

# Column experiments to investigate transport of colloidal humic acid through porous media during managed aquifer recharge

Dan Liu<sup>1,2</sup> · Jingjing Zhou<sup>1,2</sup> · Wenjing Zhang<sup>1,2</sup> · Ying Huan<sup>1,2</sup> · Xipeng Yu<sup>1,2</sup> · Fulin Li<sup>3</sup> · Xuequn Chen<sup>3</sup>

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**Abstract** Colloids act as vectors for pollutants in groundwater, thereby creating a series of environmental problems. While managed aquifer recharge plays an important role in protecting groundwater resources and controlling land subsidence, it has a significant effect on the transport of colloids. In this study, particle size and zeta potential of colloidal humic acid (HA) have been measured to determine the effects of different hydrochemistry conditions. Column experiments were conducted to examine the effects on the transport of colloidal HA under varying conditions of pH (5, 7, 9), ionic strength (<math>0.0005, 0.02, 0.05\text{ M}</math>), cation valence ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) and flow rate (0.1, 0.2, 0.4 ml/min) through collectors (glass beads) to model the properties and quality of artificial recharge water and changes in the hydrodynamic field. Breakthrough curves showed that the behavior of colloidal HA being transported varied depending on the conditions. Colloid transport was strongly influenced by hydrochemical and hydrodynamic conditions. With decreasing pH or increasing ionic strength, a decrease in the peak effluent concentration of colloidal HA and increase in deposition could be clearly seen. Comparison of different cation valence tests indicated that changes in transport and deposition were more pronounced with divalent  $\text{Ca}^{2+}$  than with monovalent  $\text{Na}^+$ . Changes in hydrodynamic field (flow rate) also had an impact on

transportation of colloidal HA. The results of this study highlight the need for further research in this area.

**Keywords** Organic colloid · Transport · Artificial recharge · Deposition · Laboratory experiments

## Introduction

Groundwater is an important component of water resources, and is widely used for irrigation, industrial and domestic water supply. Many environmental problems such as land subsidence, land collapse, and saltwater intrusion, have been caused by groundwater over-exploitation (Huang et al. 2012). Managed aquifer recharge is an effective means to solve these problems (Zhang et al. 2015). The water used during managed aquifer recharge has variable chemical and physical properties, which results in changes in the hydrochemistry and hydrodynamics of groundwater (Vanderzalm et al. 2010).

Colloidal science began in the first part of the 19th century. Colloidal contaminant transport is recognized as an important aspect of this science (Lvjiajun 2013); indeed, failure to consider colloid-facilitated contaminant transport will result in an underestimation of the transport range of contaminants (McGechan and Lewis 2002; Thorsten et al. 2014). There may be a wide variety of inorganic, organic, and microbiological colloids in the subsurface (McCarthy and Zachara 1989). Colloids facilitate the transport of a wide variety of adsorbed contaminants over significant distances (Jonge et al. 2004). Colloids have a strong contaminant adsorption capacity, and affect the rate of contaminant migration (Kretzschmar et al. 1999); thus, colloid transport in the subsurface may result in enhanced contaminant transport. To obtain an improved insight into the influence of subsurface contaminant transport by

✉ Wenjing Zhang  
zhangwenjing80@hotmail.com

<sup>1</sup> Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, China

<sup>2</sup> College of Environment and Resources, Jilin University, Changchun 130021, China

<sup>3</sup> Water Resources Research Institute of Shandong Province, Jinan 250000, China

colloids, an understanding of the transport and deposition of colloids through porous media is needed. The first step in studies of colloid-facilitated contaminant transport is therefore to gain an insight into the migration behavior of the individual colloids.

A considerable number of studies have examined the transport and deposition of colloids in porous media (Liu et al. 1995). The transport of colloids in groundwater is a very important part of this research, but artificial colloids such as carboxylated latex were mostly used in these experiments (Yan et al. 1995). In this study, natural humic acid (HA) was chosen, which originates from decayed plants and animals widely found in subsurface water. Humic acid, an organic compound or macromolecule, is widespread in aquifers because of its unique properties, and has a substantial effect on the transport of subsurface chemicals (Gao et al. 2011; Zhu et al. 2014). It contains hydrophilic aromatic rings linked by carbon chains with different functional groups including carboxyls, phenols, and alcohols (Parent and Velegol 2004). It associates easily with metal ions, minerals, and bacteria through surface interactions because of its high specific surface area, large number of negative charges, and abundant functional groups.

Many studies have shown that the physicochemical properties of colloidal HA can vary depending on the pH and ionic strength of the suspension (Balnois et al. 1999; Parent and Darrell 2014). The factors that control colloidal HA transport and fate in the subsurface have also been explored in many column experiments—for example, in their recent study, Yamashita et al. (2013) used column experiments to explore the influence of a wide range of monovalent and divalent electrolyte concentrations and found that ionic strength had a significant effect on colloidal transport, especially on divalent cations. Other researchers have conducted similar studies (Sojitra et al. 1995). While some studies have explored the transport of colloidal HA, there is still a need for a deeper insight into the transport of colloidal HA in subsurface environments during managed aquifer recharge.

