Environmental Science & Technology

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Single Collector Attachment Efficiency of Colloid Capture by a Cylindrical Collector in Laminar Overland Flow

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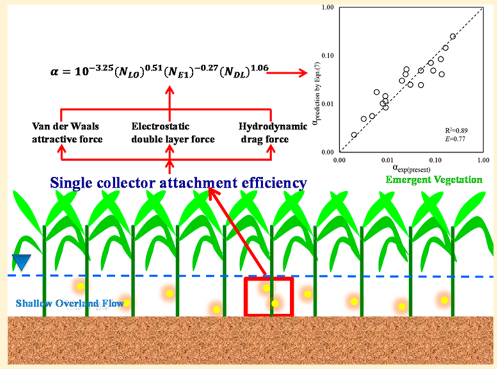
S *Supporting Information*

ABSTRACT: Little research has been conducted to investigate the fate and transport of colloids in shallow overland flow through dense vegetation under unfavorable chemical conditions. In this work, the single collector attachment efficiency (α) of colloid capture by a simulated plant stem (i.e., cylindrical collector) in laminar overland flow was measured directly in laboratory flow chamber experiments. Fluorescent microspheres of two sizes were used as experimental colloids. The colloid suspensions flowed toward a glass cylindrical rod installed in a small size flow channel at different laminar flow rates. Different solution ionic strengths (IS) were used in the experiments to simulate unfavorable attachment conditions. Our results showed that α increased with IS and decreased with flow velocity. Existing theoretical and empirical models of colloid attachment efficiency for porous media were used to simulate the experimental measurements in α and found to fall short in matching the experimental data. A new dimensionless (regression) equation was proposed that predicts the α of colloid capture by a cylindrical collector in laminar overland flow with reasonable accuracy. In addition, the equation was also effective in predicting the attachment efficiency of colloid deposition in porous media.



INTRODUCTION

Colloidal particles in surface runoff may have adverse effects on many environmental and biological processes, e.g., facilitating contaminant transport in flow, impairing water quality, disturbing life cycles of microorganisms, and altering wetland geomorphology.[1−4] It has been suggested that vegetation systems in surface flow can act as a filter or as storage to reduce contaminant loading into natural water bodies.[5−7] Recent studies found that both emergent and submergent plants were effective to remove colloids from water flow.[8,9] However, only limited research has been conducted to explore the governing mechanisms of colloid filtration by plants in overland flow.[10]

Deposition of colloids in overland flow through dense vegetation is comprised of subsurface soil infiltration and surface filtration by vegetation processes. The surface filtration of colloids by emergent plants can be considered to be governed by two sequential interactions between colloids and plants: physically controlled contact process and chemically controlled attachment process.[11−14] The transport of colloidal particles from the bulk suspension a plant stem collector is mainly controlled by the interception and Brownian diffusion mechanisms.[10,11] The single contact efficiency (η_0) theory of colloid filtration by vegetation has been established recently based on the two mechanisms.[10] Under unfavorable chemical conditions (i.e., in the presence of repulsive electric double layer interactions), however, the contact with a collector surface per se does not ensure the capture of colloidal particles by the collector as a result of the repulsive interaction forces between the colloid and collector surfaces.[11,14] Under most circumstances, the surface water environment is chemically unfavorable for the attachment of colloids on plant collectors because not only do most colloids and plants carry overall negative surface charges,[15,16] but also the ionic strength of surface water is typically low (0.0001−0.01M).[1,17] To fully understand the fate and transport of colloids in surface water, it is therefore critical to develop a theory to describe the attachment process of colloids on plant collectors.

On the basis of the framework of the classic filtration theory (CFT),[11] the concept of single collector attachment efficiency (α) was introduced together with the single contact efficiency (η_0) theory to predict the removal of colloids by vegetation in laminar overland flow under unfavorable conditions:[10]

$$\eta = \alpha\eta_0 \tag{1}$$

where η is the single collector removal efficiency of colloid filtration by plants.

Very limited literature exists on the values of α for colloid filtration by surface vegetation; however, a substantial research effort has been made to understand the attachment process of

Received: April 5, 2012
Revised: June 8, 2012
Accepted: July 16, 2012
Published: July 16, 2012

colloids in porous media under unfavorable conditions. According to the original assumptions in the CFT, α should only depend on chemical properties of the system, such as surface charge and solution chemistry, which exert significant effect on the interaction forces between the colloid and collector surfaces.[11,13,14] Derjaguin−Landau−Verwey−Overbeek (DLVO) theory is often used to predict the attachment efficiency of colloids in porous media; however, discrepancies were reported between the theoretical predictions and experimental observations.[18−20] To account for these discrepancies, various assumptions have been made to modify the DLVO-based α theory, including deposition in the secondary minimum energy well,[12,21] collector charge variability,[22] and surface charge heterogeneities.[3,23,24] Researchers have also suggested that the discrepancies may also occur as a result of physical effects that are not included in filtration theory. For example, the effect of hydrodynamic shear stress on α should not be neglected under unfavorable conditions especially when colloids are weakly deposited in the secondary minimum.[25,26] In addition, other physical factors, such as surface roughness,[27,28] pore geometry,[29,30] and stagnation zones,[31,32] were also reported to affect the α of colloids in porous media. Findings from investigations studying these effects could be very useful to the development of single collector attachment efficiency theory for plant filtration of colloids in overland flow.

