

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/24205013>

Natural and Engineered Nano and Colloidal Transport: Role of Zeta Potential in Prediction of Particle Deposition

ARTICLE *in* LANGMUIR · APRIL 2009

Impact Factor: 4.46 · DOI: 10.1021/la900134f · Source: PubMed

CITATIONS

24

READS

29

2 AUTHORS, INCLUDING:



Arturo A. Keller

University of California, Santa Barbara

145 PUBLICATIONS **3,328** CITATIONS

SEE PROFILE

Natural and Engineered Nano and Colloidal Transport: Role of Zeta Potential in Prediction of Particle Deposition

Peng Wang[†] and Arturo A. Keller*

Bren School of Environmental Science and Management, University of California, Santa Barbara, California 93106. [†] Current address: Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Received January 12, 2009. Revised Manuscript Received February 13, 2009

This study is designed to answer the question of whether the zeta-potential measurement of natural and engineered nano and colloidal particles can be used as a general predictor for their transport and deposition within porous medium. The transport and deposition of engineered zeolite particles and natural colloids (soil and sediment colloids) was studied and evaluated considering their zeta-potential measurement. The zeta-potential of Ca^{2+} or K^{+} saturated zeolite particles increased (i.e., became less negative) with increasing bulk ionic strength, independent of the cation species in the bulk solution, while the zeta-potential of Ca^{2+} or K^{+} saturated natural colloids was dependent on the cation species in the bulk solution, unexpectedly decreasing with the bulk K^{+} concentrations while increasing with bulk Ca^{2+} concentrations (10^{-5} to 10^{-2} M). The particle deposition rate coefficient (k) was sensitive to the cation species in the bulk solution and on the cation exchangeable sites of the particle surfaces. The trend of the zeta-potential of the natural colloids, especially with simple electrolytes in bulk solution, was at odds with that of k under the same conditions, indicating that the zeta-potential of these natural colloids could not be used to adequately predict their transport and deposition. The observed anomaly is a direct result of surface heterogeneity and hydrophobicity of natural colloids, and it points out the important difference between natural and engineered nano and colloidal particles in terms of their transport and deposition prediction.

Introduction

Colloidal particles are usually defined as particles less than $2\ \mu\text{m}$ in diameter. Most natural porous media, such as soils, sediments, and aquifer materials, contain a certain fraction of natural colloidal particles,^{1,2} and the mass fraction of these naturally occurring colloids can vary over a wide range. Natural colloids are generally composed of an association of clay minerals and natural organic matter (NOM),³ which makes them versatile sorbents for environmental contaminants, such as hydrophobic organic compounds (HOCs), heavy metals, and radionuclides.^{3–5} Transport of natural colloids has been observed as a result of changes in natural conditions (e.g., decreases in bulk ionic strength and increases in water flow rate),^{2,6–9} and as a result, natural colloids tend to facilitate contaminant transport underground.^{9–11}

On the other hand, due to their tunable physical and chemical properties, engineered nanomaterials are being

produced on an industrial scale, and their release into the environment is an increasing concern. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework.¹² There are currently many applications for zeolites in industry, but the potential to markedly increase the surface activity by using nanoscale particles is creating new applications. The largest volume use for engineered colloid-sized zeolites is in detergent formulations where they have replaced phosphates as water-softening agents.¹³ Divalent cations such as Ca^{2+} and Mg^{2+} that contribute to hardness are exchanged with monovalent cations (Na^{+} or K^{+}) in the zeolites.^{12,13} Zeolite particles may thus be discharged to the environment in treated wastewater.¹³ Also, it has been reported that heavy metals can significantly sorb onto zeolites.^{14,15} Thus, these engineered particles may also play an important role in transporting contaminants that would otherwise be sorbed onto an immobile surface. Therefore, it is important to understand the transport behavior of these natural and engineered colloidal particles in the environment to properly assess their risk and the risk of the contaminants associated with them.

Colloidal transport is influenced by several physical and chemical processes, i.e., advection, diffusion, dispersion, and deposition. Colloidal deposition in porous media has been studied extensively using well-characterized

*Corresponding author. Tel.: 01-805-453-1822; fax: 01-805-456-3807; email: keller@bren.ucsb.edu

(1) Roy, S. B.; Dzombak, D. A. *Colloids Surf., A* **1996**, *107*, 245.
(2) Grolimund, D.; Elimelech, M.; Borkovec, M.; Barmettler, K.; Kretzschmar, R.; Sticher, H. *Environ. Sci. Technol.* **1998**, *32*, 3562.
(3) de Jonge, L. W.; de Jonge, H.; Moldrup, P.; Jacobsen, O. H.; Christensen, B. T. *J. Environ. Qual.* **2000**, *29*, 206.
(4) Roy, S. B.; Dzombak, D. A. *Environ. Sci. Technol.* **1997**, *31*, 656.
(5) McCarthy, J. F.; Zachara, J. M. *Environ. Sci. Technol.* **1989**, *23*, 496.
(6) Sen, T. K.; Khilar, K. C. *Adv. Colloid Interface Sci.* **2006**, *119*, 71.
(7) McCarthy, J. F.; McKay, L. D. *Vadose Zone Journal* **2004**, *3*, 326.
(8) McCarthy, J. F.; McKay, L. D.; Bruner, D. D. *Environ. Sci. Technol.* **2002**, *36*, 3735.
(9) de Jonge, L. W.; Kjaergaard, C.; Moldrup, P. *Vadose Zone Journal* **2004**, *3*, 321.
(10) Keller, A. A.; Sirivithayapakorn, S.; Chrysikopoulou, C. V. *Water Resour. Res.* **2004**, *40*, W08304.
(11) Grolimund, D.; Borkovec, M.; Barmettler, K.; Sticher, H. *Environ. Sci. Technol.* **1996**, *30*, 3118.