The physicochemical properties of colloidal HA and its transportation are affected by pH, ionic strength (IS), and flow rate. However, there is a lack of information about the transport and deposition of colloidal HA during managed aquifer recharge. A systematic understanding on the colloidal HA transport in porous media under different hydrochemical and hydrodynamic conditions is still lacking. Therefore, the objective of this study was to use a laboratory model to investigate the influence of hydrochemistry and hydrodynamic conditions on the transport and deposition of colloids in porous media during managed aquifer recharge. The recharge water used in managed aquifer recharge varies, and may comprise sources such as rainfall runoff, base flow from rivers, and purified wastewater. During the recharge process, the groundwater quality will be influenced by introduced colloids and intimal

colloids. It is particularly important therefore to have reliable information about how individual colloids behave during managed aquifer recharge. In this investigation, a suspension was prepared in the laboratory to better control the hydrochemistry conditions of simulated recharge water. The influent suspension with varying conditions simulates different hydrochemistry conditions of recharge water. Flushing with deionized water was used to study the colloidal HA release process when the water chemistry conditions change; in addition, different hydrodynamic conditions were simulated by varying flow rates.

## Materials and methods

### Experimental materials

#### *Porous media*

The study used spherical glass beads, sieved with an average diameter of 0.45 mm, with a net negative charge as the model medium to eliminate uncertainties in the transport behavior of colloidal HA through porous media caused by heterogeneity and differing interface properties in natural soil. The glass beads had a chemical composition of 75.29 % SiO<sub>2</sub>, 13.26 % Na<sub>2</sub>O, 7.15 % CaO, and 4.30 % MgO by weight, and did not react chemically with the solutions. The zeta potential of the glass beads stored in deionized water at pH 7 was −18.94 mV.

Before filling the column, the glass beads were soaked in 0.1 M NaOH<sub>(aq)</sub> for about 3 h to remove surface impurities, rinsed with deionized water until the pH of the effluent became stable; they were then further soaked with 0.1 M HNO<sub>3(aq)</sub> for about 3 h, and then washed with deionized water until the pH of the effluent became stable. The glass beads were dried in an oven at 105 °C and stored in sterile beakers before being packed in the columns.

#### *Colloidal HA*

Colloidal HA, namely Suwannee River HA (SRHA) standard II, purchased from the International Humic Substance Society (Colorado, USA) was used as colloid particles in the column transport experiments. The composition and hydrochemical properties of the SRHA are shown in Table 1 (Hong and Elimelech 1997).

**Table 1** Chemical composition of SRHA standard II

Parameter	Ash	C	H	O	N	S	P
Proportion (%)	1.04	52.63	4.28	42.04	1.17	0.54	0.013

Note: Ash is inorganic components in dry sample

A 20-mg aliquot of dry HA was introduced into 100 ml of MilliQ deionized water (Millipore, Bedford, Massachusetts, USA), and sonicated for 30 min to disperse the HA uniformly. The pH of the suspension was 4.5. Based on the concentration level, total organic carbon in groundwater, and the chemical composition of HA, the preparation of colloidal HA in suspension was diluted to 10 mg/L, and stored in the dark at 4 °C and re-sonicated before use.

### Solution chemistry

The transport of colloidal HA in porous media was examined under different pH and ionic strength conditions. The pH was adjusted from 4.5 to 5, 7, and 9 by adding  $\text{NaOH}_{(\text{aq})}$ . The inorganic compounds  $\text{NaCl}_{(\text{aq})}$  and  $\text{CaCl}_{2(\text{aq})}$  were used as electrolytes to adjust the ionic strength of the suspension from 0 to 0.02 M and 0.05 M to study the effect of concentration of electrolytes and cation types. The suspensions were then sonicated again and stored at 10 °C to simulate subsurface conditions. Deionized water was used as the aqueous solvent.

## Experimental apparatus and method

### Column transport experiment apparatus

Column experiments were conducted in glass chromatography columns with an effective length of 6.0 cm and an internal diameter of 3.2 cm. The columns were packed with glass beads and were saturated with deionized water from bottom to top to minimize air entrapment. The estimated porosity of the porous medium measured by weight method ranged from 0.40 to 0.45. A filter membrane was fixed at both ends of the columns to prevent leaching of the glass beads. A peristaltic pump (BT-100, Longer Pump, Baoding, China) was used to

pump influent solution through the column at a default constant speed of 0.2 ml/min. An ultraviolet spectrophotometer (UV-1800, SHIMZU, Japan) connected to a PC and with a flow cell at a wavelength of 212 nm was used to monitor the temporal variations in the concentration of colloidal HA in the effluent. The colloid concentration-absorbance standard curve of the relationship between absorbance and the concentration of the colloidal HA was used to calculate the change in the concentrations of colloidal HA. Finally, the column effluents were collected in an automatic fraction collector at fixed time intervals of 30 min to confirm the concentration of total organic carbon in the effluent and to verify the reliability of the experimental data. To simulate the groundwater environment, the column and the experimental solution were kept in a fridge at 10 °C, and all the experiments were finished under saturated conditions. The experimental setup is shown in Fig. 1.

