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Combined effects of Ca^{2+} and humic acid on colloid transport through porous media

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Abstract We report the separate and combined effects of humic acid and Ca^{2+} ions on the transport of colloidal particles through a sand-packed column. Polystyrene latex particles with a sulfate functional group were used as model colloids. The concentrations of both the inlet solution and the effluent solutions were measured during each experimental run. Breakthrough curves were obtained by taking the ratios of each effluent sample concentration to the inlet solution concentration. In the absence of humic acid, the results indicate that increasing the concentration of Ca^{2+} increases particle attachment to the sand, thus causing decreased transport rates of latex particles through the porous bed matrix. Once 4 mg/l humic acid was added to the system, changes were observed in the effect that Ca^{2+} has on latex particle breakthrough. In a system containing calcium, increasing the humic acid concentration was shown to reduce particle attachment and increase transport rates. In the absence of calcium, the ratios for the outlet-to-inlet concentrations were similar for each concentration of humic acid. The electrophoretic mobility was also measured in order to determine the role of electrostatic repulsion in the latex particle transport. The electrophoretic mobility of the latex particles was found to be dependent on humic acid concentration in the absence of Ca^{2+} but not in its presence.

Keywords Humic acid · Divalent ions · Electrosteric mechanism

Introduction

One possible mechanism through which contaminants are transported in the subsurface environment is through attachment to dispersed colloids. Contaminants readily adsorb onto the surface of these dispersed colloids, which have low solubility and high surface area. Many inorganic particles found in groundwater, like clays, metal oxides and carbonates, have been shown to be effective at adsorbing radionuclides and metals through ion exchange and surface complexation reactions [1]. Therefore, contaminant mobilization is determined by the extent to which the colloids move through the aquifer, sediment, or soil. Conversely, conditions may favor colloidal adhesion to the immobile solid substrate in the porous medium, which in the present study was simulated by a sand-packed column, where the colloids adhere to the surface of the sand particles. Adhesion to the sand particles reduces the transport of attached contaminants since the colloids are no longer mobile. Two mechanisms by which colloids may become attached to the sand grains are interception and straining [2]. Interception capture refers to colloidal deposition on the surface of porous media by various physical forces [3]. Physicochemical forces, such as attractive van der Waals, electrostatic double-layer repulsion, or hydrodynamic forces, govern deposition by interception, which is most important when the drop size is smaller than the pore size. Deposition by straining occurs when the pore construction is clogged by particles or aggregates larger than the pore [3]. Changes in solution chemistry may alter the degree of interception or straining, thus affecting particle transport. When the repulsion between colloids and sand is increased, colloids become more mobile and transport is enhanced. Increasing the size of the colloids and their aggregates causes the particles to become strained to a larger extent, and thus may lead to decreased mobilization and lower transport rates. Understanding the factors which influence colloid transport through a sand-packed column aids in determining the fate of contaminants in the subsurface environment.

Adsorption of natural organic matter (NOM) on the surface of the colloids and the sand has been identified as one contributor to mobilization. The predominant fraction of NOM in natural waters comprises organic polyanions, known as humic substances (humic and fulvic acids) [4]. Most colloidal particles suspended in natural waters have a net negative surface charge. There is considerable evidence that an adsorption layer of NOM [5, 6] increases the net surface charge of these colloidal particles. Since the sand used in the experiments is silicate-based, it has a net negative surface charge. The sulfate latex used in the experiment also has a negative surface charge. Therefore, adsorption of NOM on sand and on the colloids increases the electrostatic repulsion already present between particles and substrate, as well as that among transporting particles, thereby enhancing colloid mobility. Studies on the effect of humic acid on the electrophoretic mobility of colloids may be found in Refs. [4–7]. In a previous study [8] we measured electrophoretic mobility and correlated changes in mobility with the transport of latex particles through a sand-packed column. Also, the role of humic acid in colloid stability is described in Ref. [9].

The presence of divalent ions may be an additional factor in the transport of colloids through porous media and, in particular, calcium has been found to increase particle deposition and to reduce transport in two ways. Tipping and Cooke [10] as well as Beckett and Le [11] provided evidence that the magnitude of the electrophoretic mobility decreases as the calcium concentration increases, thus leading to increased interception. Colloidal deposition owing to straining is also increased by the presence of calcium, since the latter lowers the colloid stability and causes an increase in aggregate size. The specific objective of our present study is to examine in a systematic way the combined and separate effects of divalent ions and humic acid on the transport of latex particles as model colloids through a sand-packed column.