The overarching goal of this work was to establish the single collector attachment efficiency (α) theory for colloid transport through dense emergent vegetation, such as vegetative filter strips, in laminar overland flow. Under such conditions, the water depth is usually below the top of the sheaths of vegetation and only plant stems are submerged to affect flow and transport processes.[10] Laboratory experiments were conducted to measure the colloid attachment efficiency on a cylindrical collector in laminar overland flow under unfavorable chemical conditions. A glass cylinder was installed in a small size flow chamber to simulate plant stem collector under laminar flow conditions. Rigid cylinders, such as glass or plastic rods and nails have been demonstrated to be effective representations of plant stems in surface runoff under various flow conditions.[10,33,34] Fluorescent microspheres were applied to the flow system as experimental colloids and the amount of colloids deposited onto the collector surface was measured to determine the attachment efficiency under various conditions. Specific objectives were as follows: (1) quantify the effect of ionic strength, colloid size, and flow velocity on the single collector attachment efficiency of colloid capture by the cylindrical collector in laminar overland flow, (2) determine whether existing single collector attachment efficiency models of porous media can be applied directly to vegetation systems, (3) establish a theory to predict the deposition of colloidal particles on vegetation in laminar overland flow conditions.

■ THEORY

The single collector attachment efficiency (α) is defined as the ratio of the rate at which particles successfully attach to the collector divided by the rate at which colloids strike the collector.[11] Under unfavorable chemical conditions, the magnitude of α is assumed to be mainly controlled by the interaction forces between the colloidal particle and the collector.[11] The classic and extended DLVO theories, which describe the attractive (van der Waals) and repulsive (electrostatic double layer) forces between colloid and collector surfaces, are often used to determine the intersurface interactions. Several models have been developed based on the DLVO theory to predict the α of colloid deposition in porous media under unfavorable conditions using either the interaction force boundary layer (IFBL) approximation or the Maxwell approach.[12,14,19]

Models based on the IFBL approximation or its extensions determine the α of colloid deposition in porous media through analytically or numerically solving the convective-diffusion equation with repulsive colloidal interactions. Previous studies, however, found the predictions from the IFBL models had rather poor agreement with measurements due to several factors.[12,14,19] The most important one was that the IFBL models do not consider the contributions of the secondary minimum energy well, which may play an important role in colloid deposition under unfavorable chemical conditions.[12] The Maxwell approach was then developed to determine colloid attachment efficiency through deposition in the secondary minimum.[12] If both primary and secondary energy minimum depositions are considered, then the single-collector attachment efficiency (α) of colloid deposition in porous media can then be expressed as follows:[12,35]

$$\alpha = \alpha_{\text{pri}} + \alpha_{\text{sec}} \tag{2}$$

where α_{pri} and α_{sec} are the fractions of single-collector attachment efficiency of colloid deposition in the primary energy minimum and secondary energy minimum, respectively. In the Maxwell model, the single-collector attachment efficiency is considered to only be influenced by chemical factors, such as solution chemistry and surface properties.[11,12,14,19] Predictions of the Maxwell model were more accurate for column experiments under unfavorable conditions than that of the IFBL models.[12,35] Some deviations from experimental measurements, however, were also observed for the Maxwell model, particularly with respect to deposition of relatively large size particles in porous media.[21,35]

Experimental measurements have shown that α of colloid deposition in porous media may also be affected by hydrodynamic factors (e.g., flow velocity).[25,36−38] The effect of hydrodynamic drag on α was determined through hydrodynamic torques analysis.[26,39] It is reported that the Maxwell model coupled with the hydrodynamic torque approach can provide an improved prediction of α of colloid deposition in porous media under unfavorable conditions.[40] The attachment efficiency can be expressed as follows:[40]

$$\alpha = f_{\text{pri}}\alpha_{\text{pri}} + f_{\text{sec}}\alpha_{\text{sec}} \tag{3}$$

where f_{pri} and f_{sec} are the fractions of single collector surface area over which the adhesive torques acting on the colloids retained in the primary and secondary minimum are greater than the fluid hydrodynamic drags, respectively.

In addition to the theoretical approach, empirical expressions (e.g., Bai-Tien model) have also been developed to predict the α of colloid deposition in porous media in terms of dimensionless parameters.[41−44] Detailed description of the theoretical and empirical models of the α of colloid deposition in porous media can be found in the Supporting Information, SI (S2).

Because of the differences in flow and transport processes between surface vegetation and subsurface porous media systems, however, it is unclear whether the existing theoretical and empirical models of α can be applied to describe the attachment processes of colloids on the plant collector under laminar flow conditions.

■ MATERIALS AND METHODS

Materials. Fluorescent, carboxylated, polystyrene latex microspheres (Magsphere, Inc.) of two sizes (0.1 and 1.05 μm) were used as experimental colloids. As reported by the manufacturer, the density of the colloids is 1.05 g/cm^3 and the surface carboxyl group coverage is 8.28×10^{17} and 1.19×10^{18} /m^2 for 0.1 and 1.05 μm colloids, respectively. Experimental solutions were made by diluting the stock colloid solution (1.05 g/mL, corresponding to 1.0×10^{15} and 8.6×10^{11} no./mL for 0.1 and 1.05 μm colloids, respectively) to the target concentration (10.5 mg/L) with deionized (DI) water.

A circular cylinder glass rod with diameter 0.5 cm was used as the collector to simulate plant stems. The glass rod was cleaned with acetone and then soaked in a 6 M HNO_3 solution for 5 h at 80 °C to remove metal oxides and other impurities on its surface.[19,26,45] For each measurement, a new glass rod without any coating was used to measure the α under various experimental conditions.

