

## COLLOID RELEASE AND TRANSPORT IN AGRICULTURAL SOIL AS IMPACTED BY SOLUTION CHEMISTRY

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**Abstract:**

Colloid release from the agricultural soil under unsaturated conditions was controlled by the hydrodynamic force, capillary force and electrostatic force that were determined by the solution chemistry in terms of solution ionic strength and pH. In this research, colloid release from the agricultural soil was investigated using an intact soil column collected from an agricultural site in Gadsden County of Florida. Colloid release was monitored and the colloid release curve was simulated using an implicit, finite-difference scheme to obtain the colloid release coefficient. It was found that the hydrodynamic force and electrostatic force overcame the capillary force under the experimental conditions of this research and consequently, colloids were released. For the colloid release, solution chemistry played a key role by controlling the colloid repulsive electrostatic force within the pore system. Colloid release exponentially decreased with the increase of solution ionic strength and increased with the increase of solution pH. Colloid release was finally found to be correlated to the colloid repulsive electrostatic force within the pore system, i.e., the greater the repulsive electrostatic force, the more colloids released.

**Keywords:** Colloid release; electrostatic forces; ionic strength; ph

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## INTRODUCTION

Naturally occurring colloidal particles are involved in many important processes in the subsurface zone (Grolimund & Borkovec, 2006; Kanti Sen & Khilar, 2006). Due to the importance of these processes in the subsurface environment, the transport of colloidal particles has been studied in several disciplines, including soil sciences, petrology, and hydrology, etc. Specifically, in environmental engineering, colloid release and transport in porous media has been extensively investigated, which is motivated by environmental concerns such as colloid-facilitated contaminant transport in groundwater and the subsurface soil (Karathanasis & Johnson, 2006; Kjaergaard *et al.*, 2004; Ryan & Elimelech, 1996). Colloid release is resulted from physical alteration of subsurface porous media. Despite the potential importance of colloid mobilization, experimental investigations of colloid release in natural porous media are scarce, and the detailed mechanisms of release and transport of colloids within natural porous media are poorly understood (Laegdsmand *et al.*, 1999; Torkzaban *et al.*, 2010). Pore media structure, properties and flow dynamics, etc. are factors that affect colloid generation, mobilization, and subsequent transport (Liu *et al.*, 2010). A thorough understanding of colloid release and transport, especially of colloid release mechanisms is required to assess the potential colloid-facilitated contaminant transport (Shani *et al.*, 2008).

Possible mechanisms of colloid generation in the subsurface soil include precipitation, erosion and mobilization by changes in pH and ionic strength and colloid release depends on a balance of applied hydrodynamic and resisting adhesive torques and forces. The coupled role of solution chemistry and fluid hydrodynamics thus play key roles in controlling colloid release and transport. Previous studies have shown that colloid release is more sensitive to changes in solution chemistry at low infiltration rates (Ryan & Gschwend, 1994; Torkzaban *et al.*, 2010). Colloid release in saturated porous media with pre-deposited colloids under steady flow conditions has been investigated and the results indicated that mobilization of deposited colloids is negligible when flow rate and solution chemistry were not altered, but did occur when a change in solution chemistry such as solution ionic strength and pH was made to the system (Torkzaban *et al.*, 2010). Changes in solution chemistry lead to variations in electrostatic forces between colloids and the porous media by influencing the electric double layer. After release, colloid transport is believed to be controlled by its interactions with the surrounding environment (Bradford *et al.*, 2002; Shani *et al.*, 2008).

Impact of solution chemistry on colloid release was investigated in this research using an intact soil column collected from an agricultural site in Gadsden County, Florida under constant and low flow rate conditions. The column was irrigated with solutions of varying ionic strength and pH. Colloid release was monitored and the colloid release curve was simulated using an implicit, finite-difference scheme to obtain the colloid release coefficient.

