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Effect of solution chemistry on kaolinite deposition behavior in silica sand

Effet de la chimie en solution sur le comportement de dépôt de kaolinite dans le sable de silice

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ABSTRACT: It is well known that the deposition of particulates in filtration and drainage infrastructures can degrade the long-term performance of the device due to the reduction of hydraulic conductivity. However, the geochemical conditions that lead to particulate retention or mobilization are less well understood. In this study, the deposition behavior of kaolinite suspensions was investigated as a function of ionic strength and pH. Experimental results revealed that the reduction of saturated hydraulic conductivity was the most significant under low ionic strength and low pH due to particle aggregation and the resulting exponential deposition profile.

RÉSUMÉ : Des recherches ont déjà montré que le dépôt de particules dans les infrastructures de filtration et de drainage peut dégrader les performances à long terme du dispositif en raison de la réduction de la conductivité hydraulique. Cependant, les conditions géochimiques qui conduisent à la rétention ou à la mobilisation des particules sont moins bien comprises. Dans cette étude, le comportement de dépôt de suspensions de kaolinite a été étudié en fonction de la dûreté et du pH. Les résultats expérimentaux ont révélé que la réduction de la conductivité hydraulique saturée était la plus importante sous une faible force ionique et un faible pH dû à l'agrégation des particules et au profil de dépôt exponentiel résultant.

KEYWORDS: particle deposition, saturated hydraulic conductivity, ionic strength, pH

1 INTRODUCTION

Physical clogging of soil filters caused by particle deposition can degrade the performance of geotechnical and geoenvironmental infrastructure by reducing the hydraulic conductivity (k). Suspended clay particles that are transported into drainage structures are a frequent source of physical clogging within filter media. Consequently, the clogging behavior of particulate media has been studied extensively, both in terms of the reduction of saturated hydraulic conductivity (k) and the retention of clay particles (Reddi et al. 2000, 2005). However, clay particles aggregate in different structures as a function of the prevailing solution chemistry (Palomino and Santamarina, 2005), which can lead to different retention profiles depending on the ionic strength and pH of the filter pore fluid. These different behaviors imply that the solution chemistry can impact to the reduction of hydraulic conductivity during filtration processes, particularly when physical clogging is caused by clay particles.

The work performed in this study quantified the reduction of the hydraulic conductivity of a sand filter medium as a function of ionic strength (IS) and pH. Laboratory scale soil column tests were performed to obtain breakthrough curves (BTC) and deposition profiles in 8 different solution chemistries, with identical flow rate and initial inlet concentrations of clay particle suspensions. Experimental results were analyzed in terms of two main mechanisms, attachment and straining, for the association and deposition of clay particles in the sand filter.

2 EXPERIMENTAL PROGRAM

2. 1 *Materials*

ASTM 20/30 sand and Georgia kaolinite were selected for the sand medium and clay particle, respectively. The sand was cleaned to remove the impurities through immersion in deionized water (Barnstead E-pure), followed by treatment in the ultrasonic bath for two hours before rinsing several times with deionized water. Specific gravities of the sand (2.65) and kaolinite (2.55) were measured according to ASTM D854, and median grain sizes were measured according to ASTM D422, with the resulting D_{50} for sand = 720 µm and D_{50} for kaolinite = 0.45 µm. NaCl was used to control the ionic strength of the pore fluid (0.001, 0.01 and 0.1 M), and HCl (1 M) and KOH (1 M) were used to control the equilibrium pH (~ 3, ~ 6 and ~ 9). All chemicals were used as received (Fisher Scientific) and high quality deionized water (~ 18 MΩ·cm) was used in all experiments.

2. 2 *Experimental methods*

Column tests were performed using an acrylic cylinder (5.08 cm (2 in.) diameter by 15.24 cm (6 in.) height) for the sand column experiment. Perforated Waluminum discs and # 200 plastic mesh were installed at the top and the bottom of the column, respectively, for the purpose of distributing the inlet flow at the top of the column and to retain the sand filter media at the base of the column. In addition, a pulse dampener was installed between the column inlet and the pump to minimize pulsations generated by the pump. A schematic drawing of experimental setup is illustrated in Figure 1. Sand was placed in the cell at relative density = 70 % (initial porosity = 0.365, maximum and minimum void ratio of sand were predetermined) using the wet pluviation method in order to obtain saturated initial conditions. The flow rate for all experiments was set to 15 $cm^3 min^{-1}$ (corresponding to a pore water velocity of 0.74 cm min^{-1}) (peristaltic pump (Cole-Parmer)) and the inlet concentration of the kaolinite suspension (C_0) was fixed at 1 g L^{-1} in all experiments. The quantity of HCl and KOH to alter the pH of 1 g L^{-1} kaolinite suspension was predetermined experimentally by titration to achieve the desired pH at equilibrium for the kaolinite suspension. Before the injection into the column experiment, the kaolinite suspension was suspended in the background solution at the chosen ionic strength and pH solution, followed by preparation in an ultrasonic bath for 2 hours, with stirring to disperse the kaolinite particles. Suspensions were then gently stirred using a magnetic stirrer for an additional hour to allow kaolinite particles to associate and develop clusters as a function of pore fluid conditions.