Analytical reagent grade KCl (Fisher Scientific) and DI water were used to prepare electrolyte solutions at desired ionic strengths. The pH for all the electrolyte solutions was adjusted to 7 with 1 mM $KHCO_3$ solution The experiments were conducted at five ionic strengths (0.001, 0.005, 0.01, 0.05, and 0.1 M) so that different attachment efficiencies could be measured. While the first three were selected to represent the typically low ionic strengths of overland flow,[1,17] the latter two (i.e., 0.05 and 0.1 M) were used to exam the effect of high ionic strength on attachment efficiency. Because carboxyl group is acidic and has a pK_a value of 5,[43] almost all (>99%) of the function groups on the colloids surface would deprotonate ($-COO^-$) and become negative charged for all the tested experimental conditions. Thus, the corresponding ξ potentials (i.e., electrokinetic potential) of the 0.1 and 1.05 μm colloids were −80.4, −70.3, −60.8, −48.1, −38.0 mV and −68.6, −63.9, −59.2, −41.2, −35.4 mV, respectively, whereas the corresponding ξ potentials of the glass collector were −57.8, −52.1, −50.5, −32.0, −18.8 mV, which were determined with a ZetaPlus (Brookhaven Instrument Co., Holtsville, NY). The ξ potentials of the glass rod were determined with colloidal glass suspensions (obtained from sonicating the glass rod) under various chemical conditions following the method developed by Johnson et al.[46]

Experimental Methods. The experimental apparatus and procedures used in this study were described in detail in our previous work.[10] Briefly, the Plexiglas flow chamber was 20 cm long, 10 cm wide, and 10 cm high. For each run, one clean glass cylinder was installed on the chamber bed as the single collector. A recirculating peristaltic pump (Masterflex L/S, Cole Parmer) was used to provide the desired system flow velocities. Once the colloid suspension was stabilized (i.e., flow rate, water table, colloid distribution), the collector was then positioned into the chamber for durations of 5, 10, 30, 60, or 120 min to determine the colloid capture rate on the collector surface over different time intervals.[10] At the end of each run, the flow was stopped and the collector was pulled out to measure the amount of colloids attached. Pre-experiments showed that colloids attached to the clean collector surface under all experimental conditions could be fully recovered in DI water after 5 min of ultrasonication. A fluorescent spectrophotometer (PerkinElmer LS 45) was used to determine the colloid concentration. Each experiment was repeated at least three times.

Two sets of experiments were conducted in the flow chamber system. The first set of experiments was designed to measure the α under different ionic strength conditions (0.001, 0.005, 0.01, 0.05, and 0.1 M) at an approach flow velocity of 2×10^{-2} cm/s for both 0.1 and 1.05 μm colloids. The second set of experiments was designed to measure the α under different flow velocity conditions (2×10^{-4}, 2×10^{-3}, 2×10^{-2}, 2×10^{-1} and 1 cm/s) at 0.01 and 0.1 M ionic strength with both 0.1 and 1.05 μm colloids (Table 1).

Table 1. Summary of Experimental Conditions and Results

test no.[a]	ionic strength IS (M)	flow velocity u (cm/s)	particle diameter d_p (μm)	attachment efficiency (α) mean ± std
I.1	0.001	0.02	1.05	$8.0 \times 10^{-3} \pm 6.2 \times 10^{-4}$
I.2	0.005	0.02	1.05	$9.1 \times 10^{-3} \pm 8.0 \times 10^{-4}$
I.3	0.010	0.02	1.05	$1.9 \times 10^{-2} \pm 3.6 \times 10^{-3}$
I.4	0.050	0.02	1.05	$8.3 \times 10^{-2} \pm 1.1 \times 10^{-2}$
I.5	0.100	0.02	1.05	$1.2 \times 10^{-1} \pm 1.5 \times 10^{-2}$
I.6	0.001	0.02	0.1	$2.6 \times 10^{-3} \pm 3.5 \times 10^{-4}$
I.7	0.005	0.02	0.1	$4.4 \times 10^{-3} \pm 6.3 \times 10^{-4}$
I.8	0.010	0.02	0.1	$1.5 \times 10^{-2} \pm 2.1 \times 10^{-3}$
I.9	0.050	0.02	0.1	$5.0 \times 10^{-2} \pm 4.3 \times 10^{-3}$
I.10	0.100	0.02	0.1	$1.0 \times 10^{-1} \pm 9.0 \times 10^{-3}$
II.1	0.01	0.0002	1.05	$2.5 \times 10^{-2} \pm 2.2 \times 10^{-3}$
II.2	0.01	0.002	1.05	$2.0 \times 10^{-2} \pm 1.9 \times 10^{-3}$
II.3	0.01	0.2	1.05	$9.0 \times 10^{-3} \pm 8.1 \times 10^{-4}$
II.4	0.01	1	1.05	$6.4 \times 10^{-3} \pm 7.0 \times 10^{-4}$
II.5	0.1	0.0002	1.05	$2.2 \times 10^{-1} \pm 2.3 \times 10^{-2}$
II.6	0.1	0.002	1.05	$1.5 \times 10^{-1} \pm 2.1 \times 10^{-2}$
II.7	0.1	0.2	1.05	$5.0 \times 10^{-2} \pm 6.3 \times 10^{-3}$
II.8	0.1	1	1.05	$3.4 \times 10^{-2} \pm 4.1 \times 10^{-3}$
II.9	0.01	0.0002	0.1	$2.3 \times 10^{-2} \pm 2.9 \times 10^{-3}$
II.10	0.01	0.002	0.1	$1.5 \times 10^{-2} \pm 2.0 \times 10^{-3}$
II.11	0.01	0.2	0.1	$2.0 \times 10^{-3} \pm 3.6 \times 10^{-4}$
II.12	0.01	1	0.1	$8.9 \times 10^{-4} \pm 1.1 \times 10^{-4}$
II.13	0.1	0.0002	0.1	$1.3 \times 10^{-1} \pm 2.1 \times 10^{-2}$
II.14	0.1	0.002	0.1	$8.9 \times 10^{-2} \pm 8.0 \times 10^{-3}$
II.15	0.1	0.2	0.1	$8.1 \times 10^{-3} \pm 1.1 \times 10^{-3}$
II.16	0.1	1	0.1	$6.0 \times 10^{-3} \pm 7.3 \times 10^{-4}$