## MATERIALS AND METHOD

### Column Experiments

*In situ* colloid release and mobilization was evaluated in intact soil columns collected from an agricultural site in Gadsden County of Florida. The columns (10.0-cm ID × 60.0-cm length) were vertically oriented. For each run of the column experiments, nano-pure de-ionized water was applied using a sprinkler from the top by a peristaltic pump (Masterflex, Cole-Parmer, Vernon Hills, IL) at an irrigation rate of 0.05 cm/min. To study the impact of ionic strength on *in situ* colloid release, the sterilized nano-pure de-ionized water was adjusted with 1 M NaCl to reach a final ionic strength of 0.03 M, 0.05 M and 0.07 M. This ionic strength range was selected to mimic the possible ionic strength scenarios of subsurface transport. To study the impact of pH on *in situ* colloid release, pH of the sterilized nano-pure de-ionized water was adjusted with 1M HCl or 1 M NaOH to pH of 4, 5.5, 8.5 and 10. This pH range covers the typical pH range of natural subsurface environment. For each column experiment, the flow was kept steady state, i.e., with inflow equal outflow rate for an extensive period of time until colloid outflow concentrations stabilized. For each of the experiment, a new sediment column was used.

During the experiments, matric potential inside the columns was monitored and recorded using a Campbell Scientific CR-7X datalogger (Campbell Scientific, Inc.). Using the matric potential information, water content within the columns was quantified by fitting the van Genuchten equation (Toride, 1995):

$$S_e = [1 + (\alpha h)^n]^{(1/n-1)} \quad (1)$$

where  $S_e$  is the effective saturation (-);  $\alpha$  is the inverse of the air-entry potential ( $\text{cm}^{-1}$ );  $h$  is the matric potential ( $\text{cm-H}_2\text{O}$ ); and  $n$  is the parameter related to pore size distribution (-). Using pressure-plate measurements,  $\alpha$  and  $n$  were determined to be  $0.025 \text{ cm}^{-1}$  and 0.177 and  $\theta_s$  and  $\theta_r$  were found to be 0.389 and 0.058 respectively.  $S_e$  is related to water volumetric content as follows (Toride, 1995),

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad (2)$$

where  $\theta$  is the volumetric water content ( $\text{cm}^3/\text{cm}^3$ );  $\theta_r$  is the residual water content ( $\text{cm}^3/\text{cm}^3$ ); and  $\theta_s$  is the saturated water content ( $\text{cm}^3/\text{cm}^3$ ).

The elution was collected by a fraction collector and the colloid concentration was measured using a spectrophotometer against a calibration curve generated using the *in situ* colloid as a reference. Colloid release is controlled by a kinetic desorption (Bradford *et al.*, 2003; Bradford *et al.*, 2002; Chen & Flury, 2005; Lenhart & Saiers, 2002):

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} = \frac{\partial}{\partial z} [D_z \frac{\partial C}{\partial z}] - \frac{J_w}{\theta} \frac{\partial C}{\partial z} \quad (3)$$

$$\frac{\partial S}{\partial t} = -\beta S \quad (4)$$

where  $C$  is the colloid concentration in the liquid phase ( $\text{g}/\text{m}^3$ );  $S$  is the colloid concentration on the sediments ( $\text{mg}/\text{g}$ );  $t$  is time (min);  $D_z$  is the apparent dispersion coefficient ( $\text{m}^2/\text{s}$ );  $\rho$  is the bulk density ( $\text{g}/\text{m}^3$ ),  $J_w$  is the specific flow rate, i.e., Darcian fluid flux;  $z$  is the coordinate parallel to the flow (cm); and  $\beta$  is the first-order colloid release coefficient ( $\text{min}^{-1}$ ).