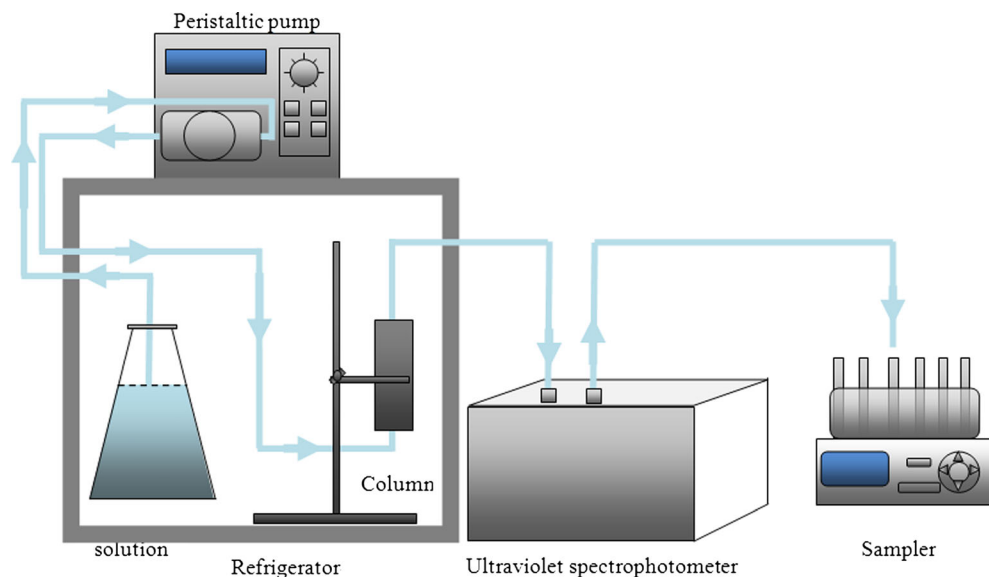
### Experimental method

Column transport experiments were conducted to determine the effect of hydrochemical and hydrodynamic conditions on the transport and deposition behavior of colloidal HA in saturated porous media. Four sets of column experiments were carried out to determine the effect of:

pH (pH = 5, 7, 9)  
 IS (IS = 0, 0.02, 0.05M)  
 cation valence ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ )  
 flow rate (0.1, 0.2, and 0.4 ml/min)

Before each experiment, the porous medium was saturated by continually injecting with deionized water from bottom to top at a constant low rate of 0.2 ml/min (corresponding to a Darcy velocity of approximately 0.9 m/d) without allowing any air to

**Fig. 1** Diagram of the experimental setup



enter for 24 h until the pH of the effluent was stable. It should be noted that the Darcy velocity is representative of field conditions.

When the columns were saturated, tracer experiments with a 10 mg/L potassium iodide solution were conducted in each group. Iodide ions were completely conserved against the surface of glass beads and were detectable at a wavelength of 280 nm by the ultraviolet spectrophotometer, and the tracer showed identical optimal breakthrough behavior. Tracer experiments also determined the PV from breakthrough curves (BTCs) of 15 ml (Kretzschmar et al. 1997).

A two-stage column test was performed for experiments 1–3. Four PV colloidal HA suspensions (stage 1) were injected at 0.2 ml/min. A three-way valve was then used to quickly replace colloidal HA solution with deionized water. This was introduced upwards into the column at the same flow rate (stage 2). This period lasted for 21 PV until there were no colloids in the effluent.

In experiment 4, the influence of flow rate on colloidal HA was determined. A 4 PV colloidal HA suspension was injected at rates of 0.1, 0.2, and 0.4 ml/min for each group of experiments, and then replaced with deionized water for 21 PV until there were no colloids in the effluent.

### Colloidal deposition rate coefficient

According to the first-order deposition kinetics theory and the convection-diffusion formula, a colloid deposition rate coefficient ( $K$ ) is needed to calculate the amount of colloidal HA deposition in the column. This coefficient was determined according to Eq. (1) (Elimelech et al. 2000):

$$K = -\frac{U}{\varepsilon L} \ln\left(\frac{C}{C_0}\right) \quad (1)$$

where  $U$  is the flow rate (m/s),  $\varepsilon$  is the porosity of the porous medium (dimensionless),  $L$  is the effective length of the column (m), and  $\frac{C}{C_0}$  corresponds to the proportion of the colloids that were recovered in the effluent after the breakthrough curve had reached a plateau.

## Results and discussion

### Characterization of colloidal humic acid

The size and zeta potential are of importance for determining the stability of colloidal HA. In this study, the major particle size and zeta potential of the colloidal HA were thus detected under different pH (5, 7, 9) and ionic strength conditions (0, 0.02, 0.05 M) in NaCl and CaCl<sub>2</sub> solutions by a zetasizer (Malvern Zetasizer, Nano ZS, Malvern, UK). The results are presented in Table 2.

#### Zeta potential of the colloidal humic acid

The stability of colloidal HA in suspension has a significant influence on colloid transport and adsorption behaviors in porous media. The zeta potential of the colloidal HA was detected in triplicate at the experimental conditions by a zetasizer. The colloidal HA with abundant functional groups and is negatively charged. The results show that the negative zeta potential of HA was  $-17.8$  mV when the pH was 5 and more negative as the pH increased from 5 to 9 for an IS of 0. Only carboxylic groups will be dissociated under acidic and neutral conditions; however, as the pH increases, both carboxylic and phenolic groups will be dissociated under alkaline conditions. In contrast, as the ionic strength increases at pH 7.0 the absolute zeta potential decreases, compression of the electrostatic double layer at higher ionic strengths results in decreases in both the electrostatic repulsive and the stability, and aggregation is likely to occur (Torkzaban et al. 2008).