A background solution at the given ionic strength and pH, but without kaolinite particles, was injected for five pore volumes (PVs) of flow to flush the column and to equilibrate the system. After five pore volumes of flow, the injection of the kaolinite suspension was initiated and continued for 20 PVs, followed by 10 PVs of flow of deionized water. The concentration of kaolinite particles in the outflow was determined by measuring turbidity (turbidimeter, Orbeco-Hellige Inc.) in every 0.4 PV of effluent collected by the fractional collector. After termination of the experiment, the kaolinite particles deposited in the sand medium was determined by carefully sampling every 1.27 cm (0.5 in.) of column depth. The column sections were vigorously stirred for ten minutes with a known amount of water to evaluate the deposition profile of kaolinite from measured turbidity. Concentration of kaolinite and turbidity showed a good positive linear relation which was evaluated prior to the column experiment (data not shown here). The pressure difference across the column was obtained from pressure transducers installed at the top and the bottom of the column (Figure 1) and the hydraulic conductivity was calculated using Darcy's equation.

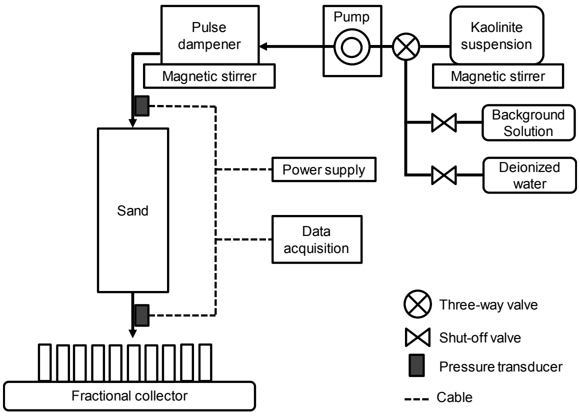


Figure 1. Schematic of experimental setup.

3 RESULTS AND DISCUSSION

The breakthrough curves for the kaolinite effluent concentration, the pressure difference between the inlet and outlet during the injection, and the kaolinite deposition profile in the sand medium were determined as a function of solution chemistry (Figure 2 - Figure 4, Table 1). Most of the kaolinite (> 99 %) was deposited in the sand, with the exception of the experiment conducted at pH ~ 6 and IS ~ 0.1 M, and the experiment conducted at pH ~ 9 and IS ~ 0.001M. As a result of the decreased deposition, low values of normalized pressure difference (dP / dP_0) were observed for those two cases after twenty pore volumes of flow ($dP / dP_0 = 2.17$ for IS ~ 0.1 M and pH ~ 9 and $dP / dP_0 = 2.15$ for pH ~ 9, IS ~ 0.001 M, Figure 3). Note that normalized hydraulic conductivity is not presented here because the hydraulic conductivity is the reciprocal of pressure difference in Darcy's equation under the constant flow rate. Therefore, the relatively large amount of kaolinite observed in effluent for the two experiments resulted in lower reduction of hydraulic conductivity compared to other cases.

In contrast, the values of dP / dP_0 after 20 PV decreased as ionic strength increased: IS ~ 0.001 > 0 > 0.01 > 0.1 at pH ~ 6, followed by pH ~ 3 > 6 > 9 at IS ~ 0.001 M, and pH ~ 3 > 9 > 6 at IS ~ 0.1 M (Figure 3). This result suggests that the reduction of hydraulic conductivity due to the deposition of kaolinite was more significant under acidic conditions than neutral or basic pH, regardless of IS. In addition, the trend of pressure difference was consistent with the trend of the amount of deposited kaolinite in the first top layer of the sand medium (Figure 4, with the exception of IS ~ 0.001 < 0 at pH ~ 6). The more exponential deposition profile resulted in a more significant reduction of hydraulic conductivity.