For colloid release, a constant flux was used for the upper boundary, i.e.,  $J_w C(0, t) = 0$ , and a zero gradient was assumed for the lower boundary, i.e.,  $\theta D_z \partial C / \partial z = 0$ . The initial conditions for colloid release were  $C(x, 0) = 0$  and  $S(x, 0) = S_0$ . For matric potential,  $J_w$  was used for the upper boundary and a constant potential of  $-10 \text{ cm-H}_2\text{O}$  was set for all times as the bottom boundary condition. The initial condition for each series was set to the measured potentials at the beginning of each experiment ( $-45 \text{ cm-H}_2\text{O}$ ). For colloid release simulations, the initial colloid source  $S_0$  for each breakthrough curve was obtained by integrating the experimental breakthrough curves to obtain the total amount of colloids eluted. The governing Eqs 1–4 were solved simultaneously with the Hydrus-1D code (Simunek *et al.*, 1998). The colloid release and transport data were fitted by adjusting the dispersion coefficient  $D_z$  and the colloid release coefficient  $\beta$ .

**ζ-potential Measurements**

To calculate electrostatic force, ζ-potential of the colloid particles was measured. Eluted colloid particle size was first measured for particle size distribution using a Malven Zetasizer 3000 Hsa (Malvern Instrument Ltd., Malvern, Worcs, UK), which was in the range of 200 nm to 650 nm. ζ-potential of the

colloids was quantified from their electrophoretic mobility in the elution corresponding to ionic strength of 0 M, 0.03 M, 0.05 M and 0.07 M as well as pH of 4, 5.5, 8.5 and 10 by dynamic light scattering (Zetasizer 3000HAS, Malvern Instruments Ltd., Malvern, UK). Each measurement was repeated five times and average results were reported.

**RESULTS AND DISCUSSION**

**Colloid Release and Mobilization**

The infiltration event was followed by a steady state flow phase, where matric potential remained constant for the sensors along the length of the column (Fig. 1). According to the van Genuchten equation, the effective water content along the length of the column was 54%, 70% and 76%, respectively from the top to the bottom. This data demonstrated that water content was not uniform in the column. Corresponding to the infiltration, colloids were observed to be released and mobilized.

The *in situ* colloid release and mobilization curves were characterized by a self-sharpening front, which became broader and diffuser at the elution limb (Fig. 2). The long-lasting tails of the curves indicated kinetic-controlled colloid release from the porous media in the columns. The colloid release coincided with the arrival of the infiltration front at the bottom of the columns.

With the increase of ionic strength, fewer colloids were released and mobilized as manifested by the smaller peak concentrations of the colloid release and mobilization curves (Fig. 2). With the increase of pH, more colloids were released (Fig. 3). By integrating the colloid release and mobilization curves, the accumulative amount of colloid release for each irrigation event was calculated. Accordingly, the accumulative amount of colloid release decreased with the increase of ionic strength (Fig. 4) and increased with the increase of pH (Fig. 5).

