of the fluid, ε_o is the permittivity in a vacuum, ζ_g and ζ_p are the zeta potential of the media grains and particles respectively, κ is the reciprocal of double layer thickness, d_M is the average adsorbed layer thickness, Γ is the mass of adsorbed polymer (i.e., surface excess), N_a is Avogadro's number, ρ_p is the macromolecule density, and M_w is the macromolecule molecular weight.

to accommodate for the reduced moisture content on η_o , the porosity term has been adjusted to account only for the fraction of the pore space that is occupied by the available moisture content to colloid transport (i.e., nS_w).

To account for reduced retention of colloids due to electrostatic repulsion, Bai and Tien²³ proposed the following semi-empirical correlation for attachment efficiency, α_{pre} (based on data with α_{exp} ranging from $10^{-2.6}$ to 10^0). This correlation employs dimensionless parameters (defined in Table 1) to account for the London-van der Waals forces (N_{LO}), electrokinetic influences (N_{EI} and N_{E2}), and a double-layer forces (N_{DL}), viz

$$\alpha_{pre} = 10^{2.527 \times 10^{-3} N_{LO}^{0.7031} N_{EI}^{-0.3121} N_{E2}^{1.5111} N_{DL}^{1.352}} \quad (2)$$

Nonetheless, studies have shown that the single effect of changing a particle's charge or zeta-potential by means of adsorbed polymers cannot always account for observed changes in transport and attachment efficiency.^{15,28} Therefore, additional repulsive parameters have been implicated in the prediction of attachment efficiencies of suspensions in polymer rich solutions (e.g., steric hindrance from adsorbed polymers). To the authors' knowledge, Phenrat et al.¹⁸ are the first investigators to propose a correlation (based on data with α_{exp} ranging from $10^{-3.5}$ to $10^{-0.04}$) that takes into account steric repulsive forces through use of a layer electrokinetic parameter (N_{LEK}) (defined in Table 1) to predict attachment efficiency, viz

$$\alpha_{pre} = 10^{-1.35 N_{LO}^{0.39} N_{EI}^{-1.17} N_{LEK}^{-0.10}} \quad (3)$$

MATERIALS AND METHODS

In previous work¹⁵ we experimentally determined deposition rate coefficients (k_d) of organic matter-coated colloid particles traveling through an unsaturated sandy medium (porosity of 0.41 and water saturation of 61%) over a range of solution compositions. Polymer-colloid properties were measured for polystyrene

microspheres of mean diameter of 2.6 μm covered with Elliott Soil Humic Acid (ESHA) and Elliott Soil Fulvic Acid (ESFA) (International Humic Substance Society) at pH 4, 6, and 9 and ionic strengths from 5.05×10^{-4} to 1.01 mM by CaCl_2 addition. Since Morales et al.¹⁵ report information on unsaturated transport deposition kinetics, colloid diameter, adsorbed polymer layer thickness, mass of adsorbed polymer, collector grain diameter, zeta potentials of the particle and the collector grains, and approach velocity of the fluid, these data were used for this study. A summary of the experimental parameters measured is presented in Table 2.

A detailed description of the experimental methods is found in Morales et al.¹⁵ In brief, direct polymeric characterization includes adsorbed polymer thickness (d_M) sizing from dynamic light scattering, mass of adsorbed NOM (Γ) from solution depletion measurements, and zeta potential (ζ) of the NOM-colloid complexes from electrophoretic mobilities. The hydrodynamic diameter of uniform and calibration-grade spherical particles was measured in the presence and absence of ESHA and ESFA. Hydrodynamic diameters in the absence of NOM were consistent with the sizing information provided by the manufacturer and confirmed that neither flocculation nor severe over-estimation of the particle size was taking place. In addition, these results demonstrated the appropriateness of light scattering characterization for measuring d_M over the solution conditions tested. It is important to note that the colloid characterizations employed in the study by Morales et al.¹⁵ are only appropriate for monodispersed and spherical particles. For the two conditions where NOM adsorption was detected, but adsorbed layer thickness not observed (ESFA at pH = 4 and IS of 1.05 mM, and ESFA at pH = 9 and IS of 1.01 mM), the detection limit for d_M (1.4 nm) was assigned to the organic coating.