(12) Dyer A. *An introduction to zeolite molecular sieves*; John Wiley and Sons: Chichester, **1988**.

(13) Davis, M. L.; Cornwell, D. A. *Introduction to environmental engineering*, 2nd ed.; McGraw-Hill: New York, **1991**.

(14) Li, Z. H.; Alessi, D.; Allen, L. J. *Environ. Qual.* **2002**, *31*, 1106.

(15) Oste, L. A.; Lexmond, T. M.; Riemsdijk, W. H. V. *J. Environ. Qual.* **2002**, *31*, 813.

engineered colloidal particles, such as latex or metal oxide particles.^{2,10,16–22} Valuable insights have been gained with these systems on the influence of physical factors, such as hydrodynamics, particle size, particle morphology, and flow rate, on the kinetics and dynamics of colloidal deposition.^{16–22} More recently, there have been a number of studies on the effect of some chemical characteristics of the bulk solutions, such as ionic strength and pH, on colloidal deposition.^{1,2,8,23–26} In quantitative and semiquantitative analyses of deposition of engineered colloids onto solid surfaces, the zeta-potentials of these colloids are commonly measured and used as a surrogate of surface potentials within the framework of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.²³ Reasonable agreement between the measured data and theoretical calculations can usually be obtained by this approach. However, Elimelech et al.²⁷ reported that, in calculating the deposition of engineered silica colloids onto quartz sand grains, the use of measured zeta-potential of the sand grains in theoretical predictions generated erroneous results largely due to patchwise chemical heterogeneity of the sand grain surfaces.

From the colloid side, the question of whether the zeta-potentials of engineered and natural colloids can be used as reliable indicators for predicting their deposition is still unanswered, since the number of experimental studies comparing the transport and deposition of engineered and natural colloids is very limited^{2,21} and with little or no evaluation of the colloidal zeta-potentials within the context of their transport and deposition.

In the past few years, the significance of surface heterogeneity on biocolloid behavior has also become better understood; some studies in the microbial field have reported that the surface chemical heterogeneity and/or surface hydrophobicity are responsible for the adhesion and/or deposition of the bacteria coated with extracellular polymeric substance (EPS), which constitutes a heterogeneous environment on the bacterial surfaces.^{28–31} Although EPS-coated bacteria have a different composition than natural colloids, given the chemical heterogeneity and hydrophobicity of bacterial surfaces, these studies with bacteria may be useful to understand the results of this study.

In this study, the zeta-potential, transport, and deposition of natural colloidal particles (soil and sediment colloids) and

engineered zeolite colloids within a porous medium, as represented by quartz sand grains, were investigated and compared under the conditions of different bulk solution and colloid surface-exchangeable cation species. The objective of the study was to determine whether the zeta-potential measurement of colloids could be used as a reliable parameter for predicting their transport in porous media.

Materials and Methods

Colloidal Particles. Three agricultural bulk soils and one sediment (denoted as Ag#1, Ag#2, Ag#3, and Sediment) were collected from Santa Barbara, California, USA, air-dried, and then gently passed through a 2 mm metal sieve. All samples were taken from topsoil layers or sediment bed (0–15 cm). Ag#1 is a sandy loam, Ag#2 and Ag#3 are loams, and Sediment is a loamy sand.³² To mimic field conditions, a low-energy separation method was applied to separate the colloidal fractions, which involved using only water as dispersant, gentle mixing, repeated wet sedimentation, dialysis desalination, and freeze–drying. The details of the natural colloid separation can be found in the Supporting Information. The separated soil and sediment colloidal particles are collectively denoted as “natural colloids” in this manuscript. Engineered zeolites particles (type A) were obtained from NanoScape (München, Germany) and were originally saturated with Na⁺.

Particle Characterization. Organic carbon (OC) content was determined for the natural colloids and their original bulk soils and sediment using the modified Walkley Black method.³³ Cation exchange capacity (CEC) of the natural colloids, the bulk soils and sediment, and the engineered zeolite particles was measured by barium acetate saturation and calcium replacement.³⁴ BET surface area (SA) measurement was conducted on a TriStar 3000 gas adsorption analyzer (Micromeritics Inc., Norcross, GA) using N₂. Iron content of the natural colloids was determined by dithionite citrate extraction, and the mineralogical composition of the natural colloids was determined by X-ray diffraction analysis.³³

Preparation of Particles with Different Surface Cation Species. For this study, one monovalent cation (K⁺) and one divalent cation (Ca²⁺) were chosen to study the effect of surface cation species on particle transport and deposition. However, the cation-exchangeable sites of the natural colloids were originally mostly saturated with divalent cations (Ca²⁺ and Mg²⁺) (Table 1). These particles were used directly as divalent cation saturated natural colloids, making no additional effort to replace the original divalent cations with Ca²⁺ since preliminary results showed that replacing the original cations with Ca²⁺ did not make a significant change in their transport behavior (c.f., Supporting Information). The K⁺ saturated natural colloids were prepared by treating 0.20 g of the original natural colloids with 40 mL of 1.0 M KCl solution for 24 h with agitation to reach the cation exchange equilibrium according to standard procedure.³³ The suspension was then desalted, quickly frozen, and freeze–dried following the same procedure as the preparation of the original natural colloids. The K⁺ and Ca²⁺ saturated zeolites were prepared using the same procedure except that, for the Ca²⁺ saturated zeolites, the original zeolites was first treated with the 1.0 M CaCl₂ instead of 1.0 M KCl.