[a]Nos. I.1–I.10 summarize the effect of ionic strength; Nos. II.1–II.16 summarize the coupled effect of flow velocity and ionic strength.

The colloid capture rate (r_c') by the single collector was determined by measuring the increases in number of colloids on the collector over different time intervals.

$$r_c' = \frac{\Delta N'}{\Delta t} \tag{4}$$

where $\Delta N'$ (no.) is the increment in number of colloids on the clean collector surface over a time interval Δt (s).Thus, the single collector removal efficiency (η) of colloids by a cylindrical collector in laminar flow can be written as follows:

$$\eta = \frac{r_c'}{N_0 u d_c l_c} \tag{5}$$

where N_0 (no./m^3) is the number concentration of colloids in the suspension, u (m/s) is the flow approach velocity, d_c (m) is the diameter of collector, and l_c (m) is the height of test area of collector. The values of the single-collector contact efficiency

dx.doi.org/10.1021/es301365f | Environ. Sci. Technol. 2012, 46, 8878–8886

(η_0) of the microspheres captured by the cylinder in the same flow chamber system had been determined previously,[10] therefore, the single-collector attachment efficiency (α) of each experiment in this work was calculated using eq 1.

RESULTS AND DISCUSSION

Effect of Ionic Strength. Measurements from the flow chamber experiments showed that the single collector attachment efficiencies (α) varied by several orders of magnitude depending on experimental conditions (Table 1). When the flow ionic strength increased, α increased for both 0.1 and 1.05 μm colloids (Figure 1), which matched the trend from the DLVO calculations. The DLVO energy profiles between the colloids and the collector surface (Figure 2) confirmed the experimental conditions were unfavorable for attachment. When the ionic strength increased from 0.001 to 0.1M, the depth of the secondary minimum energy well (Φ_{sec}) increased from 0.03 to 0.41 kT and from 0.72 to 12.8 kT for 0.1 and 1.05 μm colloids, respectively (Table 2). At the same time, however, the height of the energy barrier (Φ_{max}) decreased from 162.1 to 49.1 kT and from 1145.3 to 412.8 kT for particle diameters 0.1 and 1.05 μm, respectively. Calculations from the Maxwell theory[12,35] showed that the α_{pri} was close to zero because the Φ_{max} was too high for all of the tested experimental conditions, suggesting that deposition of colloids in the primary minimum energy well was insignificant. Instead, most of the colloid attachment was in the secondary minimum and α_{sec} was notable when Φ_{sec} was larger than 0.5 kT. For any given ionic strength, the 1.05 μm colloids had a larger α than the 0.1 μm ones, which is also consistent with both the DLVO and the Maxwell theory predictions that increase in colloid diameter would also increase the Φ_{sec} and thus enhance the deposition in the secondary minimum.

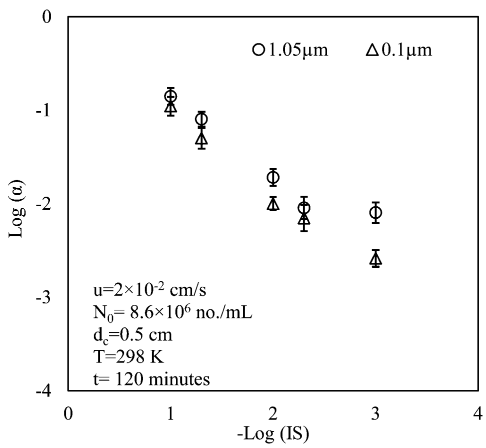


Figure 1. Experimental attachment efficiency (α) as a function of ionic strength (IS) for colloid capture by the cylinder in the flow chamber at flow velocity of 2×10^{-2} cm/s.

Although no previous investigations examined the effect of perturbations in solution chemistry or variations in particle size on the attachment processes of colloids on vegetation surfaces in overland flow, similar research has been well documented in the literatures of colloid deposition in porous media.[19,45,47−51] A number of studies of colloid transport in porous media have demonstrated that a rise in ionic strength can increase the attachment of colloids on grain surfaces by reducing the thickness of the diffuse double layer between colloid and collector surfaces and thus reducing the repulsive forces,[51,52] which is consistent with the observations in this study. Several recent studies have also shown that colloid sizes can significantly affect colloid deposition in porous media.[45,47,50] In a column transport study with different sizes latex microspheres, Hahn et al. [20] observed that larger colloids had larger α than the smaller ones and emphasized the dominance of secondary minimum deposition on colloid retention in porous media.