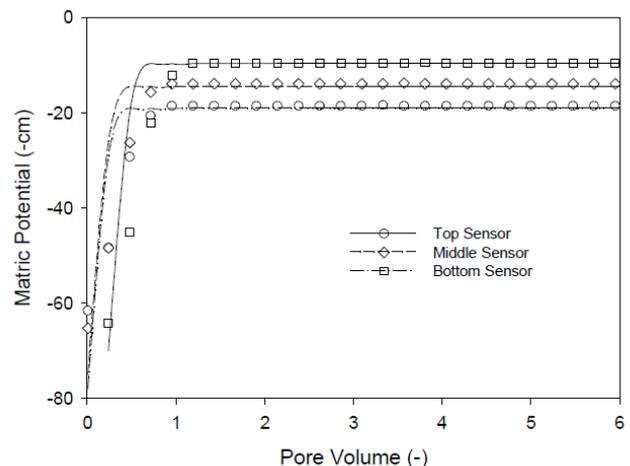
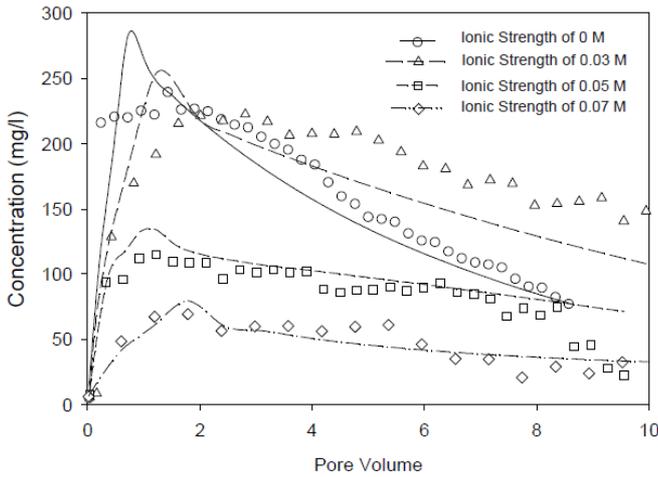
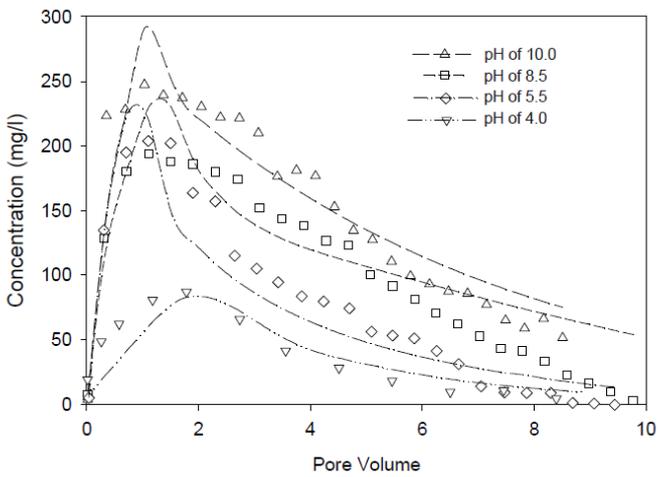


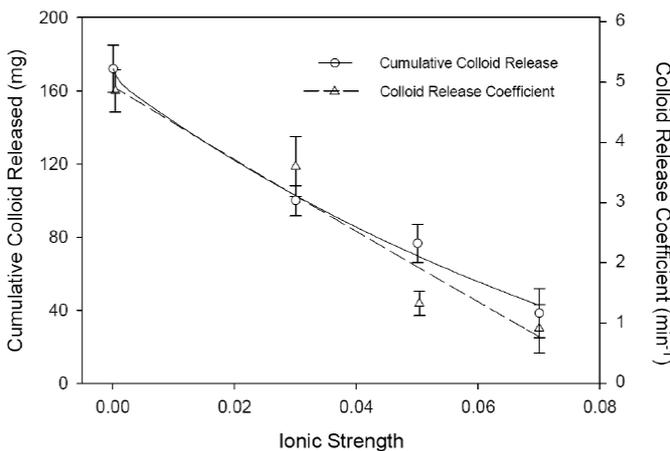
Fig. 1 System matric potential.



**Fig. 2** Colloid release curves under different ionic strength conditions.



**Fig. 3** Colloid release curve under different pH conditions.



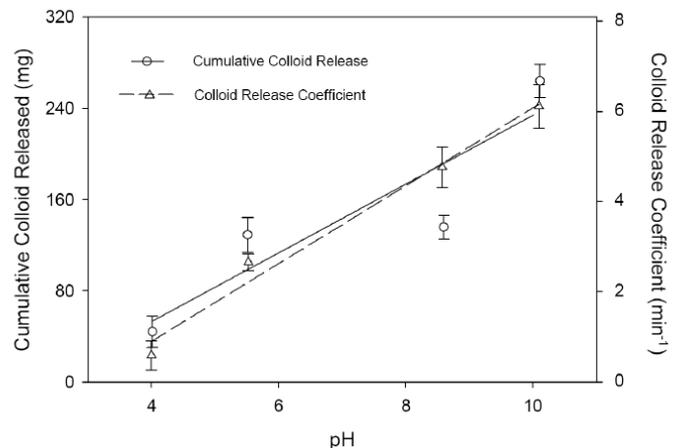
**Fig. 4** Cumulative colloid released and colloid release coefficient as a function of ionic strength.