Predicted attachment efficiency values, α_{pre} , were calculated with Bai and Tien's and Phenrat et al. correlations (eqs 2 and 3, respectively). The predicted α_{pre} were compared against observed α_{exp} as per eq 1 (yielding α_{exp} in the range of $10^{-2.20}$ to $10^{-1.02}$) to evaluate the performance of existing models against a completely empirical data set. An empirical approach was used where the power law coefficients of the constant and dimensionless parameters in the model developed by Phenrat et al.¹⁸ were adjusted through a stepwise least-squares method to fit transport data and directly measured adsorbed polymer layer characteristics and produce a correlation that fittingly captures the attachment efficiency of soft particles transported through unsaturated porous media.

Regression analysis (R^2) and Nash-Sutcliffe efficiency coefficients (E) were used as quantitative descriptors of the predictive accuracy of each model against the observed data. Briefly, Nash-Sutcliffe efficiencies range from $-\infty$ to 1, with an efficiency of 1 ($E = 1$) indicating a perfect fit of model output with observed data, an efficiency of 0 ($E = 0$) indicating that the model predictions are equally accurate to the mean of the observed data, and efficiencies less than zero ($E < 0$) indicating that the observed mean is a better predictor than the model. The Nash-Sutcliffe efficiency coefficient is defined as

$$E = 1 - \frac{\sum_{i=1}^m (\alpha_{exp\ i} - \alpha_{pre\ i})^2}{\sum_{i=1}^m (\alpha_{exp\ i} - \overline{\alpha_{exp}})^2} \quad (4)$$

where m is the number of observations, α_{exp} is the experimentally observed attachment efficiency, α_{pre} is the model predicted

Table 2. Experimental Parameters Measured To Determine Attachment Efficiency of Natural Organic Matter-Coated Particles^a

type of NOM	total DOC (mg L ⁻¹)	IS (mM)	pH	d_p (m)	d_M (m)	Γ (kg m ⁻²)	d_c (m)	ζ_p (V)	ζ_c (V)	u_s (m s ⁻¹)	k_d (s ⁻¹)
ESHA	20	5.00×10^{-2}	4	2.6×10^{-6}	3.2×10^{-8}	4.3×10^{-5}	5.0×10^{-4}	-4.4×10^{-2}	-2.8×10^{-2}	5.3×10^{-5}	7.22×10^{-5}
ESHA	20	5.05×10^{-4}	6	2.6×10^{-6}	5.3×10^{-8}	2.7×10^{-5}	5.0×10^{-4}	-4.6×10^{-2}	-4.6×10^{-2}	5.3×10^{-5}	3.06×10^{-5}
ESHA	20	5.00×10^{-3}	9	2.6×10^{-6}	1.5×10^{-9}	1.6×10^{-5}	5.0×10^{-4}	-5.1×10^{-2}	-5.1×10^{-2}	5.3×10^{-5}	1.11×10^{-4}
ESHA	20	1.05E+00	4	2.6×10^{-6}	2.5×10^{-8}	4.3×10^{-5}	5.0×10^{-4}	-2.0×10^{-2}	-2.0×10^{-2}	5.3×10^{-5}	1.19×10^{-4}
ESHA	20	1.00E+00	6	2.6×10^{-6}	5.5×10^{-8}	3.8×10^{-5}	5.0×10^{-4}	-2.1×10^{-2}	-2.1×10^{-2}	5.3×10^{-5}	1.94×10^{-4}
ESHA	20	1.01E+00	9	2.6×10^{-6}	1.2×10^{-8}	3.3×10^{-5}	5.0×10^{-4}	-2.3×10^{-2}	-2.1×10^{-2}	5.3×10^{-5}	2.14×10^{-4}
ESFA	20	1.05E+00	4	2.6×10^{-6}	1.4×10^{-9}	3.1×10^{-5}	5.0×10^{-4}	-1.9×10^{-2}	-2.2×10^{-2}	5.3×10^{-5}	4.22×10^{-4}
ESFA	20	1.00E+00	6	2.6×10^{-6}	2.9×10^{-9}	1.1×10^{-5}	5.0×10^{-4}	-2.0×10^{-2}	-2.2×10^{-2}	5.3×10^{-5}	4.27×10^{-4}
ESFA	20	1.01E+00	9	2.6×10^{-6}	1.4×10^{-9}	3.6×10^{-5}	5.0×10^{-4}	-2.2×10^{-2}	-2.2×10^{-2}	5.3×10^{-5}	4.56×10^{-4}
ESHA	10	5.05×10^{-4}	6	2.6×10^{-6}	8.7×10^{-9}	1.2×10^{-6}	5.0×10^{-4}	-5.3×10^{-2}	-2.8×10^{-2}	5.3×10^{-5}	1.17×10^{-4}
ESHA	10	2.01×10^{-1}	6	2.6×10^{-6}	7.1×10^{-9}	6.6×10^{-6}	5.0×10^{-4}	-2.8×10^{-2}	-2.2×10^{-2}	5.3×10^{-5}	1.52×10^{-4}
ESHA	5	5.05×10^{-4}	6	2.6×10^{-6}	9.1×10^{-9}	1.1×10^{-6}	5.0×10^{-4}	-4.6×10^{-2}	-3.0×10^{-2}	5.3×10^{-5}	4.99×10^{-5}
ESHA	5	2.01×10^{-1}	6	2.6×10^{-6}	6.8×10^{-9}	4.2×10^{-6}	5.0×10^{-4}	-2.8×10^{-2}	-1.9×10^{-2}	5.3×10^{-5}	1.41×10^{-4}