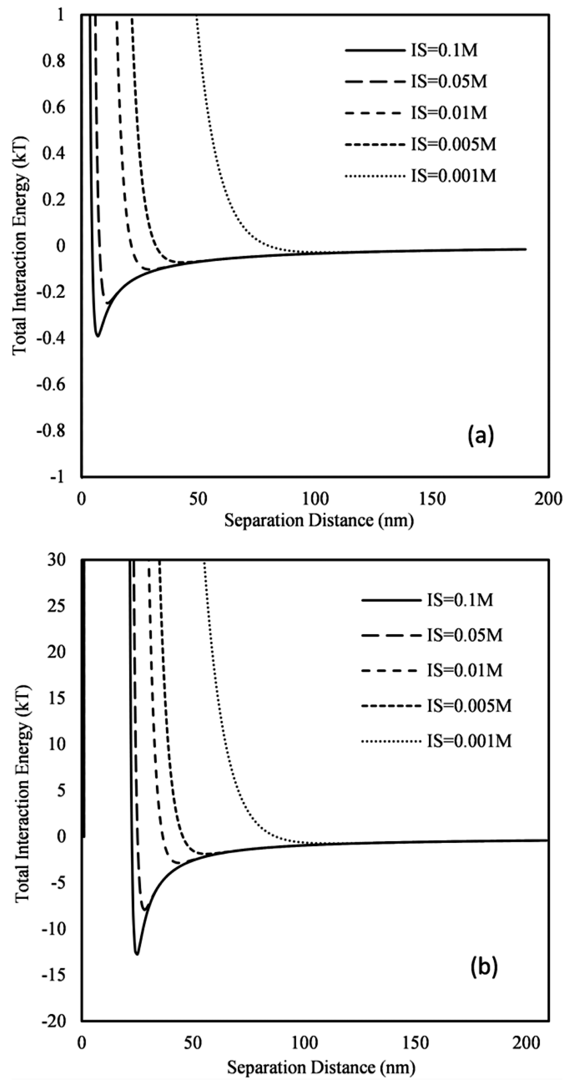


Figure 2. DLVO interaction energy between the collector and the colloids: (a) 0.1 μm colloids and (b) 1.05 μm colloids.

In this work, observations from the ionic strength experiments indicated that the secondary minima may play a dominant role in colloid deposition on the cylindrical collector under all of the tested experimental conditions. Hence, the Maxwell theory[12,35] could be used to determine the α of colloid deposition on stem collectors if the attachment processes were only controlled by chemical factors.

Effects of Flow Velocity. Flow velocity also had a strong effect on the α of the 0.1 and 1.05 μm colloids in the flow chamber at ionic strengths of 0.01 or 0.1 M (Figure 3), which suggested physical factors such as hydrodynamics also play an important role in controlling attachment efficiency of colloid deposition on cylindrical collectors in overland flow. Increases in flow velocity reduced the attachment of colloids on the

Table 2. Calculated Maximum Energy Barriers (Φ_{max}) and Primary (Φ_{pri}) and Secondary Minimum (Φ_{sec}) under Different Experimental Conditions

ionic strength	Φ_{max} (kT)[a]		Φ_{pri} depth (kT)		Φ_{pri} distance (nm)		Φ_{sec} depth (kT)		Φ_{sec} distance (nm)	
I (M)	0.1 μm	1.05 μm	0.1 μm	1.05 μm	0.1 μm	1.05 μm	0.1 μm	1.05 μm	0.1 μm	1.05 μm
0.001	162.1	1145.3	NA[b]	NA	NA	NA	0.03	0.72	103	93
0.005	148.9	1077.4	NA	NA	NA	NA	0.07	1.86	43	36
0.01	143.4	1065.5	NA	NA	NA	NA	0.11	2.83	30	25
0.05	85.8	708.8	NA	NA	NA	NA	0.25	7.9	11	9
0.1	49.1	412.8	NA	NA	NA	NA	0.41	12.8	7	6

[a]kT: k is the Boltzmann's constant (1.381×10^{-23} C^2 J K^{-1}), T is the absolute temperature, [b]NA: Not applicable, no primary minimum existing in the DLVO interaction energy profiles.

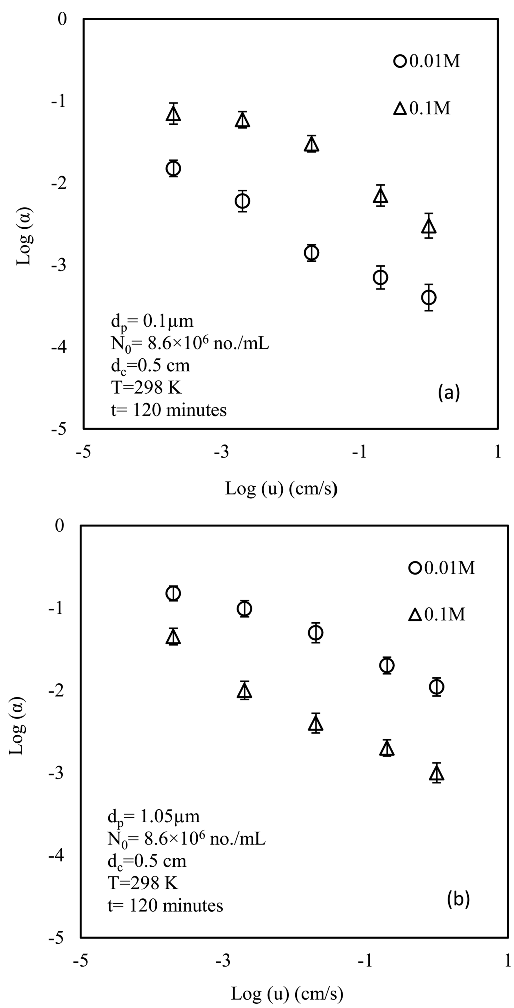


Figure 3. Experimental attachment efficiency (α) as a function of flow velocity (u) for colloids captured by the cylinder in the flow chamber: (a) 0.1 μm colloids and (b) 1.05 μm colloids.