Experimental

Materials

Surfactant-free polystyrene latex particles of the amidine and sulfate type were obtained from Interfacial Dynamics Corporation (Portland, Ore.). The sulfate latex particles had a diameter of 0.31 μm. The surface charge density of the sulfate latex was $-2.1\ \mu\mathrm{C/cm}^2$. The particle number and the weight/volume percent solids for the sulfate latex were 4.6×10^{12}/ml and 8.3%. Ottawa sand was obtained from Fischer Scientific (Houston, Tex.) and had a mesh size of 20–30, which corresponds to a mean grain diameter of 580 μm. Purification of the sand was achieved through an elaborate procedure described in Ref. [8]. Humic acid was purified from sodium humate obtained from Aldrich Chemical Company using a procedure outlined in Ref. [12]. Ultrapure water was obtained by flowing tap water through a series of ion exchangers followed by ultrafiltration and distillation in a Barnstead E-Pure water purification system. The resistivity of the water obtained was 17–17.5 MΩcm.

Column for deposition experiments

The setup for the deposition experiment, shown in Fig. 1, consists of a vessel containing the inlet solution connected to a peristaltic feed pump. The solution was pumped from the vessel through a sand-packed Plexiglas column (2.5-cm iinternal diameter, 10-cm length) from top to bottom. Steel frits on both ends support the column. A pressure drop transducer and an attached digital meter were connected at the entrance and the exit of the column in order to monitor the pressure drop across the bed. Equilibration was conducted prior to each experimental run by recirculating a solution at the desired concentration of humic acid and calcium through the bed for 24 h in the absence of latex particles. To complete the equilibration process the pump flow rate was set to 11 ml/min (about 1.2 pore volumes/min) and the solution was passed through the column for an additional 2 h. At this point the feed was switched to a 20 mg/l latex solution. Samples from the effluent solution were collected every minute for 2 h (92.9 pore volumes) and were then analyzed with a Shimadzu UV-160 spectrophotometer to measure outlet particle concentrations. The pore volume was calculated by obtaining the volume of the sand in the column from the weight and density of the sand then subtracting that volume from the total volume that may be contained in the column. Inlet particle concentrations were also measured before each experimental run. Three experimental runs were completed for each concentration, and inlet and outlet particle concentrations were determined from the scattering intensity at a wavelength of 800 nm. The pH of each solution used during the experiments was approximately 7 ± 0.5. The data represent the ratio of the outlet-to-inlet latex concentrations.

Characterization of particles and their aggregates

Since straining is enhanced by larger particle aggregates, a quantitative study was undertaken to determine the effect of calcium on the coagulation of latex particles. Flocculation experiments were conducted by first preparing a 500-ml solution containing calcium chloride and humic acid at the experimental concentrations. The latex concentration was maintained at 20 mg/l. This solution which was to be used for sampling was stirred for 2 h. The stirring rate for the sampling solution was the same as for the feed solution used in the deposition experiments. This was to help ensure that the particle diameter measured at the Ca^{2+} concentration represented the particle size of the inlet solution used in the deposition experiments. Samples were extracted from the solution