^a NOM is natural organic matter, IS is ionic strength, d_p is the particle diameter, d_M is the average adsorbed layer thickness, d_c is the mean collector diameter, ζ_p is the zeta potential of the particle, ζ_c is the zeta potential of the collector, u_s is the pore water velocity, and Γ is the mass of adsorbed polymer.

attachment efficiency, and $\overline{\alpha_{exp}}$ is the mean attachment efficiency by experimental observations.

RESULTS AND DISCUSSION

The model of Bai and Tien²³ predicts perfect attachment efficiencies (i.e., $\alpha_{pre} = 1$) for all experimental conditions tested (as illustrated in the α_{exp} vs α_{pre} plot of Figure 2a) and has an R^2 value of 0.028 with a slope of -1.0×10^{-7} , an intercept of 1.0, and a Nash-Sutcliffe efficiency coefficient value (E) of -1.1×10^3 . These statistics indicate that the model inadequately captures trends in attachment efficiency for sterically stabilized particles and that the mean of the observed data can be used with higher accuracy than the model predictions. The model from Phenrat et al.¹⁸ captures the general trend of attachment efficiency (as illustrated in the plot of Figure 2b) and has an R^2 value of 0.80 with a slope of 0.28, an intercept of 3.3×10^{-3} , and an E of -0.27 (see deviation from the 1:1 line). This indicates that the model underpredicts α_{exp} by 72%, as suggested by the slope of the regression line. The near zero E coefficient indicates that the mean of the observed data is equally accurate as the model predictions.

Based on the above statistics, the two existing models were deemed unsuitable to predict α of polymer-coated particles traveling through unsaturated systems, even under the understanding that the range of α_{exp} in the unsaturated system data is in the lower end of the range used to derive the saturated system correlations. These results underline the need to establish an expression for attachment efficiency in unsaturated porous media. To develop a correlation that satisfies these conditions, an empirical approach was used where the exponential coefficients of the constant and dimensionless parameters in Phenrat et al. correlation (eq 3) were revised through a stepwise least-squares method to fit the transport data and adsorbed polymer layer characterization reported in Morales et al.¹⁵ for organic matter-coated colloids transported through unsaturated porous media. The new correlation based on direct polymeric characteristics measurements is of the form

$$\alpha_{pre} = 10^{-0.86} N_{LO}^{0.39} N_{EI}^{-1.22} N_{LEK}^{-0.11} \quad (5)$$