cylinder probably due to the hydrodynamic shear forces.[26] Similar phenomena were observed in studies of colloid filtration and transport in emergent vegetation in wetland systems. In a field flume in the Everglades (FL), Harvey et al.[2] observed that particle attachment to vegetation stems decreased when flow velocity increased from 0.3 cm/s up to 6 cm/s. Similarly, Huang et al.[9] found that high flow velocity in their field flume in the Everglades significantly reduced the removal of colloids by the emergent vegetation. These findings are consistent with current experimental observations; however, none of the previous studies have quantitatively examined the effect of hydrodynamic shear forces on the attachment efficiency of colloid capture by vegetation surfaces.

Previous studies of colloid transport in porous media have emphasized the hydrodynamic effect on colloid deposition and demonstrated that the α decreased with increasing flow velocity under unfavorable chemical conditions.[26,39,53] In a laboratory column experiment, Tong and Johnson [53] found a decrease of attachment efficiency when flow velocity increased from 2.3×10^{-5} to 9.2×10^{-5} m/s for colloids of 0.1−2.0 μm. They attributed the changes in the α to the hydrodynamic drag force, which could shear the colloids off the porous medium surfaces. It is suggested that hydrodynamic drag may indirectly prevent colloid deposition into the primary minimum by reducing the possibility for the "attached" colloids within the secondary minimum to cross the energy barrier.[54] Under certain conditions, the hydrodynamic drag may also reduce the retention of colloidal particles in the secondary minimum via following mechanisms: (1) reduce colloid retention capacity due to reduction of stagnant flow zone volumes,[26] (2) enhance hydrodynamic collisions between mobile and surface associated colloids,[26] and (3) promote diffusion "out" of the secondary minimum driven by increased colloid concentration gradients away from zones of accumulation (i.e., rear stagnation points).[12]

Both current experimental results and findings from colloid transport studies in porous media suggest that the original assumption of chemical governing attachment processes in the CFT may need to be revisited. Physical factors such as flow velocity may play an important role in controlling the α of colloid deposition in both vegetation and porous media systems. In the literature, a hydrodynamic torque approach was introduced to improve the Maxwell theory to predict the α of colloid deposition in porous media.[40] Surface vegetation, however, may have very different flow dynamics as compared with porous media. It is anticipated that the modified Maxwell theory may not be applicable to estimate the attachment efficiency of colloid capture by cylindrical collectors even under laminar flow conditions.

Comparison of Experimental Data and Theoretical Predictions. The Maxwell model,[12] the modified Maxwell model (i.e., coupled by hydrodynamic torques),[40] and the empirical Bai-Tien model [42] were used to estimate the α of colloid capture by the cylindrical collector under all experimental conditions (Figure 4). Detailed information about the three models used in the study can be found in the Supporting Information (S2).

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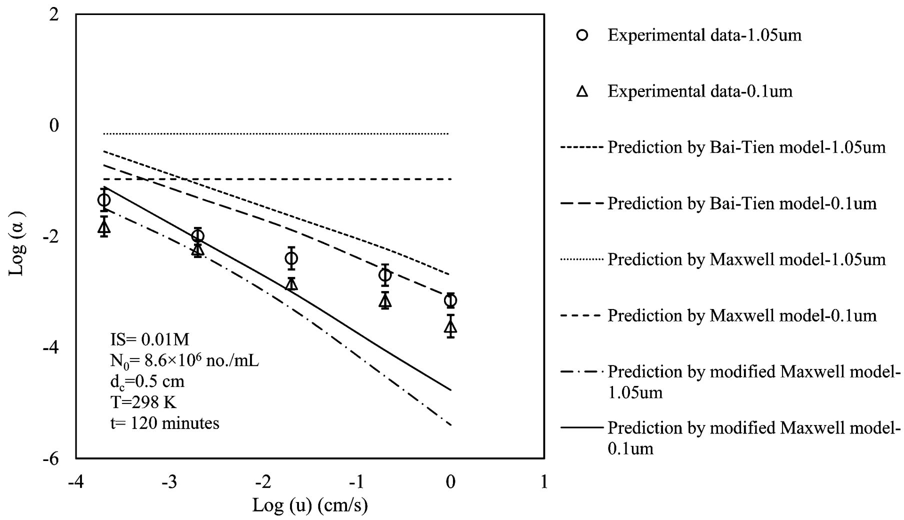

Figure 4. Comparison of experimental attachment efficiency (α) with predictions of the Maxwell, modified Maxwell, and Bai-Tien models for colloids captured by the cylinder in the flow chamber at ionic strength of 0.01 M.