Colloid release and mobilization curves were simulated against Eq. (3) and Eq. (4) against Hydrus-1D. Hydrus-1D is an implicit, finite-difference scheme, which optimizes colloid release coefficient by minimizing the sum of squared differences between

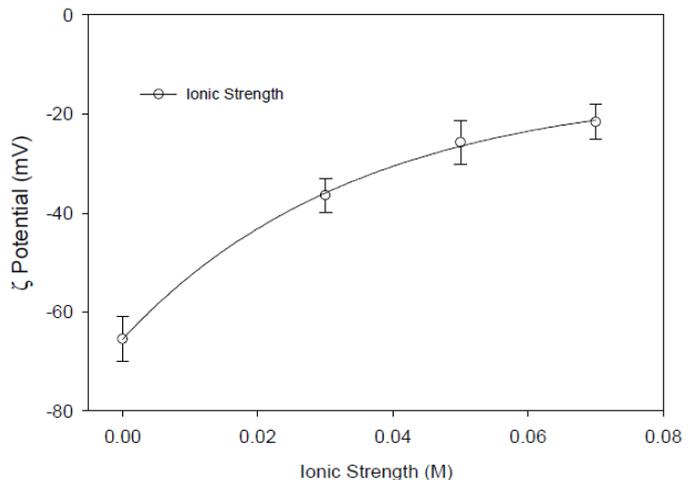
observed and fitted data using the nonlinear least-squares method (Toride, 1995). The simulation process was based on the assumption that colloid release occurred simultaneously and kinetically. Within the range of ionic strength and pH conditions of this research, colloid release coefficient had a similar trend with those of accumulative colloid release with the increase of ionic strength and pH (Figs 4–5).

**Colloid  $\zeta$  potential Values at Different Ionic Strength and pH Conditions Release and Mobilization**

The colloids had negative  $\zeta$  potential values when eluted by nano-pure de-ionized water. With the increase of ionic strength,  $\zeta$  potential exponentially increased (Figure 6). The increase of  $\zeta$  potential with the increase of ionic strength became moderate when ionic strength reached 0.05 M. The increase of  $\zeta$  potential with the increase of solution ionic strength was attributed to the fact that the Stern layer got closer to the surface owing to the compression of the double layer. Within the pH range of this research,  $\zeta$  potential linearly decreased with the increase of pH (Fig. 7).



**Fig. 5** Cumulative colloid released and colloid release coefficient as a function of pH.



**Fig. 6**  $\zeta$  potential as a function of ionic strength.

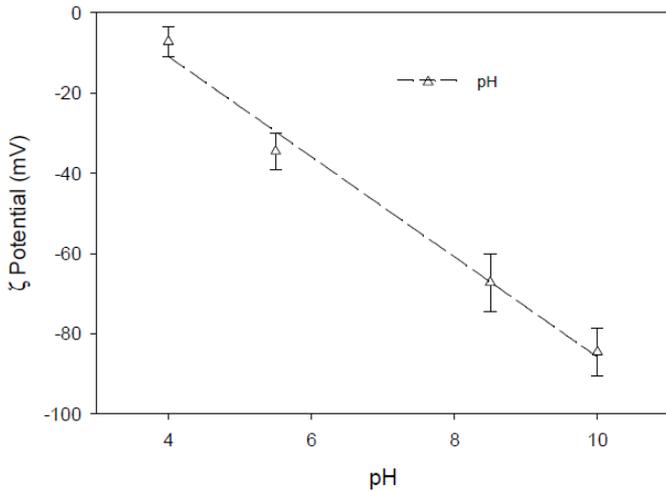


Fig. 7 ζ Potential as a Function of pH.