To facilitate the discussion, the originally Ca²⁺ and Mg²⁺ saturated natural colloids are denoted as the divalent cation saturated natural colloids.

- (16) Franchi, A.; O'Melia, C. R. *Environ. Sci. Technol.* **2003**, *37*, 1122.
- (17) Bradford, S. A.; Yates, S. R.; Bettahar, M.; Simunek, J. *Water Resour. Res.* **2002**, *38*, 1327.
- (18) Xu, S.; Gao, B.; Saiers, J. E. *Water Resour. Res.* **2006**, *42*, W12S16.
- (19) Shen, C. Y.; Li, B. G.; Huang, Y. F.; Jin, Y. *Environ. Sci. Technol.* **2007**, *41*, 6976.
- (20) Kretzschmar, R.; Barmettler, K.; Grolimund, D.; Yan, Y. D.; Borkovec, M.; Sticher, H. *Water Resour. Res.* **1997**, *33*, 1129.
- (21) Kretzschmar, R.; Sticher, H. *Phys. Chem. Earth* **1997**, *23*, 133.
- (22) Kretzschmar, R.; Sticher, H. *Environ. Sci. Technol.* **1997**, *31*, 3497.
- (23) Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. A. *Particle deposition and aggregation: measurement, modeling, and simulation*; Butterworth-Heinemann: Oxford, **1995**.
- (24) Roy, S. B.; Dzombak, D. A. *Colloids Surf., A* **1996**, *119*, 133.
- (25) Ray, J. N.; Gschwend, P. M. *J. Colloid Interface Sci.* **1994**, *164*, 21.
- (26) Lecoanet, H. F.; Wiesner, M. R. *Environ. Sci. Technol.* **2004**, *38*, 4377.
- (27) Elimelech, M.; O'Melia, C. R. *Colloids Surf., A* **1990**, *44*, 165.
- (28) Walker, S. L.; Redman, J. A.; Elimelech, M. *Environ. Sci. Technol.* **2005**, *39*, 6405.
- (29) Tsuneda, S.; Aikawa, H.; Hayashi, H.; Hirata, A. *J. Colloid Interface Sci.* **2004**, *279*, 410.
- (30) Liu, Y.; Yang, S. F.; Tay, J. H.; Liu, Q. S.; Qin, L.; Li, Y. *Enzyme Microb. Technol.* **2004**, *34*, 371.
- (31) Morales, C. F. L.; Strathmann, M.; Flemming, H. C. *Water Res.* **2007**, *41*, 2059.

(32) Wang, P.; Keller, A. A. *Environ. Sci. Technol.* **2008**, *42*, 3381.

(33) Carter, M. R. *Soil sampling and methods of analysis*; Lewis Publishers: Boca Raton, **1993**.

(34) Rible, J. M.; Quick, J. Tentative methods of analysis for diagnostic purposes, method s-9-1; University of California Agricultural Experiment Service; mimeographed report, **1960**.

Table 1. Measured Properties of Natural Colloids, Bulk Soils and Sediment, and Engineered Zeolite Particles

soil		weight %	OC (%)	CEC (cmol/kg)	surface area (m ² /g)	exchangeable Ca ²⁺ + Mg ²⁺ (cmol/kg)	Fe content
Ag #1	bulk	100%	1.51	6.20	3.5	5.8	
	colloids	5.3%	4.95	40.2	30.8	39.0	0.19%
Ag #2	bulk	100%	1.50	15.2	9.4	14.1	
	colloids	6.8%	4.36	59.0	53.1	57.5	0.14%
Ag #3	bulk	100%	1.52	15.4	14.1	15.1	
	colloids	13.8%	4.50	54.4	63.1	53.6	0.17%
sediment	bulk	100%	1.12	5.4	2.0	5.2	
	colloids	2.7%	6.02	42.2	36.6	40.7	0.19%

Zeta-Potential Measurement. The electrophoretic mobility of the particles was measured on a NanoSizer (Nano Series, Malvern Instrument Ltd., Worcestershire, United Kingdom) and the zeta-potential was calculated from the measured electrophoretic mobility using the Smoluchowski equation.²³ KCl or CaCl₂ were used to adjust the bulk ionic strength and to evaluate the effect of the bulk cation species on the zeta-potential of the particles. The solution pH was adjusted to 7.0 for the samples, and the pH adjustment was conducted using HCl and either KOH or Ca(OH)₂, depending on which electrolyte was present in the bulk solution. All zeta-potential measurements were carried out at 25 °C, which was maintained internally by the instrument. The hydrodynamic diameter of the particles was also measured on the NanoSizer as a function of time in the presence of KCl and CaCl₂ at different concentrations.

Porous Media. For the transport experiments, medium-sized quartz sand (Ward's Natural Science, Rochester, NY) was used as porous media. The sand grains were washed in DI water, bathed in a sonicator (8210R-DTH, Branson, Danbury, CT) to remove fine particles originally deposited on the grain surfaces, acid-washed with 10% sulfuric acid, and washed in DI water again to make sure they were free of fine particles.¹⁰ The cleaned sand grains were then saturated with either KCl or CaCl₂ solution at a concentration of 1.0 M for 2 days, washed thoroughly with DI water until the conductivity of the washing solution decreased to the blank level, dried at 105 °C overnight, sorted through metal sieves to obtain a grain diameter of 0.35 ± 0.05 mm, and finally stored in closed containers prior to use.