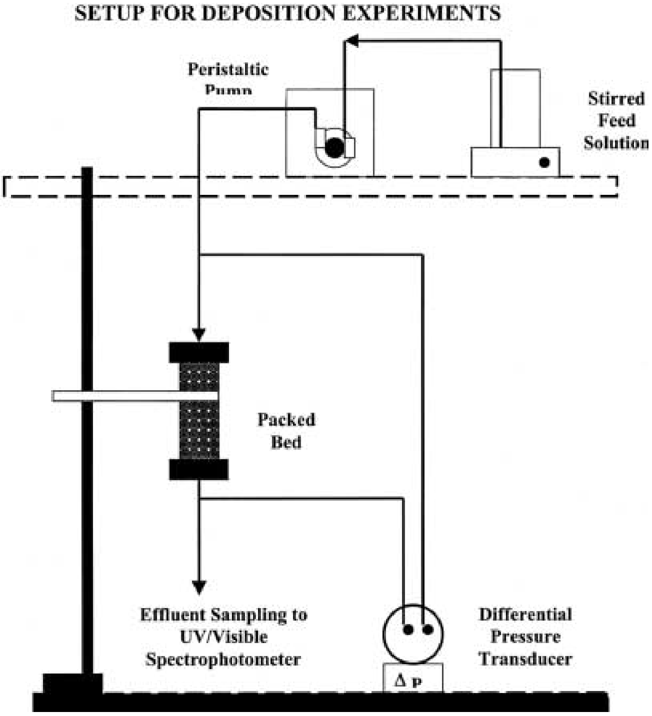

Fig. 1 Setup for the deposition experiments

every 5 min and the average particle diameters were measured using photon correlation spectroscopy (Coulter N4 MD). The instrument range for the particle size was 30–3000 nm.

Electrokinetic measurements were also conducted as a means of characterizing the surface charge properties of the latex particles. The electrophoretic mobilities of the latex particles as function of humic acid concentration, in both the presence and absence of Ca^{2+}, were measured using a Coulter Delsa instrument. Measurements were made at both stationary layers and the values reported here represent the average of the two. Differences between the two stationary layers ranged from about 10 to 15%.

Results and discussion

Effects of Ca^{2+} on the aggregation of the latex particles

Only at the low Ca^{2+} concentration of 1.7×10^{-4} M were we able to monitor conclusively the particle size of the suspension. The sulfate-based latex particle size for a 2-h period is shown in Fig. 2. Verification of the original diameter of the latex particles (0.29 μm) was done by also using the Coulter N4 MD. From Fig. 2 we observe that the presence of 1.7×10^{-4} M Ca^{2+} induced an increase in the size of the latex particles. At this Ca^{2+} concentration, the aggregate diameter reached a peak value of approximately 1.2 μm and then declined to 0.8 μm at the completion of the 2-h period, with 95% of the particles lying within 8% of this value. This particle size increase was attributed to the presence of the 1.7×10^{-4} M Ca^{2+}, while experiments at higher Ca^{2+} concentrations showed additional flocculation of the latex particles, beyond the range of the instrument. Therefore, calcium was confirmed to be a destabilizer. In view of its complexation with humic acid [13], Ca^{2+} cannot be an indifferent electrolyte and its action may not be viewed in the classical colloid-stability framework of Derjaguin–Landau–Verwey–Overbeek theory and the Schulze–Hardy rule. In addition to specific action caused by Ca^{2+} in promoting adhesion, reported numerous times in the literature, where it is termed "calcium bridging" [14, 15], the reduction of colloid stability in the presence of calcium may also be caused by a direct reduction in the absolute value of the surface charge, thus leading to a reduction in the repulsive force between latex particles, which in turn causes aggregation. Figure 2 also shows the particle size growth for a 2-h period when 2 mg/l humic acid is present. We observe from these results that when 2 mg/l humic acid was added to the system there was a reduction in the particle size. The particle size was reduced from an average value of about 0.8 μm to about 0.6 μm. Ninety-five percent of these particles were within 6% of this average value. Apparently, humic acid added to the system partially counteracts the Ca^{2+}-caused reduction in repulsion. In Ref. [8] it was shown that the presence of organic matter reduces the absolute value of the electrophoretic mobility for the same Ottawa sand and for the same concentration regime of the current work; therefore, the humic-acid-induced stabilization is not only a result of enhanced electrostatic repulsion, but may also be due to steric stabilization caused by the adsorbed humic acid on the surface of the latex particles

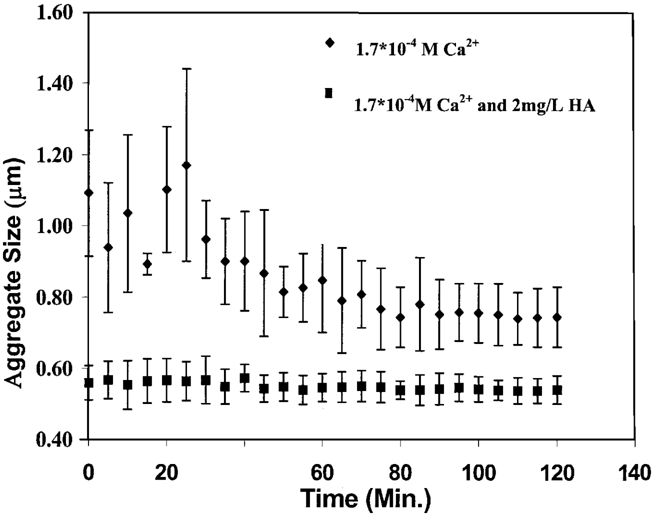

Fig. 2 Sulfate latex particle size for a 2-h period in the presence of 1.7×10^{-4} M Ca^{2+} and also upon addition of 2 mg/l humic acid

