Colloid clogging of saturated porous media under varying ionic strength and roughness during managed aquifer recharge

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ABSTRACT

Column experiments were conducted to examine the clogging effects of colloids under controlled conditions of solution ionic strength (IS) and porous media roughness. The results showed that colloids in recharge water play an important role in the clogging process of saturated porous media, such that even a small amount of colloid may cause a large reduction in the permeability of the porous medium. Clogging at the pore throat was inferred to be the main reason for the severe permeability reduction of porous media. The characteristics of colloid clogging were clearly influenced by both IS and medium roughness. Recharge water with a higher IS facilitated greater attachment of colloids to the surface of the saturated porous medium, which lead to superficial clogging, while collectors with a rough surface resulted in greater clogging than collectors with a smooth surface.

Key words | clogging, colloid, managed aquifer recharge, permeability

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INTRODUCTION

An important issue for any managed aquifer recharge (MAR) system is the decline of permeability, typically called clogging (Dillon *et al.* 2001). Clogging is an inevitable problem and recognized as perhaps the most significant challenge in MAR operations; it is attributed to physical, chemical and biological processes. According to survey data, physical clogging is the most common, affecting 70% of MAR cases (Dillon *et al.* 1994).

Suspension clogging, gas clogging and compaction clogging are all types of physical clogging, with clogging caused by suspended particles being the most common (Xiao & Reddi 2000). Suspended particles include colloids (diameter: <1 μm), intermediate (diameter: 1–30 μm) and

large (diameter: >30 μm) particles. Most research on physical clogging mechanisms has focused on large particles (Rinckpfeiffer *et al.* 2000; Rehg *et al.* 2005; Ye *et al.* 2010), with clogging that arises from a colloidal suspension in the MAR process having been much less studied. Mays & Hunt (2005) concluded that solution pH, ionic strength (IS) and exchangeable ions together determine colloid stability, and hence the morphology of the deposited colloids and the resulting permeability of the formation. However, there is little experimental data on the effects of colloid effects on clogging in the MAR process. One exception was Roth *et al.* (2015), who showed that a reduction in permeability was strongly associated with the fractal dimension of the deposited colloid's morphology. However, the transport, release and deposition of colloids in porous media are very complicated, as the colloids are simultaneously under the influence of various factors, including

IS, surface roughness and hydrodynamic conditions (Bradford *et al.* 2009a, 2009b; Bradford *et al.* 2011; Mesticou *et al.* 2014; Sasidharan *et al.* 2014). Consequently, the mechanisms of clogging by colloids need to be studied in greater detail. In this study, we examined the clogging of porous media by colloids and the influence of IS and media roughness.

MATERIAL AND METHODS

Colloids and electrolyte solution

The colloid (Thermo Scientific Corp.) was composed of polystyrene microspheres (2 μm in diameter) dyed with green fluorescent dyes and packaged as aqueous suspensions (1% (w/w) solids and a density of $1.06 \, \text{g/cm}^3$) in deionized water. The stock colloid solution was diluted 312 times with electrolyte solution for the transport experiments.

It was found that when the IS was <50 mM, the deposition behavior of the colloid was likely to be obstructed by energy barriers within the colloid particles, but when IS > 100 mM, the conditions favored irreversible colloid deposition on the sand surface (Treumann *et al.* 2014). So, the recharge water ionic strength was reproduced using Milli-Q water and NaCl with values of 0 mM, 30 mM and 150 mM.

Porous media

River sand (no manufacturers) and glass beads (Chemical Laboratory Equipment Company, China) served as the porous media in the column experiments. The river sand and glass beads were each thoroughly rinsed with Milli-Q water to eliminate background impurities and then soaked in 37% (w/w) hydrochloric acid for 24 h to remove metals from the surface. The medium was then rinsed with Milli-Q water until the liquid supernatant reached pH 5.89. The river sand had a median grain size of 254.8 μm in diameter, as determined by a laser scattering particle size analyzer (Bettersize2000, Baxter Company, China). According to the manufacturer, the median grain size of the glass beads ranged from 224 to 250 μm in diameter.

Column experiments

The experimental set-up included a column, a peristaltic pump (BT100-1F, Longer Company, China), a fraction collector (CBS-A, Huxi Company, China), two pressure transmitters (A-10, WIKA Company, Germany), and a data acquisition system (Figure 1). The column was made of plexiglass and measured 16 cm in length with a 2-cm internal diameter. Gauze mesh placed inside the end caps was used to support the porous media and also helped spread the input solution laterally throughout the column. The column was wet packed with the river sand or glass beads.