Column Transport Experiments. The column experimental setup can be seen in the Supporting Information. The glass columns used are 15.0 cm in length and 2.5 cm in inner diameter and with two ceramic membrane discs (100 μm pore size) at both ends to keep the porous medium in place. For each experiment, the cleaned, medium-sized sand grains were wet-packed into the column to minimize trapping air bubbles and to avoid creating preferential pathways. The porosity of the packed columns was 0.38. A background solution, containing KCl or CaCl₂ of varying concentrations (10⁻⁵ to 10⁻² M), was delivered into the columns from a reservoir from the bottom upward by a high-performance liquid chromatography (HPLC) pump (L-6022, Hitachi Ltd., Chiyoda-ku, Tokyo, Japan). Before each experiment, the columns were flushed with the background solution for at least four pore volumes. The effluent was collected into separate cuvettes (1.0 mL) after flowing past a conductivity meter connected to the top of the column.

Particle suspensions were prepared by weighing a certain amount of the particles and dispersing them in a desired background solution by sonicating for 10 min in a low-energy sonicator bath (8210R-DTH, Branson, Danbury, CT). The pH of the suspensions and background solutions was adjusted to be around 7.0 by using HCl and either KOH or Ca(OH)₂, depending on which electrolyte was used as background electrolyte for the transport experiments. It was determined that there was no significant contribution to the ionic strength from these acid and bases in all cases. The particle concentrations in the suspensions were between 65 and 80 mg/L. Grolimund et al.² conducted column transport experiments and found that

the colloidal transport behavior was not sensitive to the injected colloidal concentration (333–2687 mg/L) under short-pulse injection conditions.

A pulse injection was employed for all of the transport experiments: 4.0 mL (0.14 pore volume) of the particle suspension was injected into the column at the bottom via the HPLC pump. Right before the injection, the particle suspension was placed in the sonicator for 1 min to make sure the particles were well-dispersed. After the injection, the pump was immediately switched to the background solution with the same electrolyte and the same concentration as the injected particle suspensions. A constant flow of 1.0 mL/min (7.7 m/day) was used in all cases. The particle concentration in the effluent was measured on a spectrophotometer (Biospec-1601, Shimadzu, Nakagyo-ku, Kyoto, Japan) at 360 nm for all experiments. A calibration curve for each type of particle was prepared at the same wavelength on the same spectrophotometer. The results of our preliminary experiments showed that the sorption of particles onto connecting tubes, membrane discs, and glass column walls was negligible. No significant changes in pH were observed in the solutions after passing through the columns.

Tracer experiments were also conducted separately, in which 4.0 mL of KCl or CaCl₂ at 10⁻³ M was injected through the sand columns. The conductivity of the effluent was measured via a conductivity meter (09-326-2, Fisher Scientific, Pittsburgh, PA) to determine the tracer concentrations by using the calibration curves of KCl or CaCl₂.

Results and Discussion

Colloid Characterization. The measured properties of the natural colloids and their original bulk soils and sediment are presented in Table 1 along with the properties of the engineered zeolite particles. Although the natural colloids make up only 2.7% to 13.8% of the bulk soils and sediment by weight, they have significantly higher OC, CEC, and SA than their bulk soils and sediment. The higher SA of natural colloids, relative to the bulk soils, results in higher capacities for NOM binding, and the higher fraction of secondary minerals contributes to their higher CECs.³⁵ Divalent cations (Ca²⁺ and Mg²⁺) were found to be the dominant species in the cation exchangeable sites of the natural colloids in all cases (> 92%) (Table 1). There was no significant presence of iron species associated with the natural colloids. The dominant clay mineral in all cases was Illite, which is non-swelling.

The engineered zeolite particles have a SA comparable to the natural colloid, but have a significantly higher CEC than the natural colloids, which makes them an effective water softening agent. The engineered zeolites consist of pure mineral phase, while the natural colloids are the association of organic matter and clay minerals (Table 1).

(35) Bohn, H. L.; McNeal, B. L.; O'Connor, G. A. *Soil Chemistry*, 3rd ed.; John Wiley & Sons, Inc.: New York, 2001.

The stability curves, as denoted by the variation in the measured hydrodynamic diameter as a function of time for the natural colloids (Ag#1 and Ag#3) and engineered zeolite in the presence of 0.01 M KCl or 0.01 M CaCl₂ in bulk solution, are presented in Figure 1. TEM images of the natural colloids (Ag#1 and Ag#3) and zeolites are provided in the Supporting Information. The measured zeolite diameter was consistently higher than 250 nm, which was the primary diameter of the zeolites reported by the manufacturer, suggesting that in aqueous suspension, as is the case for many engineered nanoparticles, the zeolite particles are present mainly as aggregates of individual primary particles, minimizing their surface energy.

As indicated by Figure 1, the hydrodynamic diameter of both natural colloids and engineered zeolites was generally stable in the presence of 0.01 M KCl, but it increased gradually in the presence of 0.01 M CaCl₂ probably due to higher charge density of Ca²⁺ and thus its higher ability to neutralize surface charges on the particles than K⁺. However, even in the presence of 0.01 M CaCl₂, within the time framework of the transport experiments (~56 min for two pore volumes), the hydrodynamic diameter of the natural colloids was comparable to the engineered zeolite particles.