and the sand grains. A measurement of the floc size of the effluent solution for a Ca^{2+} concentration of 1.7×10^{-4} M revealed that the floc size remained the same when the solution flowed from the top to the bottom of the column. This suggests that at low Ca^{2+} concentrations (smaller aggregate sizes) particles may not aggregate within the column. Owing to instrument limitations, measurements at higher Ca^{2+} concentrations were not possible. For this reason, we cannot exclude the fact that at high Ca^{2+} concentrations particles may indeed aggregate within the column.

Effect of Ca^{2+} on breakthrough curve

The hypothesis in our experiments was that Ca^{2+} may lead to an increase in straining and to an increase in interception, in which case the transport of latex particles through porous media would be expected to decrease. Deposition experiments were thus conducted in the presence of Ca^{2+} in order to quantify the effect that a divalent ion has on the transport of latex particles through porous media. Breakthrough curves for the sulfate latex at various concentrations of Ca^{2+} in the absence of humic acid are shown in Fig. 3. The ordinate depicts the ratio of outlet-to-inlet particle concentrations and the abscissa shows the number of pore volumes that have passed through the porous bed. These results demonstrate that increasing the concentration of calcium in the system decreases the transport rates of the latex particles through porous media. A concentration of 0.01 M Ca^{2+} produced very little breakthrough of latex particles. It is noteworthy that even a monovalent ion at high concentrations, 0.1 M KCl, caused very low breakthrough in the work of Elimelech and O'Melia [16]. The deposition rate of particles in granular porous media can be further quantified through the single collector efficiency, η, defined as the ratio of the particle deposition rate to the rate at which the particles approach the collector. Values for η were obtained from the single-collector-efficiency expression [8, 17]:

$$\eta = -4a_c/3L(1-f)\ln(c/c_0) \ , \tag{1}$$

where a_c is the radius of the sand grains, L is the length of the bed, f is the porosity of the bed, and c/c_0 is the near-steady-state value for the concentration ratio.

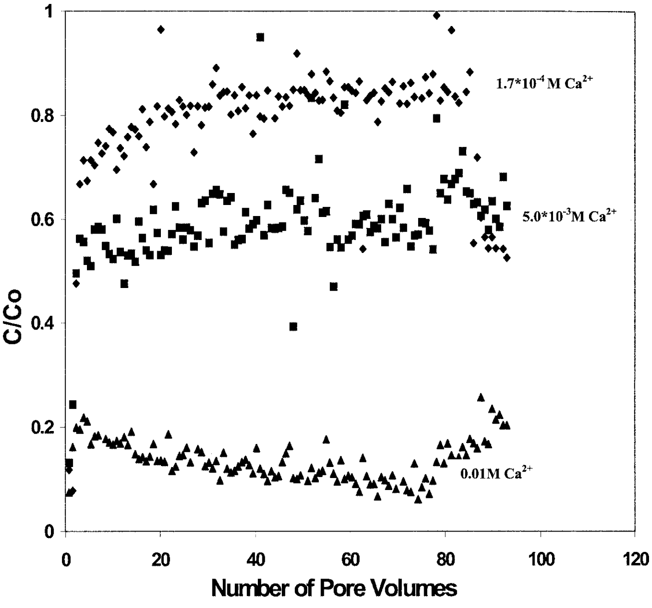

Fig. 3 Breakthrough curves for the sulfate latex system at various Ca^{2+} concentrations in the absence of humic acid

The single-collector efficiencies at varying Ca^{2+} concentrations are listed in Table 1 and the results indicate increased attachment and reduced transport rates at higher calcium concentrations. The reduction in the transport of latex particles is explained by the interception and straining. The level of straining may be assessed from measurement of the particle diameter of the effluent solution containing 1.7×10^{-4} M Ca^{2+}. This experiment revealed that the floc diameter did not increase as the solution flowed from the top to the bottom of the column, indicating that there was no flocculation of the latex particles in the column. This demonstrates that interception is the predominant mechanism when the aggregate size is small, i.e., at low Ca^{2+} concentrations. Straining certainly becomes important as the calcium concentration is increased and the particles become larger.