**Colloid Release and Colloid Interactions**

Colloid release in the subsurface soil was attributed to rolling by hydrodynamic forces. The detachment criterion under water unsaturated conditions is given by the torque balance (Sharma *et al.*, 1992):

$$1.399F_s \frac{H}{2} = (F_{cap} - F^{EL})R \sin \phi \tag{5}$$

where  $F_s$  is the shear force (N);  $H$  is the water film thickness (m);  $F_{cap}$  is the capillary force (N);  $F^{EL}$  is the critical filling angle (degree); and  $R \sin \phi$  is the radius of the contact area on which the capillary force acts (m).  $F_s$  is calculated by (Sharma *et al.*, 1992):

$$F_s = 1.7(6\pi)\mu \frac{H}{2} V \tag{6}$$

where  $\mu$  is the water dynamic viscosity (N·s/m<sup>2</sup>) and  $V$  is the fluid velocity measured at a distance  $H/2$  from the surface of the pore wall. If colloids are completely covered with water, then  $H/2 = R$ , radius of the colloid.  $F_{cap}$  is calculated as (Chateau *et al.*, 2002):

$$F_{cap} = \pi R \gamma [2 \sin \phi \sin(\theta + \phi) + \cos \theta (1 + \cos \phi)^2 - \sin \phi] \tag{7}$$

where  $\gamma$  is the water surface tension (N/m) and  $\theta$  is the colloid-water contact angle (degree) and was determined to be 24.5° for this research. We approximated the fluid velocity  $V$  as the pore water velocity. If the left-hand-side of **Eq. (5)** is larger than the right-hand-side, colloids are released.

The value of the right-hand-side of **Eq. (5)** was heavily relied on  $F^{EL}$ . Since colloids were originated from the porous media surfaces, we assumed that the

media surface had similar  $\zeta$  potential values as the colloids. Therefore, the electrostatic force between colloids and the porous media was repulsive. The distance-dependent repulsive electrostatic force,  $F^{EL}$  between colloids and the porous media can be evaluated by (van Oss, 1994):

$$F^{EL} = \pi \epsilon \epsilon_0 \frac{R}{y} [2\psi_{01}\psi_{02} \text{Ln}(\frac{1+e^{-\kappa y}}{1-e^{-\kappa y}}) + (\psi_{01}^2 + \psi_{02}^2) \text{Ln}(1-e^{-2\kappa y})] \tag{8}$$

where  $\epsilon$  and  $\epsilon_0$  are the relative dielectric permittivity of water (78.55 for water at 25°C) and permittivity under vacuum ( $8.854 \times 10^{-12}$  C/V·m) respectively;  $R$  is the colloid radius (m);  $1/\kappa$  is the Debye-Hückel length, which is also an estimation of the effective thickness of the electrical double layer [18];  $y$  is the distance between colloid surface and the porous media surface measured from the outer edge of the sphere (m); and  $\psi_{01}$  and  $\psi_{02}$  are potentials at colloid and porous media surfaces (V), which can be calculated by (Dukhin, 1993):

$$\psi_0 = \zeta(1 + z/R^*) \exp(\kappa z) \tag{9}$$

where  $\zeta$  is the zeta potential measured at the slip plane (V);  $z$  is the distance from the colloid or porous media surface to the slip plane (m); and  $R^*$  is the radius of the colloid or the porous media. The  $\kappa$  value in above equations can be estimated by (Chen & Flury, 2005):