Although it was reported that the Maxwell model works well for describing attachment processes of colloids (particularly small size colloids) in porous media,[12,55] it failed to match the experimental data obtained from the flow chamber (Figure 4). The model overestimated the α of colloid deposition on the cylinder up to 1−2 orders of magnitude for almost all experimental measurements. This result further confirmed that physical factors, such as hydrodynamics, should be considered in the theory of colloid attachment efficiency. The modified Maxwell model, which considers the hydrodynamic factor, did show a better agreement with the experimental measurements than the original Maxwell model (Figure 4). However, significant differences between model and experimental results were still observed, especially when flow velocity became high (e.g., 0.2 and 1 cm/s), suggesting that, even after the consideration of hydrodynamic effect, the modified Maxwell model cannot be applied directly to describe the α of colloid deposition on vegetation in laminar overland flow. Similarly, the Bai-Tien model [42] overestimated up to 1 order of magnitude to the corresponding experimental results.

In general, the experimental attachment efficiencies of colloid capture by the cylinder in laminar overland flow were much smaller than the predictions of the porous media models, which could be mainly attributed to the different flow dynamics in surface vegetation and porous media. Other possible causes of the discrepancy between the experimental data and theoretical predictions (i.e., Maxwell approaches) might include (1) the Maxwell models (original and modified) use the deepest point of the secondary minimum well to determine the α, but colloid may be initially attached in other positions with the secondary minimum; and (2) non-DLVO forces, such as short-range hydration and hydrophobic forces are not included in the Maxwell models.[12,56] Although progress has been made, current understanding of the governing factors of colloid attachment process in porous media is still quite limited.

Because the surface properties and geometry of the stem collector, as well as flow dynamics in vegetation systems could be much more complicated than that in porous media, it may not be feasible to establish a theoretical model to describe the α of colloid capture by the cylinder under laminar flow conditions at this point. However, the direct experimental measurements obtained in this work provide an opportunity to develop an empirical model to predict the attachment efficiency of colloid filtration by plants in overland flow.

Dimensionless Equation. On the basis of the Buckingham- π theorem, the α of colloid deposition on the cylinder could be a function of 8 dimensionless parameters[41,42] (defined in Supporting Information, Table S1). The experimental data were divided into a calibration/development subset with 58 data points randomly selected from the original 78 point data set (Table 1) while ensuring a good distribution that covers the experimental conditions, and a verification subset consisting of the remaining 20 data points. The stepwise least-squares method was used in this study to fit the development data subset. The coefficients of determination (R^2) and Nash-Sutcliffe efficiency (E) were used as quantitative descriptors of the predictive accuracy of the new correlation equation. The Nash-Sutcliffe efficiency coefficient is defined as follows:

$$E = 1 - \frac{\sum_{i=1}^{m} (\alpha_{\exp i} - \alpha_{\text{pre}i})^2}{\sum_{i=1}^{m} (\alpha_{\exp i} - \overline{\alpha_{\exp}})^2} \quad (6)$$

where m is the number of observations, $\alpha_{\exp}$, α_{pre}, and, $\overline{\overline{\alpha_{\exp}}}$ are the experimentally observed, model predicted, and mean single collector attachment efficiency, respectively. The R^2 value reflects strength of the linear relationship between observed and simulated data and the E value indicates how well observed and simulated data fit the 1:1 line. Predictions of the new correlation equation are near perfect when both R^2 and E are close to one.

The analysis of the development data subset showed that only three dimensionless parameters (defined in Table 3) were strongly correlated with the α (p-value smaller than 0.05). The results of stepwise regression are presented in the Supporting Information (Table S2). A dimensionless/regression equation (Supporting Information, Figure S1, $R^2 = 0.92$ and $E = 0.85$) can be written as follows:

$$\alpha = 10^{-3.25}(N_{\text{LO}})^{0.51}(N_{\text{E1}})^{-0.27}(N_{\text{DL}})^{1.06} \quad (7)$$

It is worth noting that although α is less sensitive to the electrokinetic parameter (N_{E1}) than to other two dimensionless parameters, the N_{E1} term is a key component of the equation to reflect the effect of surface potential (Supporting Information, Table S2).

Table 3. Summary of Dimensionless Parameters Governing Attachment Efficiency

parameter	definition	
N_{LO}	$\frac{4A}{9\pi\mu d_p^2 u}$	London number
N_{E1}	$\frac{\varepsilon\varepsilon_0(\xi_p^2+\xi_c^2)}{3\pi\mu u d_p}$	first electrokinetic parameter
N_{DL}	kd_p	double-layer force parameter

[a] A is the Hamaker constant, μ is the fluid viscosity, d_p is the colloidal particle diameter, u is the flow velocity, ε is the relative permittivity of the fluid (78.4 for water), ε_0 is the permittivity in a vacuum (8.854×10^{-12} C^2 N^{1-} m^{-2}), ξ_p and ξ_c are the surface potential of the colloidal particles and collectors respectively, k is the reciprocal of double layer thickness.

To further validate the new correlation equation of the α, it was tested against the rest of the 20 experimental data (Figure 5a, R^2 = 0.89 and E = 0.77), which indicate that the new correlation equation is effective in fitting the experimental observations of colloid attachment efficiency on the cylinder with reasonable accuracy. Unfortunately, it was not possible to further validate the correlation equation for field conditions because only a few studies have been conducted to measure the removal of colloidal particles by plant stems in laminar overland flow. Hence, additional investigations, particularly experimental studies, are needed to measure the removal of colloids by plant stems in laminar overland flow.