When the Ca^{2+} concentration was changed in the presence of a constant humic acid concentration of 4 mg/l the results were not as clear. As Fig. 4 demonstrates, at this humic acid concentration, initially the breakthrough for 5.0×10^{-3} M Ca^{2+} is lower than that for 0.01 M Ca^{2+}. After approximately 25 pore volumes had passed through the column, the value for the latex breakthrough at these two concentrations became almost equal. The breakthrough for the latex particles was higher at a lower Ca^{2+} concentration of 1.7×10^{-4} M. The difference in these results from those obtained when no humic acid is present in the system may be explained by a recent study [18], which showed that humic acid adsorption to the surface of colloidal particles increases with increasing salt concentration.

Table 1 Single-collector efficiencies at various calcium ion concentrations

Calcium concentration (M)	Single-collector efficiency
0	4.38×10^{-5}
1.7×10^{-4}	3.53×10^{-4}
5.0×10^{-3}	8.11×10^{-4}
1.0×10^{-2}	1.84×10^{-3}

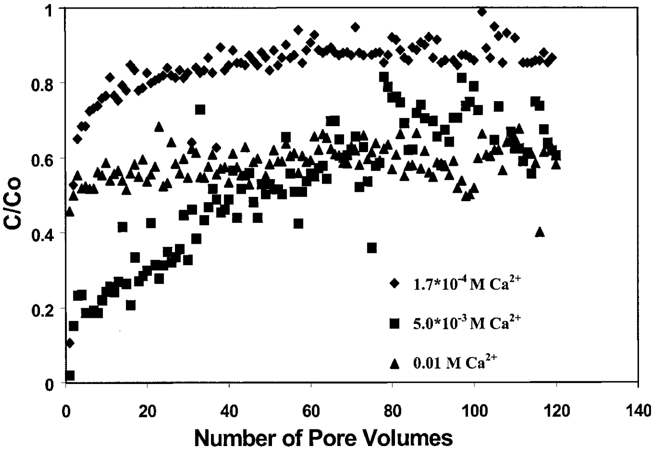

Fig. 4 Breakthrough curves for the sulfate latex system at various Ca^{2+} concentrations in the presence of 4 mg/l humic acid

Therefore an increase in Ca^{2+} concentration from 5.0×10^{-3} to 0.01 M may cause more humic acid to adsorb onto the latex particle surface and this could explain the difference in transport rates.

Effect of humic acid

The effect of humic acid on the sulfate latex breakthrough curve in the presence of 0.01 M Ca^{2+}, a typical calcium-ion concentration used by previous researchers in simulating soils [19, 20], is shown in Fig. 5. This graph compares the breakthrough for the latex particles at various concentrations of humic acid, while maintaining a constant Ca^{2+} concentration. Figure 5 clearly demonstrates that at this calcium concentration the transport rates of latex particles are dependent on the humic acid concentration. When the humic acid concentration was increased from 0.5 to 4 mg/l the breakthrough of latex particles increased from 0.2 to 0.6. In a study by Deshiikan et al. [8], in the absence of calcium ions, varying the humic acid concentration did not produce a consistent effect on the breakthrough of sulfate latex particles, as there was no correlation between NOM concentration and the transport rate for the sulfate latex. On one hand, as the NOM concentration was increased from 0 to 5 mg/l, there was an increase in the absolute value of the electrophoretic mobility and a subsequent increase in the transport rate; however, when the NOM concentration was increased to 10 or 15 mg/l, in the case of the positively charged amidine latex there was a charge reversal and the absolute value of the mobility was slightly increased. This may explain why the breakthrough for 5 mg/l humic acid was higher than that for 10 and 15 mg/l humic acid. Owing to these previously reported inconsistencies at high humic acid concentrations, we examined a lower concentration range in the current study. The concentration range in the current study is 0.5–4 mg/l, which is representative of the actual humic acid presence in soils. Also, in the current study, the humic acid was purified from sodium humate obtained from Aldrich, whereas in Deshiikan's study Georgetown NOM was used. Additionally, the latices used in the two studies had different surface properties and different sizes, and the pH of the solution was also higher in the present work, in the range 6.5–7.5. These differences may explain the variation in some of the results. The trend seen in Fig. 6 shows a slight increase in breakthrough upon addition of humic acid,