Zeta-Potential of the Colloids. The measured zeta-potentials of the natural colloids and engineered zeolite particles are presented in Figure 2. For the range of salt concentrations tested (10⁻⁵–10⁻² M), the zeta-potential of all the natural colloids showed similar trends, with Ag#1 colloids having the lowest and Ag#3 colloids the highest zeta-potentials in all cases. Thus, only the zeta-potentials of Ag#1 and Ag#3 colloids are presented, for clarity. The zeta-potentials of either K⁺ or Ca²⁺ saturated zeolites consistently increased (i.e., became less negative) with increasing bulk CaCl₂ or KCl concentration, while the zeta-potentials of K⁺ and divalent cation saturated natural colloids consistently increased with the increasing bulk CaCl₂ concentration but decreased with increasing bulk KCl concentration, which was unexpected. Engineered colloids generally have a homogeneous surface composition, or at least they are designed so that the surface exhibits regular patterns. In our study, since the engineered zeolites only have mineral surfaces, their zeta-potential behavior is easier to predict, increasing monotonically as the ionic strength increases.

In contrast, most natural colloids have significant patchwise surface charge heterogeneity^{7,36–38} and hydrophobicity.^{28,39} The unusual zeta-potential behavior exhibited by the natural colloids in the presence of K⁺ in solution may be due to the heterogeneity of their surfaces, which includes hydrophobic patches. The presence of significant hydrophobic sites on the natural colloidal surfaces is evidenced by their high OC and the significant sorption capacities of hydrophobic organic compounds onto the natural colloids as reported in our previous work (relevant data are presented in the Supporting Information).^{32,39} Studies by Elimelech and O'Melia²⁷ showed that latex particles, which contain a significant amount of surface hydrophobic sites, also exhibit an inverted zeta-potential behavior. According to the model used and tested by Elimelech and O'Melia, as the bulk salt

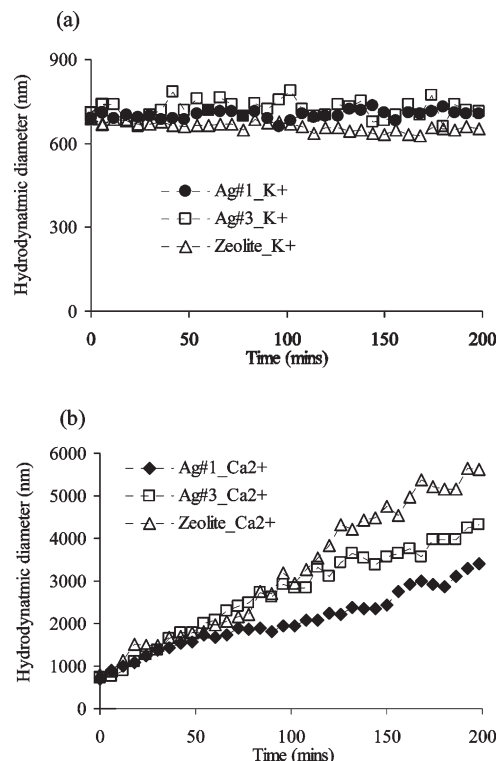


Figure 1. Stability curves of natural colloids and engineered zeolite particles under different bulk cation species: (a) 0.01 M KCl and (b) 0.01 M CaCl₂.

concentration increases, bulk coions (e.g., Cl⁻) enter into the interfacial region adjacent to the surface hydrophobic sites and decrease the zeta-potential of the particles. Concurrently, the increase in bulk cation concentration tends to increase the zeta-potential due to compression of the electric double layer and charge neutralization. Due to its higher charge density, Ca²⁺ in solution can approach the negatively charged surface sites more closely, thus neutralizing more surface charges, rendering the influence of the coions less significant. However, in the presence of K⁺ in solution, the effect of coions (Cl⁻) approaching the surface hydrophobic patches is much more significant, resulting in the unusual decrease in zeta-potential with increasing ionic strength. Thus, the presence of hydrophobic moieties on the natural colloidal surfaces results in a zeta-potential behavior that is quite different from that of engineered zeolites or other pure mineral surfaces.

It is possible that the location of the cation exchangeable sites (edge vs interlayer) can also play a role, but since the zeta potential is a macroscopic parameter that reflects the net or average charge at a significant distance away from the particle surface (i.e., shear plane), it is less likely that the location of the exchangeable sites is the dominant effect. For the same reason, the zeta-potential measurement is not sensitive to small local-scale variations on a particle surface. Therefore, the zeta-potential does not capture the subtle differences in charge heterogeneity on the surface²⁸ and the standard deviation of zeta-potential measurements bears no information on the charge heterogeneity of the natural colloidal surfaces.

As can be seen from Figure 2, with the same bulk electrolyte, the same trend in zeta-potential was preserved for divalent cation saturated natural colloids and zeolites as for K⁺ saturated natural colloids and zeolites. It suggests

(36) Majzik, A.; Tombácz, E. *Org. Geochem.* **2007**, *38*, 1330.

(37) Tombácz, E.; Libor, Z. S.; Illés, E.; Majzik, A.; Klumpp, E. *Org. Geochem.* **2004**, *35*, 257.

(38) Zukoski, C. F.; Saville, D. A. *J. Colloid Interfacial Sci.* **1985**, *107*, 322.

(39) Wang, P.; Keller, A. A. *Water Res.* **2008**, *42*, 3781.