The peristaltic pump was used to move solutions from the supply bottle into the column at a constant Darcy velocity (v) of 5 m/d. Flow direction was vertically upward. Note that the potential effect of gravity on the kinetics of colloid transport and deposition was not considered in the present study. Colloid transport was assessed by injecting of a pulse of the colloid suspension into the column for 460 min (i.e., phase 1), followed by the injection of a colloid-free solution of the same chemistry for 100 min (i.e., phase 2). A fully-automated sample collector continuously gathered the effluent samples at specified time intervals (approximately every 11.5 min) and then measured them with an ultraviolet spectrophotometer (PerkinElmer, USA) at a wavelength of 486 nm. A linear correlation was established between the absorbance reading
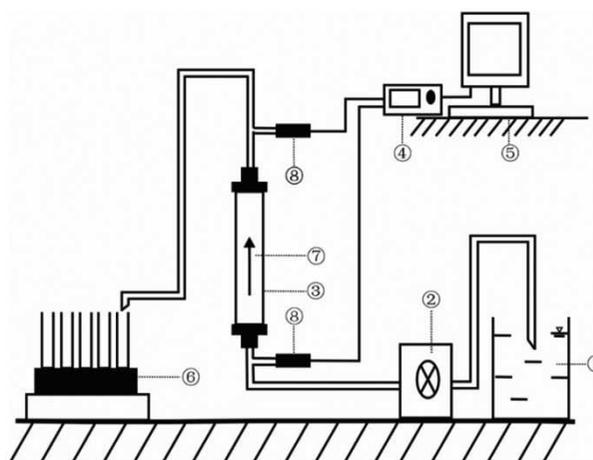

Figure 1 | Experiment set-up for the colloid clogging experiments. ① Solution; ② Peristaltic pump; ③ Column; ④ Data acquisition system; ⑤ Computer; ⑥ Fraction collector; ⑦ Flow direction; ⑧ Transducer.

Table 1 │ Summary of the conditions used in column experiments

Number	Porous medium	IS (mM)	Flow velocity (m/d)	Phase1	Phase2
Ec1	River sand	0	5	Colloid solution	Background solution
Ec2	River sand	30	5		
Ec3	River sand	150	5		
Ec4	Glass beads	0	5		

and the colloid concentration following the procedure described by Grolimund *et al.* (1996). The pressure at the inlet and outlet of the column was monitored via transmitters. The sequence of influent solutions and flow rates for each experiment are summarized in Table 1.

At the end of the experiment, the sand or beads were excavated at 1 cm intervals from the column and placed in a centrifuge tube that contained the same electrolyte solution as used in phase 1. The tube was shaken vigorously with a vortex mixer for 3 min to separate the retained colloids from the collector surface. Next, the colloid concentration in the electrolyte solution was measured by an ultraviolet spectrophotometer.

Hydraulic conductivity

The hydraulic conductivity (K) of the porous medium in each column was calculated by Darcy's law (Mbonimpa *et al.* 2002).

$$K = \frac{QL}{A\Delta H} \tag{1}$$

where Q (m³/d) is the flow rate, L (m) is the length of the column, A (m²) is the cross-sectional area of the column, and ΔH (m) is the difference in hydraulic head between the inlet and outlet points of the column.

RESULTS AND DISCUSSION

Effect of ionic strength on clogging

The effect of IS on the permeability decline of the porous medium is shown in Figure 2. A fast reduction in permeability occurred within 10 min for experiment Ec3,
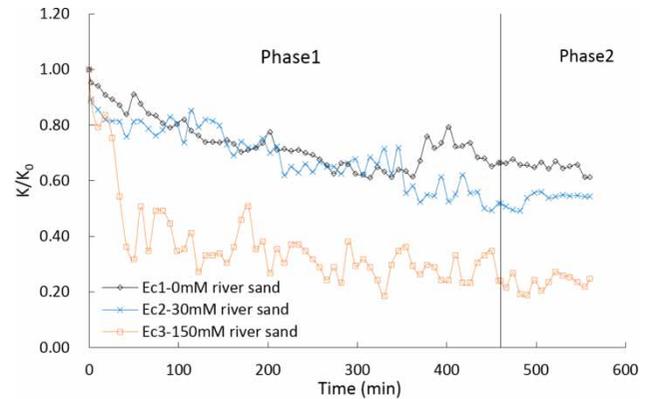
Figure 2 │ Comparison of permeability change at different ionic strengths.