In the proposed correlation for unsaturated systems, the equation constant was increased from $10^{-1.35}$ to $10^{-0.86}$, which

reflects the increase in attachment for NOM-coated colloids traveling through unsaturated media. The relative contribution from N_{LO} did not require adjustments, indicating that the input from van der Waals interactions is properly accounted for in the correlation from Phenrat et al.¹⁸ The exponents for N_{EI} and N_{LEK} were changed from -1.17 to -1.22 and -0.1 to -0.11 , respectively. The changes in weighed contribution of N_{EI} and N_{LEK} suggest that both the first electrokinetic and layer-electrokinetic parameters affect the attachment efficiency to smaller degrees in unsaturated systems than established by the original correlation from Phenrat et al.¹⁸ The output of the new correlation (eq 5) plotted against the experimental data yielded an R^2 value of 0.81 with a slope of 1.0, an intercept of 9.0×10^{-3} , and an E value of 0.67 (Figure 2c), indicating that the model is effective at fitting the unsaturated system observations with reasonable accuracy. These results demonstrate that the correlation from Phenrat et al.¹⁸ provided a good basis to empirically tune α_{pre} for polymer-coated colloid transport in unsaturated systems given a comprehensive data set of particle attachment kinetics and direct polymeric shell measurements.

The primary and most significant difference between Phenrat et al.'s correlation and the one proposed in the present study is in the constant of the models, which quantitatively describes system-specific phenomena associated with particle behavior in fully- and partially saturated porous media (100% and 61% water saturation, respectively). In Phenrat et al.'s equation, a constant of $10^{-1.35}$ represents the cumulative interactions experienced by particles in saturated systems and retention at the solid-water interface and/or grain-to-grain contacts; while in the new equation, a constant of $10^{-0.86}$ represents the cumulative particle interactions in unsaturated systems, including those acting in saturated systems as well as those with the air–water and air–water–solid interfaces. It is those interactions, which are characteristic of unsaturated systems, that Phenrat et al. correlation fundamentally does not capture. The specific mechanisms behind the suggested reduction in attachment efficiency for unsaturated media fall beyond the scope of this study because they cannot be discerned through direct comparisons of the breakthrough data used in this study and those in the studies used by Phenrat et al.¹⁸ Additionally, the performance of the correlation may change with changes to the saturation if the distribution of