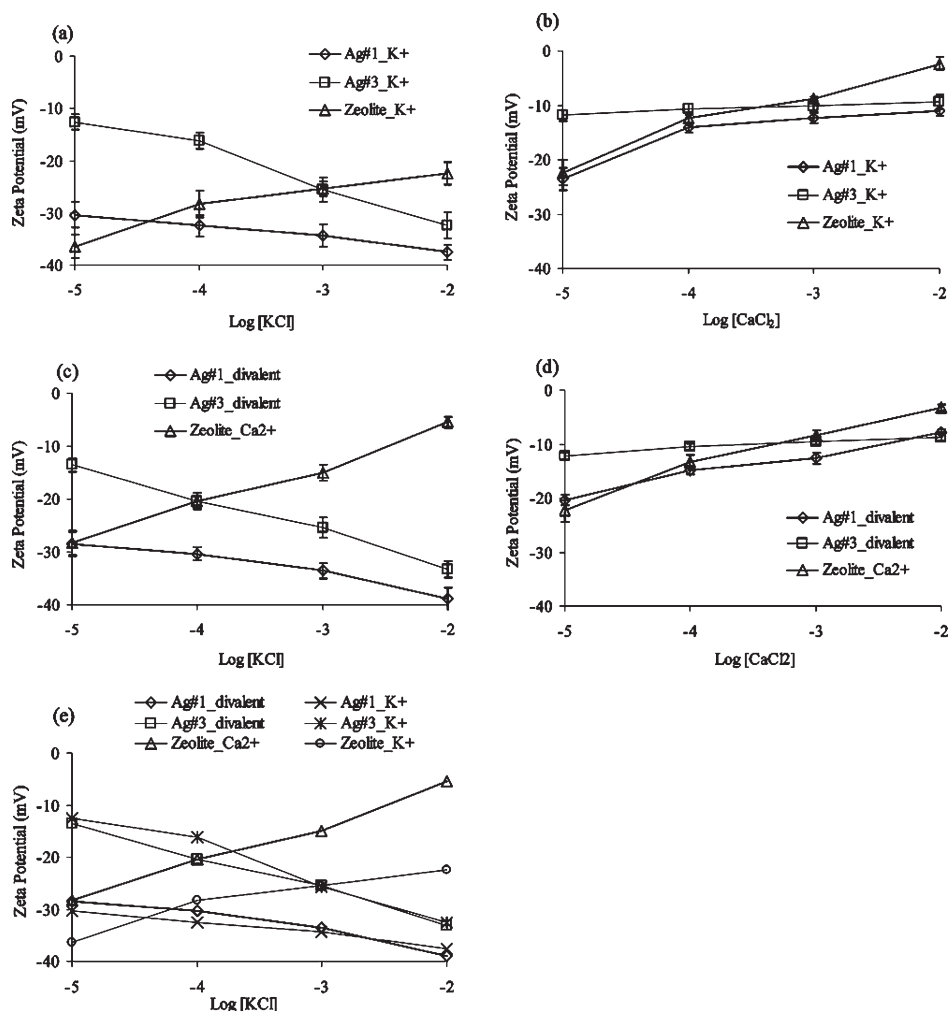


Figure 2. Zeta-potentials of the original and cation-exchanged natural colloids (Ag#1 and Ag#3) and engineered zeolite as a function of log molar concentrations of KCl and CaCl_2 (pH 7.0): (a) K^+ saturated colloids with KCl in the bulk solution; (b) K^+ saturated colloids with CaCl_2 in the bulk solution; (c) divalent cation saturated colloids with KCl in the bulk solution; (d) divalent cation saturated colloids with CaCl_2 in the bulk solution; (e) comparison of K^+ and divalent cation saturated colloids with KCl in the bulk solution.

that the species of the exchangeable cations of the natural colloids and zeolites and thus the cation exchange interaction between the bulk and exchangeable cations does not play a significant role in determining the zeta-potential in these experimental systems, which is especially true for the natural colloids. As shown in Figure 2e, the zeta-potentials of the Ag#1 and Ag#3 were almost independent of the cation species on their exchangeable sites, while with Ca^{2+} on their surfaces, zeolites showed significantly higher zeta-potential than with K^+ on their surfaces. Also, the zeta-potential of the natural colloids was less sensitive to the bulk CaCl_2 concentration than the zeolites as indicated by the lower slopes of the zeta-potential curves of the natural colloids than the zeolites (Figure 2b,d). Presumably, the special composition of the natural colloids confers them a certain buffering capacity to variation in bulk Ca^{2+} concentrations.

General Particle Breakthrough. The transport of the natural colloids and engineered zeolites generated similar breakthrough curves, although with significant differences in particle retention. To demonstrate, the breakthrough curves of the Ag#1 and Ag#3 colloids, as well as the zeolites, are presented in Figure 3.

Inspection of the breakthrough curves in Figure 3 reveals two distinct features. First, all particles break through earlier than the solute tracers (KCl or CaCl_2). Early particle

breakthrough due to size or anion exclusion has also been observed by several other researchers.^{2,10,20–22,40} The particles that break through are likely to be those that remain most of the time near the central streamlines, where the fastest velocities occur.⁴⁰ If these particles were transporting sorbed contaminants, there would be a higher likelihood that these contaminants would arrive earlier at a drinking water well or point of discharge.⁴¹ Due to the similar hydrodynamic diameter of the particles in the aqueous solution (Figure 1), the breakthrough of the particles occurred consistently around 0.90 pore volume, which is a function of the particle size and is independent of the bulk ionic strength. Second, as indicated by the reduced peak area of the normalized particle breakthrough curves, only a fraction of the injected particles was recovered in the effluent, meaning that particle deposition onto the porous medium surfaces took place as the particles traveled through the porous media. The percent recovery of the particles under each condition was calculated as the percentage of the mass of the particles recovered in the effluent to the total mass of the particles injected (Table 2).

An analysis of the effect of cation species provided two additional important findings. First, under otherwise

(40) Auset, M.; Keller, A. A. *Water Resour. Res.* **2006**, *42*, W12S02.