35 min for experiment Ec2, and 90 min for the experiment Ec1 (Figure 2). Experiment Ec3 had both a greater rate of decrease in permeability and lower permeability than experiments Ec1 and Ec2. The effluent concentrations (C) were normalized against the inlet concentrations (C_0) to describe colloid transport. The corresponding breakthrough curves (relative effluent concentrations (C/C_0) were plotted as a function of time) showed that almost no colloids were able to penetrate the column under high ionic strengths of 30 mM and 150 mM NaCl, whereas around 80% of colloids could move through the column under a very low ionic strength of 0 mM NaCl (Figure 3). These phenomena thus showed that high ionic strength facilitated a greater attachment of colloids in sand (Gamerdinger & Kaplan 2001; Zhou *et al.* 2011; Torkzaban *et al.* 2015). Hence, the clogging process was highly dependent on the IS of the recharge suspension used.
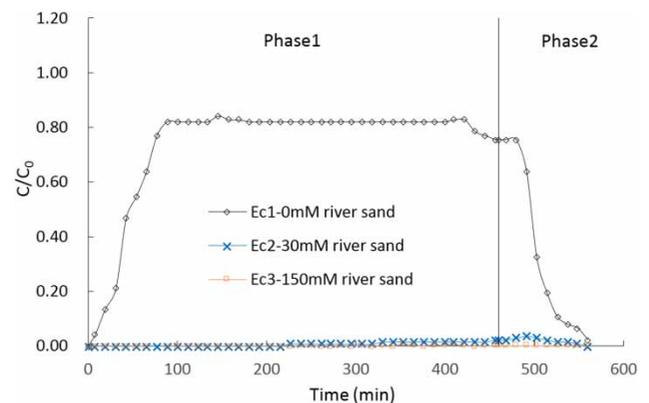
Figure 3 │ Breakthrough curves of colloidal suspension at different ionic strengths.

The results of dismantling the columns of experiments Ec1, Ec2 and Ec3 are shown in Figure 4. An exponential distribution of deposited colloids was found under high ionic strengths of 30 mM and 150 mM, while a relatively even deposition profile was found under a low ionic strength of 0 mM. Therefore, the colloid clogging in porous media was prone to superficial clogging under high ionic strength and mixed or inner clogging (Du *et al.* 2014) under low ionic strength.

The results shown in Figures 2–4 can be explained using Derjauin–Landau–Verwey–Overbeek (DLVO) theory (Deraguin & Landau 1941; Verwey & Overbeek 1948). A DLVO interaction energy profile is constructed from the total interaction energy (the sum of van der Waals attraction and double layer forces) as a function of the separation distance between a colloid and a collector surface. When the interacting surfaces are like-charged, the double layer force is repulsive and a typical DLVO energy profile is characterized by a deep attractive well (the primary minimum) at a small separation distance, a maximum energy barrier and a shallow attractive well (the secondary minimum) at a larger distance (Shen *et al.* 2007). According to DLVO theory, increasing ionic strength decreases the height of the energy barrier and increases the depth of the secondary minimum, and ultimately, the energy barrier disappears, leaving only the primary minimum well in the energy profile (Hahn & O'Meliae 2004). Therefore, increasing the ionic strength of an injected solution facilitates colloid deposition on the grain surface; this can then block the pore throats between porous particles, leading to severe clogging.
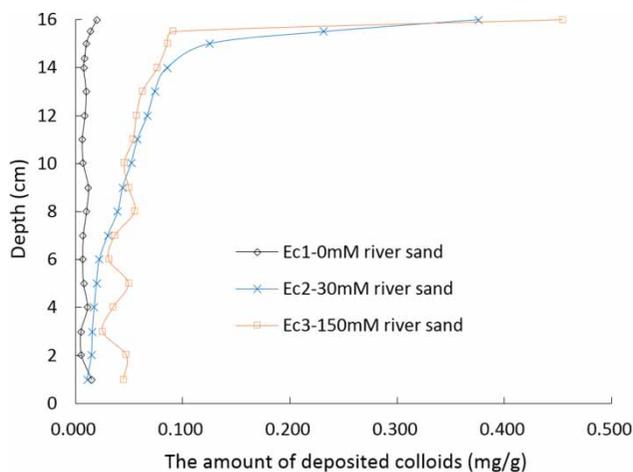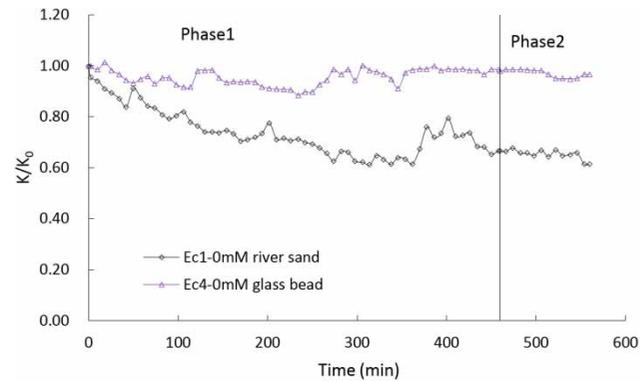