Table 1. Experimental Conditions and Kaolinite Mass Balance (MB)

Experimental Condition		Recovered Fraction (%)			MB (%)
pH	IS (M)	M_s	M_e	M_d	
~ 6	~ 0	99.05	0.95	0.02	95.90
~ 6	0.001	99.91	0.09	0.09	104.82
~ 6	0.01	99.88	0.12	0.74	99.12
~ 6	0.1	87.63	12.37	0.34	96.82
~ 3	0.001	99.90	0.10	0.03	98.70
~ 3	0.1	99.93	0.07	0.03	101.63
~ 9	0.001	43.51	56.49	0.95	99.07
~ 9	0.1	99.96	0.04	2.41	94.63

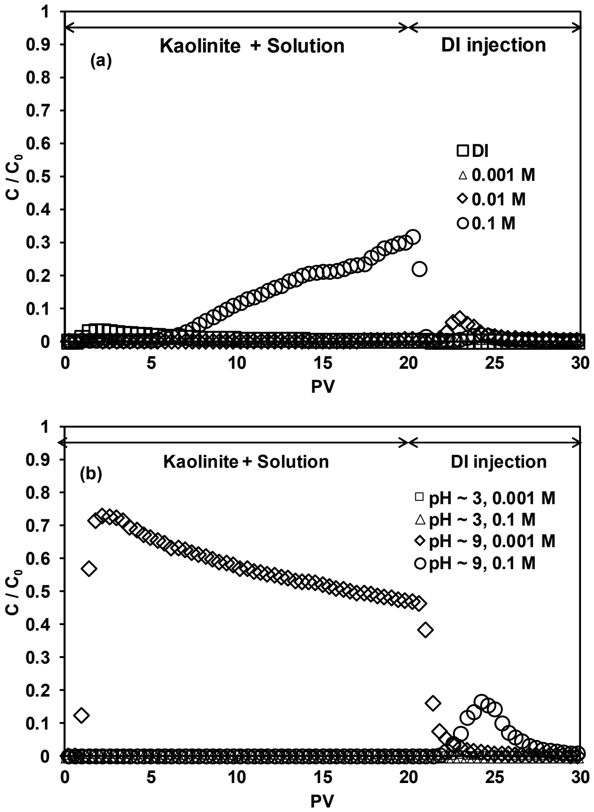
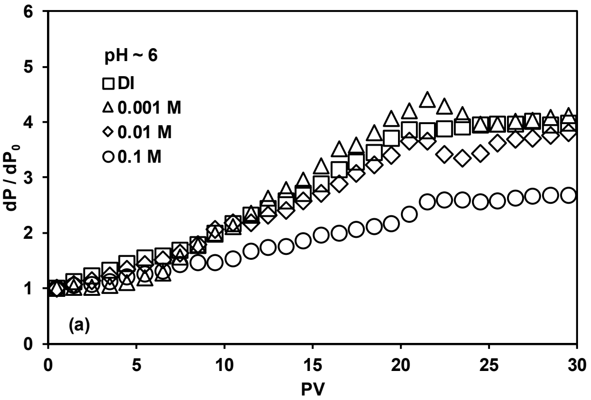


Figure 2. BTCs of kaolinite (a) pH ~ 6 under different IS and (b) pH ~ 3 and 9 with IS = 0.001 and 0.1 M.