#### Size of colloidal humic acid

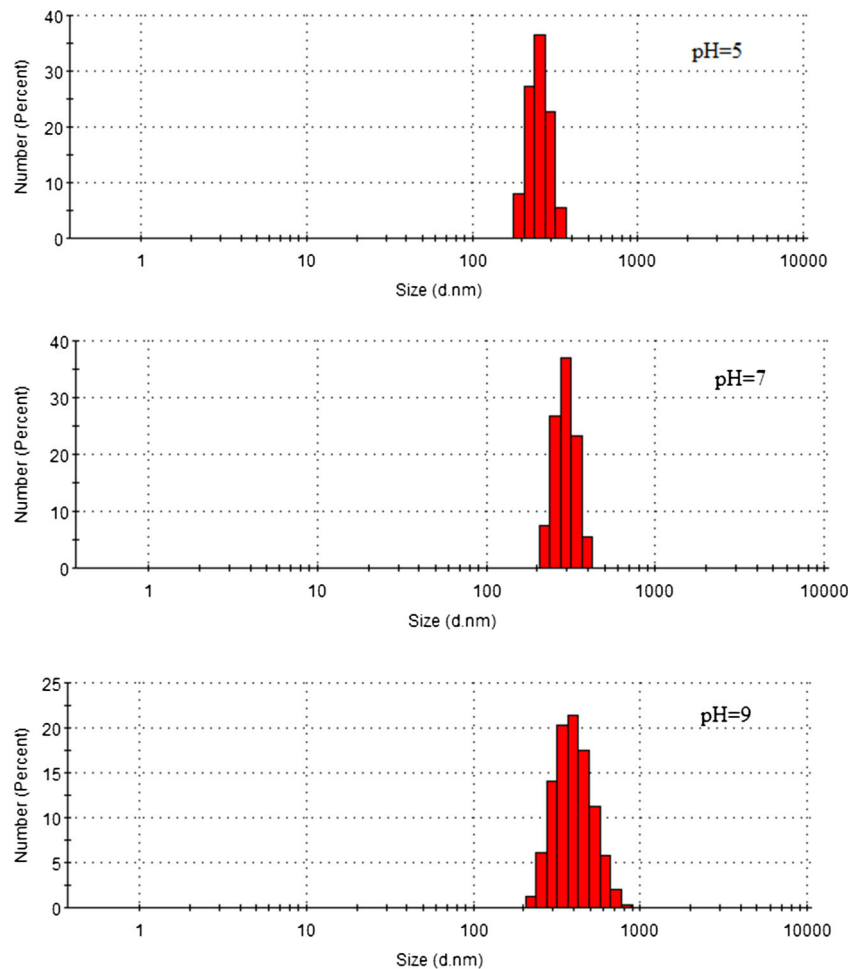
Previous research results (Alvarez-Puebla and Garrido 2005) showed that particle size of colloidal HA varied under different conditions, and that it had an influence on the stability and aggregation in the suspension. Changes in pH had an obvious influence on particle size (Fig. 2). When the pH was 5 (acidic

**Table 2** Characterization of colloidal humic acid suspension

pH	IS (M)	Humic acid (mg/L)	PdI	Pk1 Mean (d.nm)	Pk2 Mean (d.nm)	Pk3 Mean (d.nm)	Pk1 area (%)	Pk2 area (%)	Pk3 area (%)	ZP (mv) ( $\pm 0.8$ –2.5)
5	0.00	10	0.794	259.8	0	0	100	0	0	-17.8
7	0.00	10	0.554	300.8	0	0	100	0	0	-27.0
9	0.00	10	0.530	448.4	5441	0	91.9	8.1	0	-42.4
7	0.02 (NaCl)	10	0.891	331.4	0	0	100	0	0	-22.6
7	0.05 (NaCl)	10	0.726	432.7	5351	0	76.6	23.4	0	-21.5
7	0.02 (CaCl <sub>2</sub> )	10	0.746	562.6	0	0	100	0	0	-9.25
7	0.05 (CaCl <sub>2</sub> )	10	0.922	641.1	0	0	100	0	0	-8.82

Note: IS ionic strength; PdI poly dispersity index; ZP zeta potential; Pk Mean and Pk Area display the size and percentage by number for up to three peaks within the result

**Fig. 2** Particle size distribution by number in different pH conditions (IS = 0)



conditions), the majority of HA had a particle size of around 259.8 nm; when the pH was adjusted to 7, it was about 300.8 nm, and was larger than that in acid conditions; when the pH increased to 9, it was 448.4 nm. This is because with increasing pH, the particle size also increases, because of the dissociation of functional groups. Besides, changes in ionic strength also had an effect on the particle size (Fig. 3), when the ionic strength was adjusted from 0 to 0.05 M with NaCl, the particle size increased from 300.8 to 432.7 nm; when the ionic strength was adjusted with CaCl<sub>2</sub>, the particle size increased sharply from 300.8 to 641.1 nm. Small basic units that occur individually at low ionic strength interconnect together at high ionic strength. Besides, divalent cations (Ca<sup>2+</sup>) have a greater influence than monovalent cations (Na<sup>+</sup>); divalent cations have a greater capacity to neutralize more negative charges, resulting in increases in particle size.