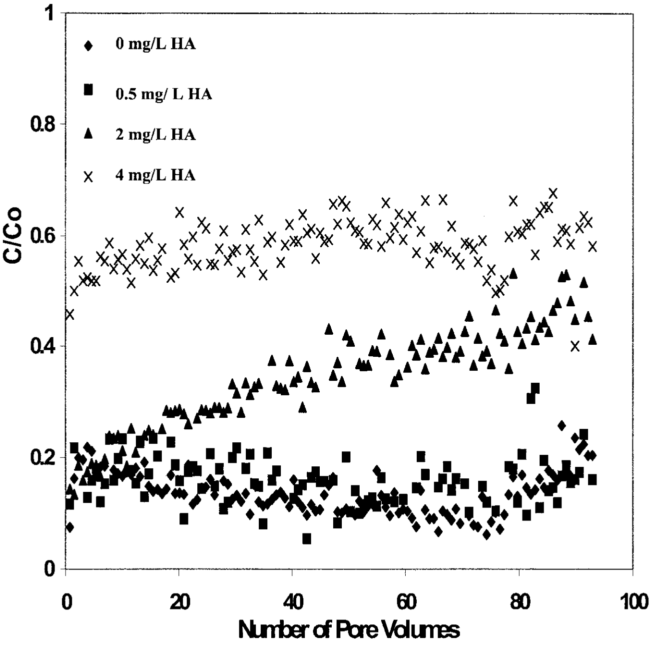

Fig. 5 Breakthrough curves for the sulfate latex system at various humic acid concentrations in the presence of 0.01 M Ca^{2+}

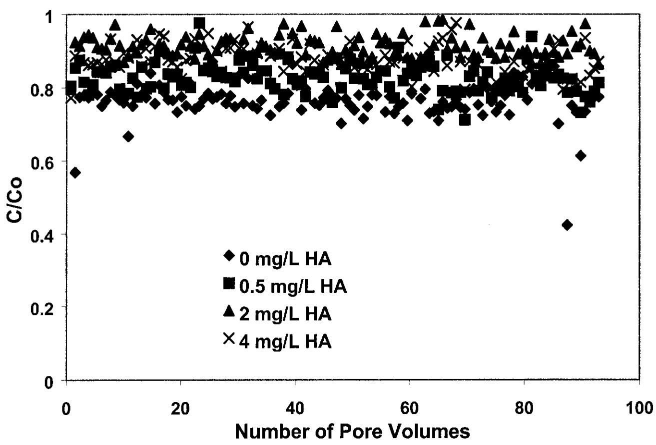

Fig. 6 Breakthrough curves for the sulfate latex system at various humic acid concentrations

although there is no significant difference between the results for 2 and 4 mg/l. This indicates that the effect humic acid has on sulfate latex particle transport through the packed bed is significant only when Ca^{2+} is present. An explanation for this is that the presence of the divalent ion may increase the adsorption of humic acid on the surface of the sand, as also reported in Refs. [21, 22]. These studies show, through batch adsorption experiments on various types of sand, that divalent ions increase the adsorption of humic acid. The structure of humic acid is also affected by the presence of divalent ions [23, 24], which may bring about changes in the configuration of the humic acid and in the number of attachment points on the surface of the sand. Table 2 demonstrates that increasing the concentration of humic acid in the presence of 0.01 M Ca^{2+} decreases the single-collector efficiency, thereby increasing attachment and interception.