(41) Wang, P.; Keller, A. A. *Water Res.* **2009**, in press.

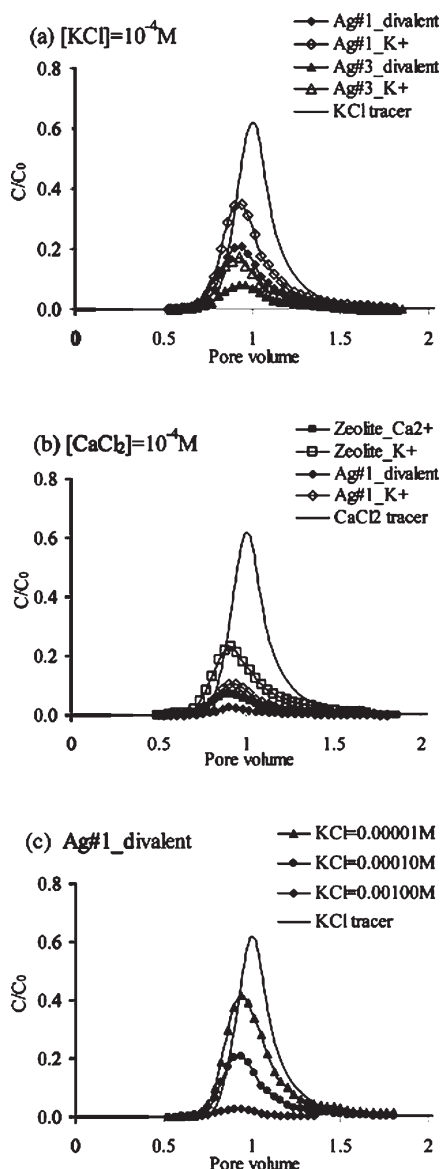


Figure 3. Breakthrough curves of divalent cation and K^+ saturated natural colloids and engineered zeolites for (a) divalent cation and K^+ saturated Ag#1, Ag#3 at $[KCl] = 10^{-4} M$; (b) divalent cation and K^+ saturated Ag#1 and zeolites at $[CaCl_2] = 10^{-4} M$; (c) divalent cation saturated Ag#1 at different KCl concentrations.

identical conditions, with the divalent cations either in the bulk solution or on the cation exchangeable sites, all particles had much lower recovery compared with K^+ (Figure 3a,b, Table 2), which can be partially explained by the difference in colloid stability as presented in Figure 1. Colloid stability influences the size of colloids, the interaction with sand grains, and, to certain degree, mechanisms of colloid retention. However, further discussion and quantification of these complex interactions is out of the scope of the manuscript. Second, as the salt concentration increased, the percent recovery decreased sharply (Figure 3c), which is consistent with other studies.^{1,2,20} In addition, under the same conditions, there were pronounced differences in percent recovery between the natural colloids and the zeolites (Figure 3b), which indicates that surface heterogeneity plays a significant role in colloid fate and transport. To a lesser extent, the cation species in the exchangeable sites can also play a role in the fate of the particles as they travel through porous media.

Colloid Deposition Rate. Deposition refers to the removal of particle mass from solution via collision with and attachment onto porous media and is usually assumed to be the primary process controlling particle transport.¹⁷ For breakthrough curves resulting from short-pulse injection, the particle deposition rate coefficient (k) can be estimated using^{20–22}

$$k = -\frac{1}{t_p} \ln \left[\frac{q}{N_0} \int_0^{t_f} C(t) dt \right] \quad (1)$$

where t_p is the average travel time of the particles through the column, $C(t)$ is the particle concentration in solution, q is the volumetric flow rate, N_0 is the total amount of particles injected into the column, and t_f is the time at which the particle pulse has completely moved through the column. The term in brackets in eq 1 corresponds to the percent recovery of the particles presented in Table 2.

The derived k for the natural colloids and engineered zeolites are depicted in Figure 4 as a function of the bulk salt concentrations. The results are presented as deposition curves: i.e., the logarithm of the deposition rate coefficient k as a function of the logarithm of counterion concentrations. The slope of the deposition curves, $d(\log k)/d(\log C_s)$, where C_s is the molar salt concentration, can be indicative of the difference in the chemistry of the bulk solution and surface

Table 2. Percent (%) Recovery of the Natural Colloids and Engineered Zeolites under a Range of Bulk Salt Concentrations and with Different Surface Exchangeable Cations

salt conc. (M)	KCl									
	divalent-saturated colloids					monovalent cation saturated colloids				
	Ag#1	Ag#2	Ag#3	sediment	zeolite	Ag#1	Ag#2	Ag#3	sediment	zeolite
0.00001	79.2	63.2	32.1	51.2	65.4	85.4	78.0	61.8	71.3	98.9
0.0001	40.6	34.5	16.6	28.3	30.1	70.2	59.3	37.2	52.4	96.8
0.001	6.1	3.7	1.2	2.2	4.1	30.1	21.3	7.2	18.2	66.5
0.01	0.1	0.1	0.1	0.1	0.1	2.5	1.0	0.1	0.1	12.0
salt conc. (M)	CaCl ₂									
	Ag#1	Ag#2	Ag#3	sediment	zeolite	Ag#1	Ag#2	Ag#3	sediment	zeolite
	Ag#1	Ag#2	Ag#3	sediment	zeolite	Ag#1	Ag#2	Ag#3	sediment	zeolite
0.00001	32.1	28.5	14.2	24.2	55.1	52.3	45.3	35.2	41.2	90.1
0.0001	11.4	9.5	3.5	9.5	16.2	21.3	18.7	12.3	16.0	55.2
0.001	0.1	0.1	0.1	0.1	1.2	9.2	6.2	2.2	5.0	10.2
0.01	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1