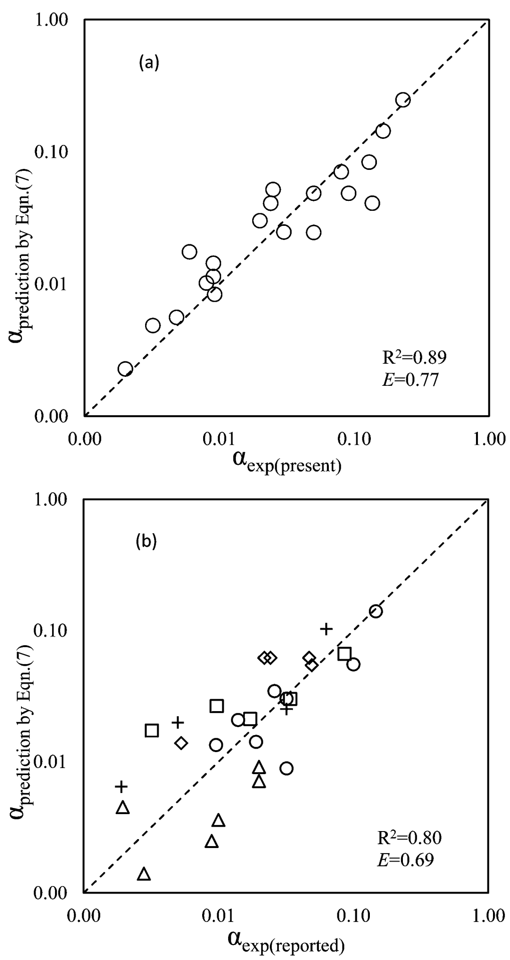

Figure 5. Comparison of experimental attachment efficiency (α) with predictions of the new correlation equation: (a) experimental data (verification subset, n = 20) from present study, (b) experimental data of colloid deposition in porous media: (Δ) Elimelech et al.,[13] (○) Tufenkji et al.,[18] (+) Shen et al.,[21] (□) Tong et al.,[53] (◊) Bradford et al.[30,57] Symbols are experimental data and dash lines are the 1:1 lines.

Although its generality still needs to be tested, the dimensionless equation can be used to determine the attachment efficiency of colloid capture by a single vegetation stem in laminar overland flow with stem-diameter-based Reynolds number ($Re_c = ud_c/\nu$) smaller than 50. If stems in a vegetation system have similar physicochemical properties, this equation, when coupled with spacing and geometry factors, can be applied to describe the attachment efficiency of colloid capture by stems in the vegetation system.[10,11]

Because most of the flow in porous media is the creeping flow with Reynolds number smaller than 1,[51] the regression equation could also be applicable to describe the attachment processes of colloid deposition in porous media when the hydrodynamic effect is negligible (i.e., α is dominated by chemical factors). To test this hypothesis, simulations of the new correlation equation were tested against measurements of α obtained from well-controlled column experiments of colloid transport in porous media under unfavorable conditions[13,18,40,53,57] (Figure 5b). The results showed that the new correlation equation indeed can be used to predict the α of colloid deposition in porous media with an R^2 value of 0.80 and E value of 0.69.

■ ENVIRONMENTAL IMPLICATIONS

Only a very limited number of studies have been made to examine colloid transport in surface runoff, particularly with respect to develop theories or models to predict the filtration processes of colloid capture by vegetation collectors in overland flow. For the first time, laboratory experiments were conducted to directly measure attachment efficiency of colloid capture by a cylindrical collector in surface runoff under laminar flow conditions. Our results showed that both solution chemistry and hydrodynamic shear played important roles in colloid attachment processes. Because existing attachment efficiency models overestimated the α of colloid attachment onto cylinders in laminar overland flow, a dimensionless equation was thus derived from experimental data and was found to predict the colloid attachment onto cylinders in surface water flow with reasonable accuracy. In addition, this new equation may also be used to predict colloid attachment efficiency in porous media if the attachment processes were mainly controlled by chemical factors.

This attachment efficiency equation, when combined with the contact efficiency equation reported previously,[10,58,59] can be used to determine kinetic deposition rate (k_d) of colloidal particles in both vegetation and porous media systems. On the basis of this work, for the case of colloid filtration and transport in a vegetation system on a real field under laminar flow conditions, the kinetic deposition rate at the field scale can be written as follows:

$$k_d = 4 \times 10^{-5.6} \frac{(1-f)}{\pi d_c} \frac{u}{f} \mathrm{Re_c}^{-0.94} N_{Pe}^{-0.03} N_{LO}^{0.51} N_{E1}^{-0.27} N_{DL}^{1.1} \quad (8)$$

dx.doi.org/10.1021/es301365f | Environ. Sci. Technol. 2012, 46, 8878−8886

where f is the ratio of the empty area among the plant stems divided by the total vegetated area, d_c is diameter of the vegetation stem, u is the approaching velocity, Re_c and N_{pe} are Reynolds number ($Re_c = ud_c/v$) and Peclet number ($N_{pe} = ud_c/D$), respectively. Because eq 8 is completely untested, additional experiments would need to be designed to test the suitability of this equation to monitor and predict the fate and transport of colloids in vegetation in laminar surface flow, and perhaps inform the design of engineered/natural surface runoff filtration systems, such as vegetative filter strips and constructed wetlands, to remove colloidal contaminants from surface runoff.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

DLVO interaction energy profiles; definitions of dimensionless parameters; summary of stepwise-least square regression results; and attachment efficiency predictions (two tables and a figure). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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