Figure 5 | Comparison of permeability change profiles for different surface roughness conditions.

Surface roughness effects on clogging

The hydraulic conductivity change (Figure 5) and breakthrough curves (Figure 6) for experiments Ec1 and Ec4 show that the most important difference between experiments Ec1 and Ec4 was the roughness of the infiltration medium. For the glass beads, there was no obvious clogging observed and the permeability stayed relatively stable in both phases. However, the permeability change of river sand differs entirely from that of glass beads. The result indicates that the grain surface roughness contributes to porous medium clogging.

The breakthrough curves for experiments Ec1 and Ec4 are very similar. During phase 1, both curves rose rapidly and then reached a stable state, but the rate of increase and the stable peak value of effluent colloid concentration
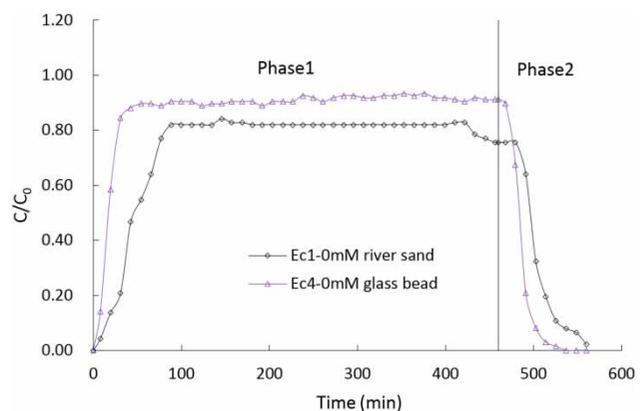

Figure 4 | Deposition profile of colloids at different ionic strengths.

Figure 6 | Breakthrough curves of colloidal suspension under different surface roughness conditions.
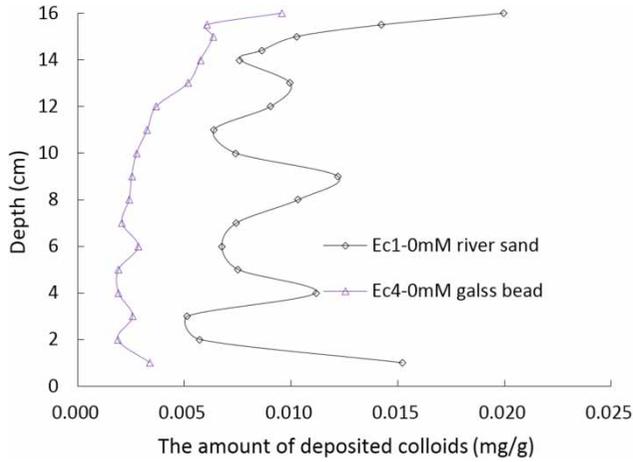
Figure 7 | Spatial distribution of deposited colloids under different surface roughness conditions.

in experiment Ec4 were faster and higher than those seen in experiment Ec1. During experiment phase 2, the injection suspension was changed into a colloid-free background solution, and the effluent concentration in experiment Ec4 declined more rapidly than it did in experiment Ec1. Therefore, under the same conditions, a porous medium with a smooth surface facilitates the transport of colloid.

The deposition profile of colloids in experiment Ec1 and Ec4 are shown in Figure 7. Along the whole column, the spatial distribution of the deposited colloids was similar to each other. The total amount of deposited colloids in experiment Ec4 was only 0.66 mg more than that in experiment Ec1.