### Column transport experiment

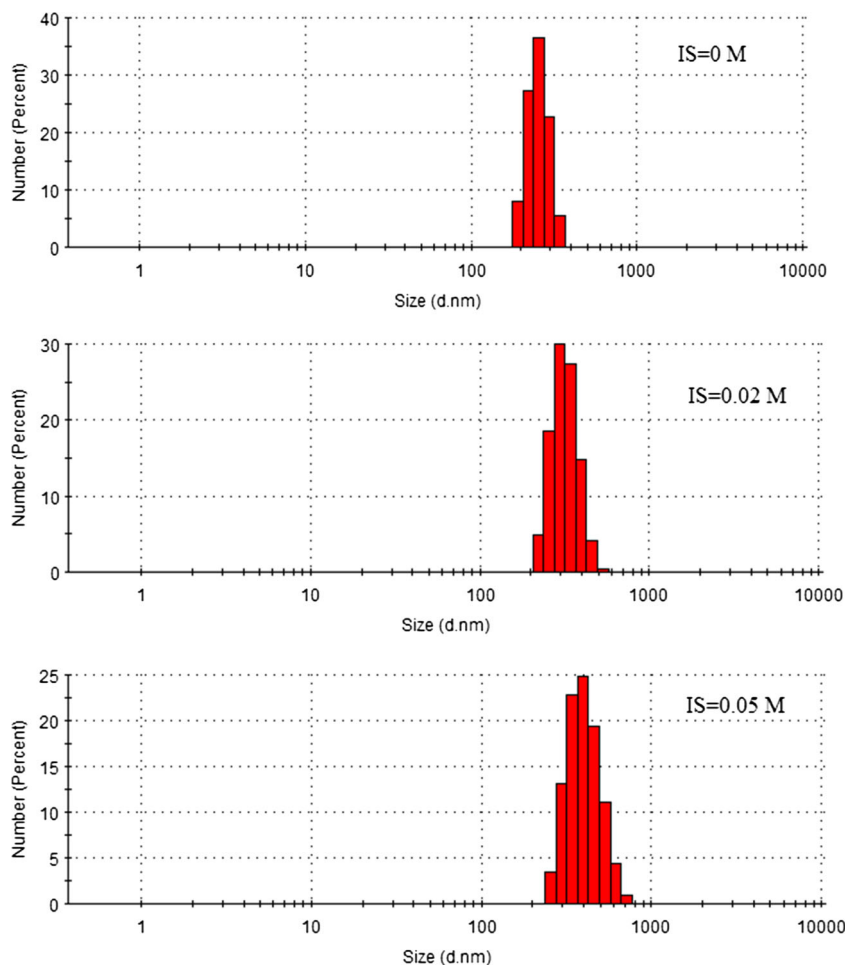
Ten groups of experiments were carried out. The experimental conditions and results are listed in Tables 3 and 4.

### Effects of pH on the transport of colloidal HA

The effects of pH on the transport of colloidal HA were identified in column transport experiments (tests A1, A2, and A3) and breakthrough curves shown in Fig. 4 at pH values of 5, 7, and 9. As shown in Fig. 4, under different pH conditions, the transport velocity is equal to the velocity of the tracer, and the peak concentration was reached at approximately 1.5 PV from the introduction of particles to reach peak concentration and remain stable. As shown, colloids were retained at a pH of 5, and not all the colloids were transported through the porous medium; however, as the pH increased, there was less deposition and peak concentration increased from 0.98 to 1.00. According to the colloid sedimentary dynamics, the colloid deposition rate coefficient  $K$  was  $3.94 \times 10^{-6}$ ,  $1.74 \times 10^{-6}$ , and  $4.63 \times 10^{-7}$ , for the pH values of 5, 7, and 9, respectively. The results for the different pH conditions showed that, when the pH increased from 5 to 7, various changes occurred because of the character of the colloids, as follows: the particle size of the colloidal HA and the absolute value of the zeta potential increased, the repulsion between colloids increased, and colloids were stable and facilitated colloid movement. These changes indicated that pH had a



**Fig. 3** Particle size distribution by number in different ionic strength conditions (pH = 7)



minimal influence on colloidal transport. A previous study (Sujoy Roy and Dzombak 1997) reported that transport of latex colloids in Eustis sand increased significantly when the pH increased, and the greater degree of increase in the earlier study relative to this study may have been attributable to the different

porous media. The breakthrough curve for pH 9 showed a slightly downward trend after the peak concentration was reached, because of variations in the structural properties at different pH values. When pH was between 5 and 9, the zeta potential changed from  $-17.8$  to  $-42.4$  mV. In acidic conditions,

**Table 3** Experimental conditions and results for column tests under different hydrochemical conditions

Influence factors	Test No.	pH	IS (mol/L)	Flow rate (ml/min)	Stage 1 (%)	Stage 2 (%)	Retain (%)	Peak $C/C_0$	$T_{peak}$ (min)	$R$	$K$ ( $s^{-1}$ )
pH	A1	5	0.00	0.20	72	12	16	0.98	135	1.06	$3.94 \times 10^{-6}$
	A2	7	0.00	0.20	74	14	12	0.99	120	1.06	$1.74 \times 10^{-6}$
	A3	9	0.00	0.20	59	32	9	1.00	112	1.11	$4.63 \times 10^{-7}$
IS (NaCl)	A1	5	0.00	0.20	72	12	16	0.98	135	1.06	$3.94 \times 10^{-6}$
	A4	5	0.02	0.20	74	17	9	0.95	190	1.10	$8.86 \times 10^{-6}$
	A5	5	0.05	0.20	64	15	21	0.92	210	1.13	$1.44 \times 10^{-5}$
IS (CaCl <sub>2</sub> )	A1	5	0.00	0.20	72	12	16	0.98	135	1.06	$3.94 \times 10^{-6}$
	A6	5	0.02	0.20	71	5	24	0.92	205	1.31	$1.44 \times 10^{-5}$
	A7	5	0.05	0.20	59	18	23	0.88	220	1.81	$2.21 \times 10^{-5}$

Note: *IS* ionic strength; *Stage 1* is the relative mass recovery in the effluents during the HA injection process; *Stage 2* is the relative mass recovery in the effluents during the deionized water washing process; *Retain* is the relative mass withheld in the glass beads; *Peak  $C/C_0$*  is the peak value of colloid recovered in the effluent after the HA breakthrough curve reached a plateau;  $T_{peak}$  is the time to reach the peak  $C/C_0$ ;  $R$  is the retardation coefficient calculated according to the breakthrough curve; and  $K$  is the deposition rate coefficient

**Table 4** Experimental conditions and results for column tests under different hydrodynamic conditions. (pH = 5, IS = 0)

Test No.	Flow rate (ml/min)	Stage 1 (%)	Stage 2 (%)	Retain (%)	Peak $C/C_0$	$T_{\text{peak}}$ (min)	$R$	$K$ ( $\text{s}^{-1}$ )
A8	0.1 ml/min	64	8	28	0.85	245	1.20	$7.05 \times 10^{-5}$
A1	0.2 ml/min	72	12	16	0.98	135	1.06	$3.94 \times 10^{-6}$
A9	0.4 ml/min	75	14	11	1.00	75	1.06	$4.34 \times 10^{-7}$

Note: Terminology is the same as Table 3

the carboxyl and hydroxyl groups are protonated, and the molecular electrostatic repulsion will decrease, which will cause shrinkage of the spherical particle shape. In alkaline conditions, the negative charge of the HA surface increases, the molecular electrostatic repulsion is higher than that in acidic conditions, and the molecular size of HA increases in chainlike structures. As the HA suspension is injected, the pH of the water in the column is changed to alkaline, and the HA is in chainlike structures, which will influence the transport of HA, resulting in a tendency to decrease slightly after the peak concentration is reached.