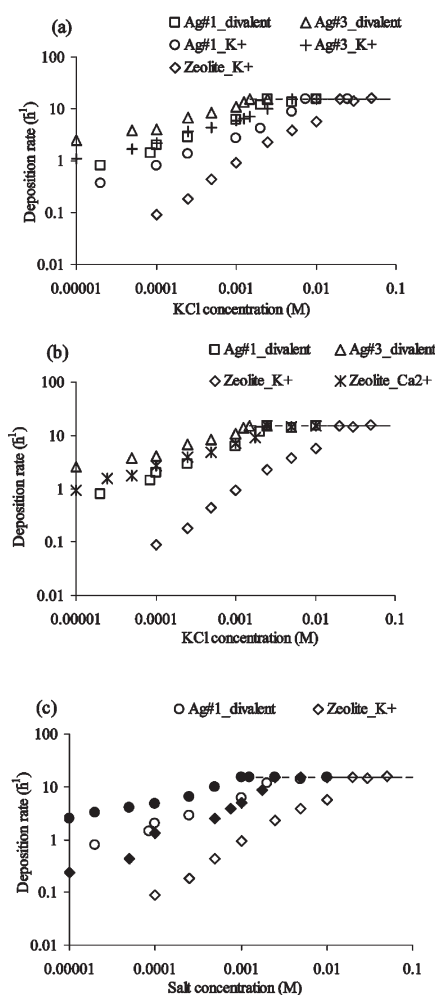


Figure 4. Deposition rate coefficient (k) of the natural colloids (Ag#1 and Ag#3) and engineered zeolites for (a) original and cation-exchanged Ag#1 and Ag#3 colloids and original zeolite with bulk KCl; (b) original Ag#1, Ag#3, original and cation-exchanged zeolite colloids with bulk KCl; (c) original Ag#1 and zeolite with bulk KCl or CaCl₂. Note: the open symbols in (c) represent bulk KCl and closed symbols represent bulk CaCl₂.

charges and cation species. To avoid undesirably high numbers generated by eq 1 at low particle percent recovery ($<0.1\%$), k was calculated by intentionally setting the particle percent recovery to be 0.1% when it was below 0.1% .

First, our results showed that there is a clear difference in particle deposition depending on the species of cations either in bulk solution or on cation exchangeable sites (Figure 4), indicating the important role of the cation species in determining k . Second, for the K^+ saturated zeolites, their deposition curves were a certain distance away from those of the K^+ saturated natural colloids (Figure 4a), indicating that, with the same monovalent cation on the cation exchangeable sites, the natural and engineered colloidal particles behave considerably differently in terms of their deposition onto porous media. However, for Ca^{2+} saturated zeolites, their deposition curves were within the range of the divalent cation saturated natural colloids (Figure 4b), suggesting that, with the divalent cation on the cation exchangeable sites, the engineered and natural colloidal particles deposit onto porous media in a similar manner.² It is worth mentioning that, since the mineral phase of natural colloids has a similar

composition as zeolite (aluminosilicate minerals),³⁵ their specific density is expected to be similar, and thus, the effect of density difference on the particle deposition should be minimal.

The deposition curves of the natural colloids have a lower slope than the zeolites, regardless of whether they are saturated with K^+ or divalent cations. This is probably related to the special composition (patchwise hydrophobic and mineral surfaces) of the natural colloids compared with that of the zeolites. Furthermore, as shown in Figure 4b,c, with K^+ either on cation exchangeable sites or in the bulk solution, the slopes of the deposition curves were always higher than in the case with divalent cations.

Relating k to Zeta-Potential. It is widely accepted that k is controlled by interparticle forces between particles and porous medium surfaces, such as van der Waals and electric double layer (EDL) forces.²³ Generally speaking, the zeta-potentials of particles are believed to be a reasonable surrogate for surface potential for prediction of colloidal particle deposition within the framework of the DLVO theory.²³ However, the anomalous decrease of the zeta-potential of the natural colloids with the increasing bulk KCl concentrations is at odds with the increasing k under the same conditions, suggesting that DLVO calculation will break down if zeta-potentials are used in these cases. Thus, the zeta-potential of the natural colloids, especially with simple electrolytes in bulk solution, is not an appropriate surrogate for their surface potential and is largely irrelevant for predicting deposition. Presumably, the charge property at the shear plane at which the zeta-potential is measured is less important in particle deposition prediction than the Debye length of the EDL, which evaluates the overall magnitude of the EDL, irrespective of the charge distribution near particle surfaces.

In summary, the observed anomaly is a direct result of surface heterogeneity of the natural colloids, and it points out the important difference between natural and engineered colloidal particles in terms of their transport and deposition prediction.

Acknowledgment. This work was supported by the University of California Lead Campus for Nanotoxicology Training and Research, funded by University of California Toxic Substances Research & Training Program (UC TSR&TP). This material is also based upon work supported by the National Science Foundation and the Environmental Protection Agency under Cooperative Agreement Number EF 0830117. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or the Environmental Protection Agency. This work has not been subjected to EPA review and no official endorsement should be inferred.

Supporting Information Available: Natural colloid separation procedure, transmission electron microscopy (TEM) images of the natural and engineered colloids, sorption of hydrophobic organic compounds (HOCs) onto the natural colloids and zeolite particle, comparison of the transport behavior of the original and Ca^{2+} saturated natural colloids, schematic representation of the column setup. This material is available free of charge via the Internet at <http://pubs.acs.org>.