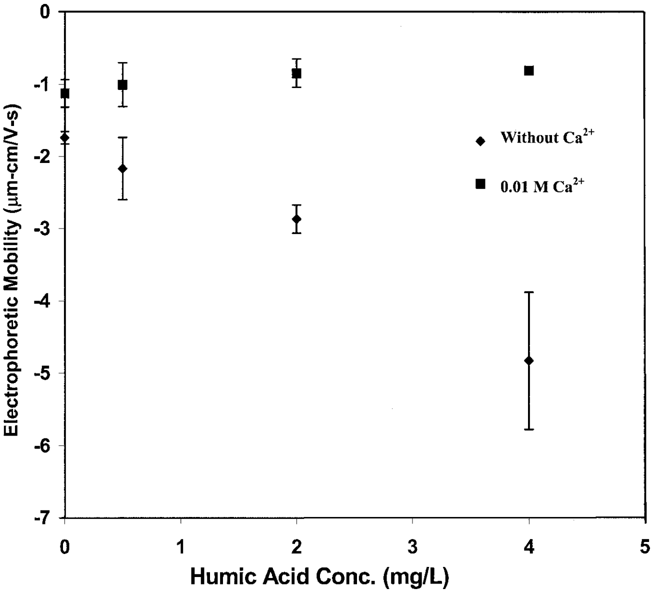

Fig. 7 Electrophoretic mobility versus humic acid concentration for the sulfate latex system with and without addition of 0.01 M Ca^{2+}

Table 2 Single-collector efficiencies at various humic acid concentrations in the presence of 0.01 M Ca^{2+}

Humic acid concentration (mg/l)	Single-collector efficiency
0	1.84×10^{-3}
0.5	1.73×10^{-3}
2	9.84×10^{-4}
4	5.49×10^{-4}

Electrokinetic studies

Electrokinetic studies were conducted in order to characterize the surface charge properties of the latex particles. Electrophoretic mobility measurements for the two systems (with and without calcium) are presented in Fig. 7, which shows that increasing the concentration of humic acid in the absence of calcium increases the absolute value of the mobility. The values for the mobility are different from those seen by Deshiikan et al. [8]. This may be explained through the differences in the system parameters, as mentioned earlier. Electrostatic repulsion between latex particles and sand grains is expected to increase because of increases in the magnitude of the mobility. Once calcium was added to the system, the mobility did not vary. If we examine Fig. 7 we can see that the mobility only varies between -0.80 and -1.0 μmcm/Vs. These results are in agreement with those of Tipping and Cooke [25], who also showed that increasing the Ca^{2+} concentration reduces the dependence of colloid surface charge on humic acid concentration. An explanation for this is offered in Ref. [26]: adsorption of humic acid on the surface of the colloid will cause coadsorpion of cations. Therefore, increasing the humic acid concentration increases the adsorption of cations and there should not be any substantial change in the mobility values. These electrokinetic results in conjunction with the breakthrough curves suggest the dominance of steric repulsion. Amirbahman and Olson [27, 28] described an "electrosteric" mechanism for colloidal attachment when humic acid is present, indicating a combination of electrostatic and steric interactions. Figure 7 shows that in the absence of calcium ions, humic acid may cause an increase in electrostatic repulsion among the latex particles and between the latex particles and the sand, whereas in the presence of Ca^{2+} humic acid does not have the same effect. Here it is assumed that the electrophoretic mobility behavior of sand is similar to that of latex vis-à-vis the change in electrophoretic mobility with humic acid concentration when Ca^{2+} is present. Comparing Figs. 5 and 6 shows that the influence of humic acid on colloid-facilitated transport is enhanced by the presence of the calcium ions. Since electrokinetic experiments have shown that electrostatic repulsion is not significantly enhanced by humic acid when Ca^{2+} is introduced into the system, steric repulsion must be the key parameter responsible for the facilitation of latex particle transport by humic acid.

Conclusions

The results from the breakthrough curves for a sulfate latex suspension through a sand-packed column, show that increasing the Ca^{2+}concentration decreases particle transport. However, changes in the divalent ion concentration yielded very different results when humic acid was absent compared to when it was present. The decrease in breakthrough with increasing calcium ion concentration was not as pronounced in the latter case. Also, changing the humic acid concentration affects the breakthrough of sulfate latex particles to a larger extent when Ca^{2+} is present. The effects that result upon calcium ion addition may be explained by the fact that Ca^{2+} causes more humic acid to be adsorbed on the surface of both the sand grains and the latex particles. Evidence from single-collector efficiencies and latex particle size measurements shows that at small aggregate sizes or at low calcium concentrations interception is the more important mechanism for increased transport rates. In addition, our work shows that in the presence of calcium the electrophoretic mobility of the latex does not change significantly, yet we see increases in the breakthrough of the colloid particles with increasing humic acid concentration. In the absence of Ca^{2+}, there is a consistent trend of latex electrophoretic mobility absolute value increases with increasing humic acid concentration, yet we see no evidence of a correlation between such differences in mobility and the breakthrough of latex particles. This suggests that humic acid steric repulsion may dominate when calcium is present.

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