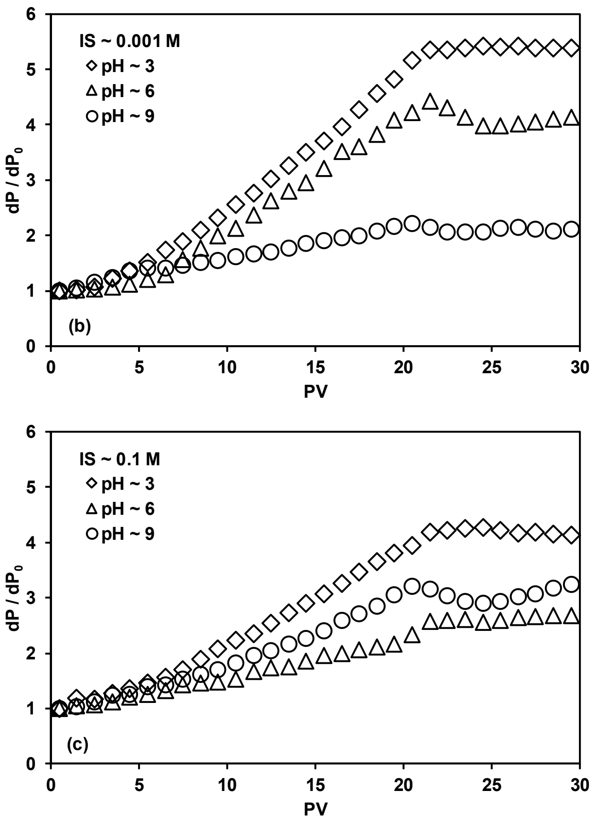
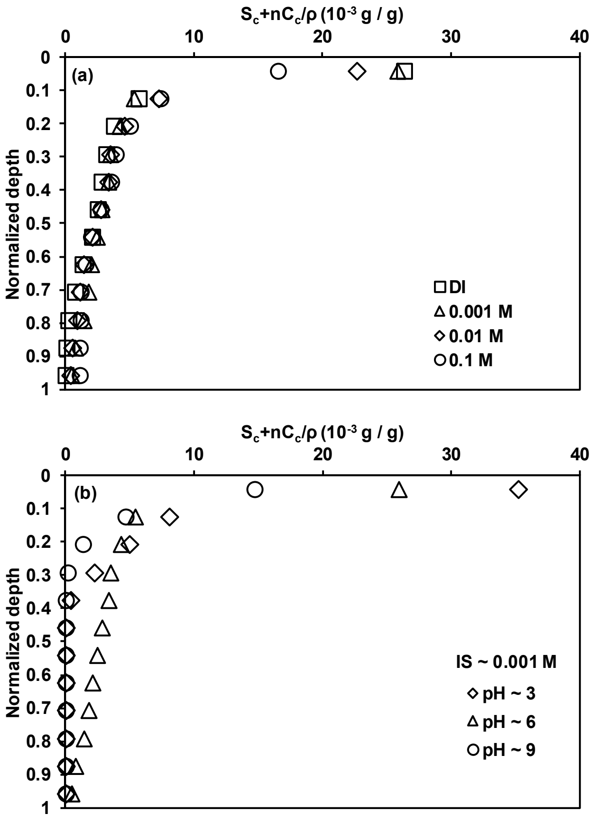


Figure 3. Normalized pressure difference (dP / dP$_0$) during the injection: (a) as function of ionic strength at pH ~ 6, (b) as function of pH at IS ~ 0.001 M and (c) as function of pH at IS ~ 0.1 M.



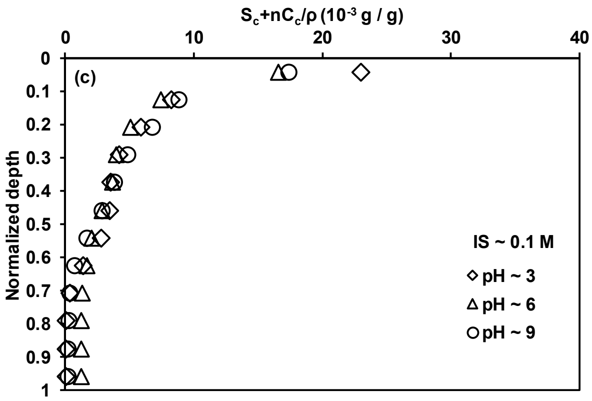


Figure 4. Kaolinite deposition profile after the injection: (a) as function of ionic strength at pH ~ 6, (b) as function of pH at IS ~ 0.001 M and (c) as function of pH at IS ~ 0.1 M.

Straining and attachment mechanisms can be taken into account to fundamentally explain the differences in the breakthrough curves and deposition profiles as a function of the solution chemistry. Straining is defined as particle immobilization due to narrow pore size of the sand medium (Auset and Keller 2006; Xu et al. 2006). Therefore, the size ratio between the kaolinite and sand particles is the most important factor affecting the mass of strained kaolinite particles because larger grain sizes of sand generally lead to larger pore openings and throats (Arya et al. 1999). In contrast, attachment of particles can be explained by the net attractive interaction energy between the particle and the sand grain. The theory, originally proposed by Derjaguin, Landau, Verwet and Overbeek (DLVO theory), has been used to account for the attachment mechanism of particles (Torkzaban et al. 2007), with van der Waals attraction and double layer repulsion representing the two key interaction energies that can affect particle attachment. If the sizes of the kaolinite clusters formed as a function of solution chemistry are relatively large, most of them are more likely to be deposited at the filter surface by straining, which results in a more exponential deposition profile. In contrast, attachment mechanisms may be dominant when the sizes of kaolinite cluster are relatively small, which allows kaolinite aggregates to penetrate more deeply into the filter. This deep penetration of kaolinite results in a less exponential deposition profile.