To test whether colloids were deposited and released during the transport experiments, scanning electron microscopy (SEM; JSM-6700 F, JEOL, Japan) and energy spectrum analysis (EDX; 333, JEOL, Japan) were used to characterize the microstructure and element composition of the porous medium. The results (pH = 5, IS = 0) are shown in Fig. 5. Before the transport experiments, the original glass beads had smooth surfaces and were composed of  $\text{SiO}_2$  and some metal oxides (Fig. 5a). Beyond 4PV, when colloidal HA suspension was passed through the glass beads, colloidal particles were adsorbed to the surface of glass beads and the carbon element emerged in the energy spectrum analysis, further illustrating colloid attachment to the surfaces of the glass beads (Fig. 5b). During the flushing process, there was still adsorption of colloidal HA on the surface of the glass beads and very little colloid detachment (Fig. 5c).

#### Effect of electrolyte valence on the transport of colloid

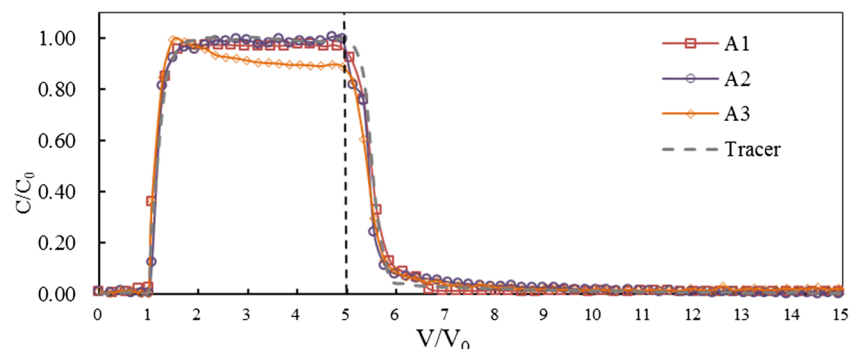
To determine the effect of solution IS and electrolyte valence on the transport and deposition of colloidal HA, column

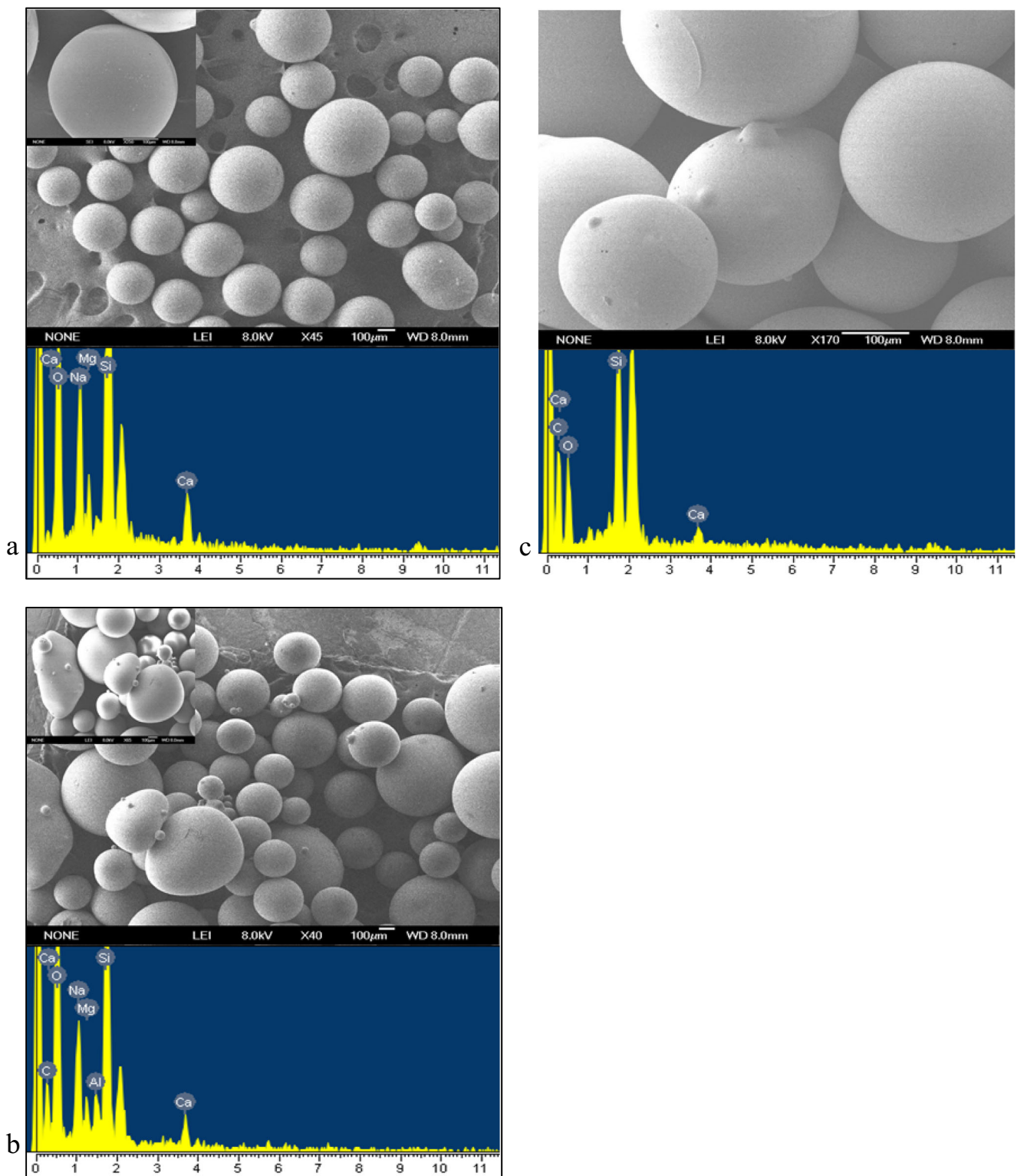
experiments were conducted. The breakthrough curves of the colloidal HA suspension at a specific pH of 5 at various IS concentrations (0, 0.02, 0.05 M) of two types of electrolytes ( $\text{NaCl}$  and  $\text{CaCl}_2$ ) are shown in Figs. 6 and 7.