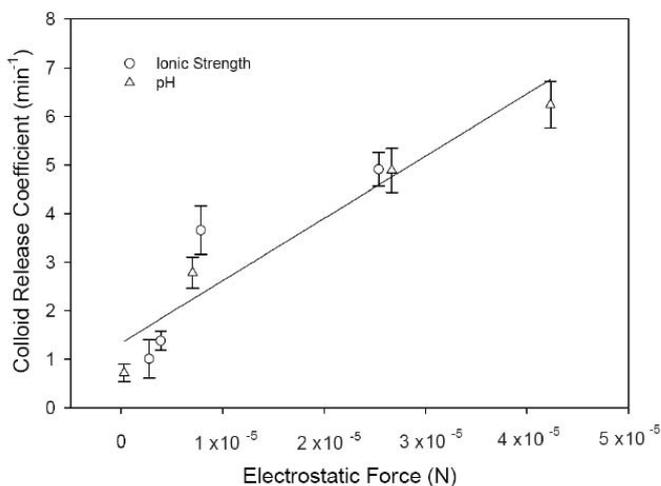
$$\kappa = \sqrt{4\pi e^2 \sum_i \frac{v_i^2 n_i^2}{\epsilon \epsilon_0 kT}} \tag{10}$$

where  $e$  is the charge of the electron ( $1.6 \times 10^{-19}$  C);  $v_i$  is the valence of each ionic species (-);  $n_i$  is the number concentration of ions of each species in the bulk liquid (number/m<sup>3</sup>);  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K); and  $T$  is the absolute temperature (K). The typical distance from the colloid surface or porous media to the slip plane, i.e.,  $z$  is usually in the range of 0.3 nm to 0.5 nm. 0.5 nm was used for this research.

For this research, the capillary force was up to  $4.12 \times 10^{-7}$  N and the electrostatic force was in the range of  $2 \times 10^{-7}$  N to  $4.23 \times 10^{-5}$  N (**Table 1**). Therefore, the electrostatic force was the controlling force for colloid release under the conditions of this research. Especially, when the electrostatic force was greater than the capillary force, hydrodynamic force was not that important for colloid release, instead, it contributed to colloid mobilization. By plotting the colloid release coefficient against the electrostatic force, it was found

**Table 1.**  $\zeta$  potential and colloid electrostatic force,  $F^{EL}$ 

| Ionic strength<br>(M) | $\zeta$ Potential<br>(mV) | $F^{EL}$<br>( $10^{-5}$ N) |
|-----------------------|---------------------------|----------------------------|
| 0                     | -65.5                     | 2.54                       |
| 0.03                  | -34.6                     | 0.78                       |
| 0.05                  | -25.7                     | 0.39                       |
| 0.07                  | -21.6                     | 0.27                       |
| pH                    | $\zeta$ Potential<br>(mV) | $F^{EL}$<br>( $10^{-5}$ N) |
| 4.0                   | -7.1                      | 0.03                       |
| 5.5                   | -34.5                     | 0.70                       |
| 8.5                   | -67.2                     | 2.67                       |
| 10.0                  | -84.6                     | 4.23                       |

**Fig. 8** Colloid release coefficient as a function of electrostatic force.

that the colloid release coefficient increased linearly with the increase of the repulsive electrostatic force (Figure 8). It should be noted that the electrostatic force was evaluated at the equilibrium distance, i.e.,  $y = 1.57 \times 10^{-10}$  m when colloids physically contacted the media surfaces (van Oss, 1994).

## CONCLUSIONS

Colloid release from the agricultural soil under unsaturated conditions was investigated using intact soil columns in this research. Hydrodynamic force and electrostatic force overcame the capillary force under the experimental conditions of this research to release the colloids. With the increase of solution ionic strength, colloid repulsive electrostatic forces decreased, and subsequently, colloid release decreased. With the increase of pH, colloid repulsive electrostatic force increased, leading to more colloid release. Colloid release displayed a linear exponential relationship with respect to the repulsive electrostatic forces between colloids and the porous media.

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