Based on the shape of the deposition profile (exponential) and the absence of kaolinite particles within the deep sand medium at low ionic strength, straining was likely the dominant removal mechanism for kaolinite deposition at pH ~ 3 and pH ~ 9 (Figure 3b). In contrast, the less exponential deposition profile and deposited kaolinite particles measured at all depths demonstrated that attachment of kaolinite occurred in experiments performed at pH ~ 6. According to the kaolinite fabric map proposed by Palomino and Santamarina (2005), kaolinite particles at pH ~ 3 will form clusters with face to face aggregation while kaolinite particles will disperse at pH ~ 9. Additionally, the surface charge of the sand and kaolinite particles tend to be same sign due to the protonation / deprotonation of surface hydroxyl groups on the silica faces of kaolinite particles. This leads to low attachment efficiency and high repulsive energy between sand and kaolinite at pH ~ 3 and 9. In addition, a lower mass of kaolinite was deposited at pH ~ 9 when compared to pH ~ 3 (56 % of kaolinite was observed in effluent at pH ~ 9 compared to pH ~ 3 (Table 1) due to the highly dispersed kaolinite particles). In contrast, pH ~ 6 is located between the edge and face isoelectric points, meaning that negative and positive sites coexist on the kaolinite particles, which will likely lead to more significant attachment of kaolinite at pH ~ 6 than at other pH levels. From the observed deposition profiles, roughly 28 % of total injected kaolinite was recovered at pH ~ 6 at the normalized depth (depth divided by total depth) of sand medium larger than 0.3 while only 1.4 and 0.5 % were recovered at pH ~ 3 and 9 respectively. At the high ionic strength, the significance of pH as a factor in the form of the deposition profile and pressure difference decreased due to prevalent Na^+ ions that can potentially compensate for the impact of pH.

At pH ~ 6, the quantity of strained kaolinite increased as ionic strength decreased (Figure 4a). Based on DLVO Theory, kaolinite particles (or clusters) may more preferably attach to the sand grain as ionic strength increased due to a decrease in double layer repulsion. However, the lower amount of deposited kaolinite was observed at ionic strength ~ 0.1 M, and 12 % of kaolinite mass was recovered in the effluent. This may be mainly attributed to the smaller size of kaolinite clusters under high IS at pH ~ 6. The adsorption of Na^+ to the kaolinite particles may also decrease the available negative sites available to associate with positive sites of another kaolinite particle. This leads to the smaller size of kaolinite clusters and less exponential deposition profiles under higher ionic strength, which resulted in the lowest pressure difference at ionic strength ~ 0.1 M.

Overall, the most significant decrease in hydraulic conductivity was $k / k_0 = 0.2$ (at pH ~ 3, IS ~ 0.001 M) while the least decrease was $k / k_0 = 0.46$ (at pH ~ 9, IS ~ 0.001M), when measured after twenty pore volumes of kaolinite suspension flow. Consequently, it can be concluded that the solution chemistry of the kaolinite suspension was a crucial factor for the reduction of hydraulic conductivity under identical kaolinite concentration and flow rate. From the observed BTCs and deposition profiles, this may be attributed to the different size of kaolinite clusters because of different association behavior between kaolinite particles and different interaction energy (attraction or repulsion) between kaolinite clusterd (or particled) and sand graind according to the solution chemistry. As was anticipated, the straining of kaolinite more substantially affected the reduction of hydraulic conductivity in a sand medium than the attachment of kaolinite.

4 CONCLUSIONS

In this study, reduction of hydraulic conductivity in a sand medium during the injection of kaolinite suspensions was experimentally quantified as a function of different solution chemistries. Based on the observed deposition profiles and breakthrough curves of kaolinite, the following conclusion can be drawn:

1. Relatively large amounts of kaolinite were observed in effluent when pH ~ 6, IS ~ 0.1 M and pH ~ 9, IS ~ 0.001 M which resulted in relatively lower decrease in hydraulic conductivity when compared to other cases where most of the kaolinite deposited in the sand medium.

2. The reduction of hydraulic conductivity was greatest at pH ~ 3 (pH ~ 3 > 6 > 9 under low ionic strength) while it exhibited different order at high ionic strength: pH ~ 3 > 9 > 6. This suggested that the reduction of k was more significant at acidic conditions regardless of ionic strength, which may be attributed to the large kaolinite clusters that formed by face to face association of kaolinite particles.

3. At pH ~ 6, kaolinite was observed in the effluent at ionic strength ~ 0.1 M and a more exponential deposition profile was observed as ionic strength decreased, in spite of higher attractive interaction energy at high ionic strength as predicted by DLVO theory. Thus, the size of kaolinite clusters can explain the straining mechanism as well as the attachment mechanism and their impact on the deposition behavior of kaolinite particles.

4. From the observed deposition profiles and pressure difference, it can be concluded that the solution chemistry was one of the crucial factors that can impact to the reduction of hydraulic conductivity, as observed in the shape of the resulting retention profiles.

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