It can be seen that IS has a strong effect on the transport and deposition of colloids. The transport velocities of the colloid and the tracer were initially the same, but with increasing IS, the peak effluent concentration decreased and the deposition of colloidal HA increased. When the IS was 0.02 M, it took about 1.5 PV for  $\text{NaCl}$  to reach the peak  $C/C_0$  of close to 0.95. However, for an IS of 0.05 M, it took around 3 PV to reach the peak  $C/C_0$  of close to 0.92, which is slower than the tracer. The breakthrough curves indicate that the colloid deposition rate coefficient ( $K$ ) were  $3.94 \times 10^{-6}$ ,  $8.86 \times 10^{-6}$ , and  $1.44 \times 10^{-5}$ , as IS increases from 0 to 0.05 M. The colloid deposition rate coefficient ( $K$ ) increased as the IS increased and more colloids were deposited. The results are similar to those for  $\text{CaCl}_2$  and agree with those of many other researches on the transport and deposition of colloids (Yan et al. 1995).

Changes in the deposition and detachment of colloidal HA passing through the porous medium with increases in IS are consistent with the predictions of the classical DLVO theory, and support the findings of earlier studies. The deposition process depends on the interactions between the colloid and collector. The surfaces of both colloidal HA and glass beads were negatively charged in the experiments. With the increasing of IS in the aqueous phase, the thicknesses of the electrical double layer decreased, leading to a reduction in electrostatic repulsion between colloidal HA and collectors, and to an increase of colloidal HA deposition. The van der Waals attractive

**Fig. 4** Breakthrough curves of humic colloidal suspension under different pH conditions (A1, A2, A3 are test numbers)





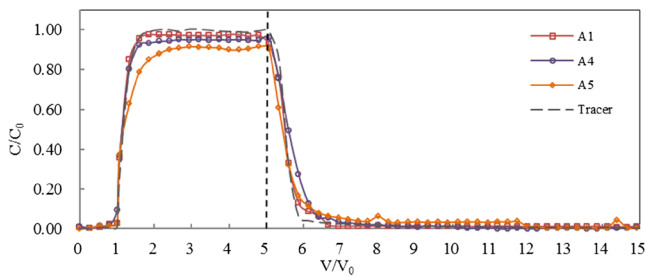
**Fig. 5** Transport experiments with porous media: scanning electron microscopy (SEM) and energy spectrum analysis (EDX). **a** Original porous medium of the transport experiments, **b** Porous medium after

the adsorption of colloidal HA, **c** Porous medium after the desorption of colloidal HA

forces are independent of solution chemistry (Sojitra et al. 1995). The breakthrough curves showed tailing when IS

was 0.05 M. Comparison showed that the release results at high and low IS values were different because of an





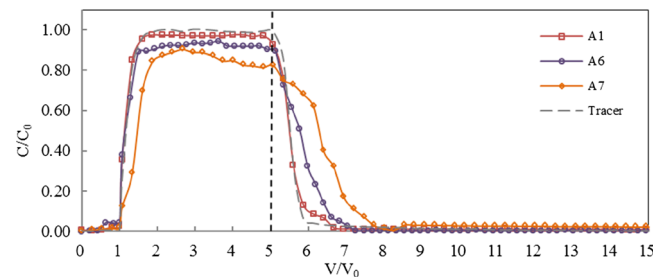
**Fig. 6** Breakthrough curves of colloidal HA suspension under various concentrations of NaCl

increase in the secondary minimum calculated by DLVO theory.

The type of cation also influences the transport of colloidal HA. The divalent cation  $\text{Ca}^{2+}$  has the same trend of breakthrough curves as NaCl electrolytes in the colloidal HA suspension, but the increase in the rate of deposition is considerable. The colloid transport rate decreased, and the time taken to reach a plateau increased as the IS increased, which clearly shows that  $\text{Ca}^{2+}$  has a greater influence on the transport of HA than NaCl. The value of  $C/C_0$  quickly reached a plateau of 0.92 with 0.05 M of NaCl, whereas it only reached 0.88 with 0.05 M of  $\text{CaCl}_2$ . The  $C/C_0$  values at each plateau decreased as the electrolyte concentration increased because the divalent cation had more influence on the conformation of HA. Divalent cations can neutralize more negative charges on the surface of HA than monovalent cations, thereby resulting in more compact networks of HA, similar to the results of other studies (Jada et al. 2006; Baalousha et al. 2006).