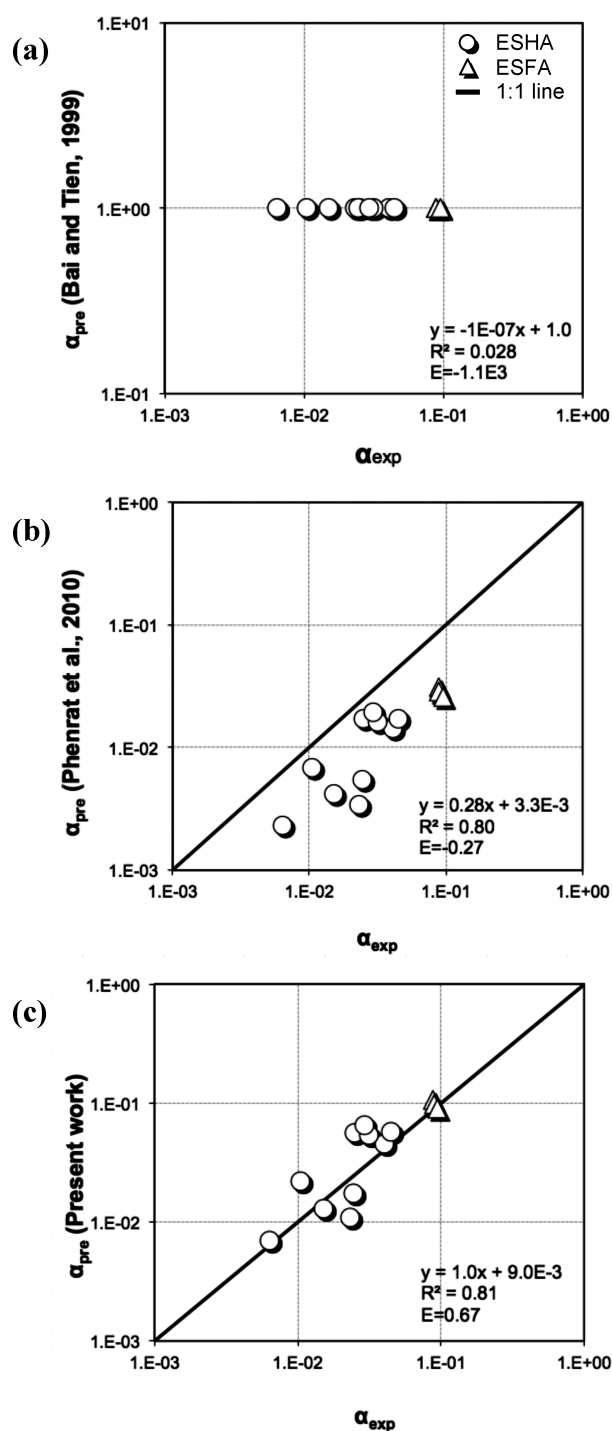


Figure 2. α_{exp} for polystyrene particles coated with ESHA and ESFA¹⁵ vs α_{pre} from (a) Bai and Tien's²³ correlation, (b) Phenrat et al.'s¹⁸ correlation, and (c) correlation from present study. Solid black line represents the 1:1 correlation for α_{exp} to α_{pre} . Regression analysis equation and R^2 and, as well as Nash-Sutcliffe model efficiency coefficient value, E , are reported.

air–water interfaces is significantly affected. Nonetheless, pore-scale observations of organic matter-coated colloid transport from our prior work¹⁵ corroborate the significant role that air–water interfaces play on enhancing colloid retention in unsaturated media.

Secondary differences between the two models lie in the weighted contribution of the dimensionless electrokinetic and layer electrokinetic parameters, which can be explained by two possible bias sources in the data sets used by Phenrat et al.¹⁸ to develop the correlation. First, the decrease in relative contribution in N_{LEK} may be due to the generic NOM adsorption values for Γ , which Phenrat et al.¹⁸ used to supplement published data sets that did not measure or report these parameters. Second, the increase in relative contribution of N_{LEK} can likely be attributed to the use of Ohshima's indirect approach for estimating d_M , which can yield theoretical values that are larger than their true physical magnitude. Uncertainties in the parameters Γ and d_M justify the slight differences in exponential coefficient for parameters N_{EI} and N_{LEK} between the correlation proposed by Phenrat et al.¹⁸ (eq 3) and the one presented here (eq 5), which is based on values obtained from direct measurements of all parameters on which α_{pre} depends.

The importance of the adsorbed layer thickness parameter is highlighted by the power function dependence of d_M on N_{LEK} , which exponentially magnifies any errors associated with the value used for d_M . As discussed earlier in the text, Ohshima's method is not valid for determining d_M of suspension in asymmetric and/or non-indifferent electrolyte solutions, such as those in CaCl_2 used in the current study. The nonindifferent properties of this divalent electrolyte are discussed in detail in our previous work¹⁵ and were corroborated with salting out experiments, as illustrated in Figures S.1a and b. As a result, the experimental conditions in the data from Morales et al.¹⁵ breach the principal assumptions in Ohshima's soft particle theory, so comparisons of d_M values from direct measurements and values calculated with Ohshima's approach were not possible. Still, the use of direct measurements of polymer layer thickness to determine d_M values of suspensions where Ohshima's theory does not apply and to revise the contribution of layer electrokinetic forces on attachment efficiency contributes to the improvement of soft-particle predictive models in general.

Our efforts to develop a correlation for the attachment efficiency of sterically stabilized colloids in unsaturated media represent an important step in advancing the current understanding and improvement of predictive models for colloid transport in the vadose zone. As presented, the new correlation describes well the transport behavior of polymer-influenced particles in unsaturated media by capturing the physical restrictions and system-specific interactions (e.g., air–water interface attachment) in the correlation constant, and accounting for the relative contribution to steric stability in the power law terms of N_{LO} , N_{EI} , and N_{LEK} . The sensitive relationship between polymer-coated particle characteristics with α for both saturated and unsaturated systems highlights the importance of reporting adsorbed layer characteristics, in addition to standard particle and collector size and zeta potential, in order to draw meaningful insights from comparisons of available data sets and to improve existing models. This study circumvents the nonideal electrolyte limitations of Ohshima's approach through the use of a dynamic light scattering technique to directly measure adsorbed layer thickness. However, our approach holds its own set of limitations in terms of particle sphericity and of suspension monodispersity. As such, the development of a universal method to determine d_M in any given environmental condition is an issue that remains unresolved.

■ ASSOCIATED CONTENT

S Supporting Information. Brief description of the electrolyte indifference test and plots of dissolved organic matter

concentrations by CaCl_2 and NaCl addition as illustrated in Figure S.1 for ESHA and Figure S.2 for ESFA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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