The study indicated that a relatively rough porous medium contributed to the deposition of colloids. Here, DLVO theory is also employed to explain the results. Knowledge of the interaction energy between a colloid and a collector surface is of great importance in the prediction of colloid attachment behavior in porous media. A number of theoretical studies have shown that surface roughness reduces interaction energy barrier and thus favors colloid attachment in primary minima (Huang *et al.* 2010; Henry *et al.* 2011; Shen *et al.* 2012; Torkzaban & Bradford 2016). Whereas at a low ionic strength, the secondary minimum decreases and can disappear from the DLVO interaction energy (Hahn & O'Meliae 2004). Thus, the colloids in experiment Ec1 and Ec4 are mainly attached in the primary minima and a rough surface facilitates colloid deposition on porous media.

Mechanism of colloid clogging

Permeability reduction was found in all of the experiments (Figures 2 and 5), which means that colloid plays an important role in the clogging of porous media. The recharge mass of colloid (M_R) and the retained mass of colloid (M_{Re}) in the sand columns can be calculated based on the colloid concentration of the suspension, the experiment duration and the transport breakthrough curves. The volume of retained colloid (V_{Re}) in the column can be calculated by considering colloidal particle densities of 2.1 g/cm^3, and the volume of pore space (V_P) in column can be calculated based on a porosity of 0.4. The occupied proportion of retained colloid to the pore space volume of the sand column (V_{Re}/V_P) was calculated as small values of 8.79×10^{-6} to 1.55×10^{-4}, and the stable relative hydraulic conductivity of around 96%–30% can be determined from Figures 2 and 5 (Table 2).

Based on the data from Table 2, the retained colloid only occupied a very small proportion of the pore space, so a change of porosity can be neglected. Obviously, the relationship between hydraulic conductivity and porosity could not be interpreted by using the Kozeny–Carman equation (Equation (2)), which is the most common approach for estimating the permeability of the porous media (Roth *et al.* 2015). So, the decrease of hydraulic conductivity was not caused by clogging of the whole pore space, but only at the pore throat (Figure 8).

$$K = \frac{n^3}{(1 - n^2)} \frac{d_{50}^2}{180} \tag{2}$$

where K is hydraulic conductivity (m/s), n (−) is the porosity of porous media and d_{50} is median grain size (mm).

Table 2 | Comparison of V_{Re}/V_P and K/K_0

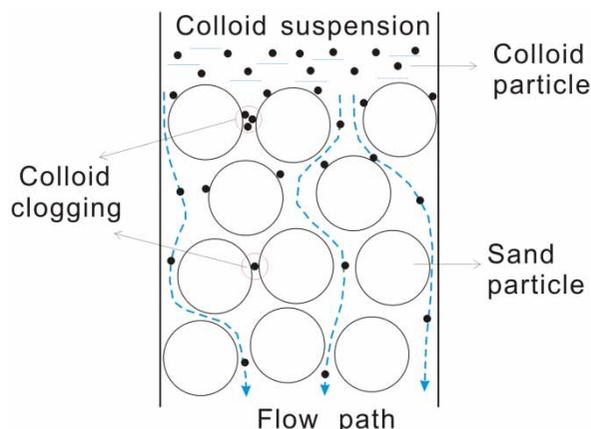| Porous media	River sand			Glass beads
IS (mM)	0	30	150	0
M_R (mg)	7.092	7.092	7.092	7.092
M_{Re} (mg)	1.050	6.992	7.057	0.390
V_{Re} (cm^3)	0.00050	0.00333	0.00336	0.00019
V_P (cm^3)	21.61			
V_{Re}/V_P (−)	2.31×10^{-5}	1.54×10^{-4}	1.55×10^{-4}	8.79×10^{-6}
K/K_0 (−)	65%	55%	30%	96%

Figure 8 │ A conceptual illustration of colloid clogging position in porous media.

CONCLUSIONS

The set of experimental results showed that colloids in recharge water play an important role in the clogging process of saturated porous media, and even a very small quantity of colloid may cause a large reduction in the permeability of porous media. Clogging at the pore throat was inferred as the main reason for the severe permeability reduction of the porous media. The temporal and spatial distribution and the extent of colloid clogging were both influenced by factors that affect the transport and release of colloids in a porous medium, and this may usually be explained by DLVO theory. A high ionic strength of recharge water enables more colloids to attach onto the surface of saturated porous media, thus leading to superficial clogging, while a rough surface of collectors leads to greater clogging than a smooth surface.

Considering the rapid and severe colloid clogging of porous media, further detailed investigations of the mechanisms and quantitative relationships between permeability change and colloid transport and retention in porous media are being investigated. In a further study, the colloid concentration, flow velocity, and other influencing factors in colloid clogging should be studied.

ACKNOWLEDGEMENTS

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