$\text{Ca}^{2+}$  is absorbed to the colloidal particle surface and the organic polymer on the surface of the colloidal HA bridges with divalent cations in the solution, which increases the complexation of functional groups of colloidal HA (Amirbahman and Olson 1995), promoting the union between colloidal particles, and decreases the transport ability of colloidal HA (Kai and Elimelech 2007). When there is  $\text{Ca}^{2+}$ , the breakthrough curves show significant tailing at colloid release stage, especially for an IS of 0.05 M conditions. In this study, the deionized water (IS = 0) used in the flushing process can be used to study the release of colloidal HA when the hydrochemical properties of the recharge water differ from those of previous processes. In contrast to previous studies, as the ionic strength decreased during the flushing process, the electrostatic interaction force between the colloids and porous medium was rebalanced and deposited colloidal HA was released.

Other studies have reported that as the ionic strength increased, the concentrations of colloidal HA in the effluent decreased (Yamashita et al. 2013). Previous studies (Akbour et al. 2013) did not report desorption of colloidal HA, irreversible attachment of colloidal HA onto porous media can be seen. It should be noted that in earlier studies, the same experimental conditions and colloid-free electrolyte solution were used in the flushing process to examine whether the



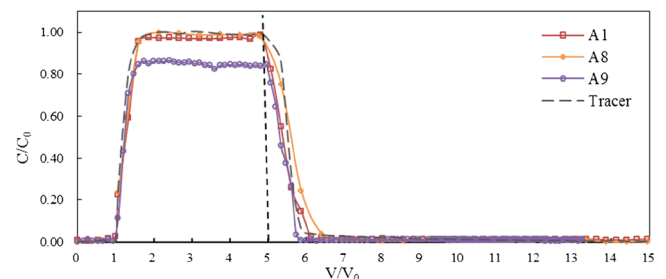
**Fig. 7** Breakthrough curves of colloidal HA suspension under various concentrations of  $\text{CaCl}_2$

attachment of colloidal HA onto the porous media was reversible. In this study, when deionized water was used in the flushing process, the deposition was reversible and tailing occurred, as shown in Fig. 7. Changes in hydrochemical conditions have a strong influence on desorption of colloidal HA, and should be considered in the process of managed aquifer recharge. Results from this study agree well with those reported by Shen (2007).

#### Effect of flow rate

The purpose of these experiments was to study the effect of flow rates on the transport of HA through the column. The breakthrough curves for injecting the HA suspension under different flow rates were measured (Fig. 8) and showed that the flow rate also had a significant effect on the transport and deposition of colloids. With high flow rates, the relative concentrations of the breakthrough curves were higher than for low flow rates. Colloid concentrations increased substantially when the flow rate increased from 0.1 to 0.2 ml/min. The peak  $C/C_0$  increased from 0.85 to 0.98, and the retardation coefficients calculated from the breakthrough curves were 1.20 and 1.06, respectively; however, further increases in the flow rate from 0.2 to 0.4 ml/min caused little increase in the transport of colloids. The peak  $C/C_0$  increased and was close to 1, less was retained in the column, and the retardation coefficient did not change.

These observations can be explained by kinetic effects. At a low flow rate such as 0.1 ml/min, the colloidal deposition process is mainly the result of colloid adsorption reactions to the porous medium. Colloidal HA has more contact time with



**Fig. 8** Breakthrough curves of colloidal HA suspension under different flow rates

the porous medium, adsorption of colloidal HA is enhanced, and there is less colloidal HA in the effluent. When the flow rate is increased to 0.2 ml/min, hydrodynamic shear stresses on the solid matrix increase can overcome the electrostatic and van der Waals interactions. With increases in the flow velocity, the equilibrium of the forces between the colloidal particles and porous medium are affected so that there is less contact time with the porous medium, which promotes the mobility of colloidal HA, and less colloidal particle deposition occurs (Torkzaban et al. 2008). When the flow rate is further increased to 0.4 ml/min, however, there is little increase of peak  $C/C_0$ , although it may reach a certain critical value of flow rate to facilitate colloidal HA transport in the porous medium (Yin et al. 2010). In addition, when the flow rate is 0.4 ml/min, there is little tailing because when the flow rate increases, the hydrodynamic shear stress increases and adsorbed colloidal HA is detached and is found in the effluent. Results from this study were consistent with the findings reported by Bradford et al. (2002) and Albarran et al. (2011), who found that decreasing flow rates resulted in decreased colloid concentrations effluents.

## Conclusions

Four sets of column transport experiments were used in this study to determine the effect of recharge water with a range of chemical properties and different hydrodynamic conditions on the transport and deposition of colloidal particles. The breakthrough curves clearly showed that the transport of colloids can be significantly enhanced when conditions favor less deposition. Colloid transport increased slightly when the pH was increased from 5 to 9, and the peak concentration increased from 0.98 to 1.00. Colloidal HA transport in a porous medium is also controlled by IS; as the IS increased, the thickness of the electrical double layer decreased, leading to a reduction in the electrostatic repulsion between colloidal HA and collectors, and less HA in the effluent. Decreases in the IS during the flushing process caused significant tailing in the release stage. Transport increased significantly when the flow rate increased, as it was influenced by the balance of forces among the colloidal particles, the porous medium and the contact time with the porous medium, as also reported by Sätmark et al. (1996) and Kretzschmar and Sticher (1998). The aim of this study was to obtain greater insight into the transport and deposition behavior of colloidal HA during managed aquifer recharge, and the results provide a basis for further studies on the transport and deposition of colloid-associated subsurface contaminants.

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