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Assessment of Colloid Filtration in Natural Porous Media by Filtration Theory

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Mobile colloids in groundwater aquifers can act as carriers for sorbing contaminants and thereby facilitate contaminant transport. Therefore, the removal efficiency of two natural porous media for colloids with regard to the ionic strength of the solution and the counterion valence has been investigated. Short-pulse experiments were conducted using fluorescence labeled latex colloids in order to investigate their transport behavior. The predictions of the *filtration theory* concerning the filtration of colloids were confirmed qualitatively. The removal efficiency of a filter bed is influenced by both the type of electrolyte and its concentration as well as the type of the porous medium. An attachment parameter α, which was introduced into Happel's *Sphere-in-Cell-Model*, describes the dependence of the removal efficiency on the electrolyte concentration qualitatively. The normalization of α by the valence of the dominant counterion describes the removal efficiency independent of the kind of electrolyte.

Introduction

Recent evidence of transport of colloidal particles in groundwater aquifers has led to a concern that mobile colloids may enhance the transport of sorbing contaminants or, as in the case of certain bacteria or viruses, can be considered hazardous pollutants themselves *(1−3)*. Mobile subsurface colloids may have different origins. The major source of colloids in groundwater is the mobilization of existing colloids by chemical and physical perturbations, e.g. decreasing ionic strength of the solution or increasing flow velocities *(4)*. Another source can be the precipitation of colloids from supersaturated solutions along chemical gradients, e.g. by the infiltration of wastewater *(5)*. Colloids may also originate from external sources such as landfills or from the translocation of inorganic and organic substances from the vadose to the saturated zone *(1)*.

The transport and deposition of colloids in aquifer systems are influenced by certain physical processes *(6)*, known as Brownian or molecular diffusion, interception, and sedimentation. In addition, the transport of colloidal particles also can be limited by the sieve-effect *(7)*. The *filtration theory* has been applied quantitatively to predict the removal of colloidal particles at single collectors from a flowing fluid through model systems of granular porous media, assuming that repulsive double layer interactions are absent *(8−11)*. A more detailed description of the filtration theory will be given in the materials section.

In natural sediments, repulsive double layer interactions resulting from the negative surface charges of the colloidal particles and matrix grains must be considered. These interactions are qualitatively described by the DLVO theory *(12)* and play an important role in the deposition of colloidal particles on sediment matrices. Laboratory experiments concerning the deposition rates of colloidal particles have been observed to be several orders of magnitudes larger than predictions based on the DLVO theory *(13−16)*. This discrepancy may be a consequence of local roughness and variation of charge distribution at the surface of colloidal particles and sediment matrices. Thus, the interaction energy of a given particle may vary widely with position across these surfaces. Due to the influence of parameters such as the ionic strength, the valence of the dominant counterion, and the pH on colloidal deposition rates, the surface charges of colloidal particles and matrix grains must be considered, too *(17−22)*.

The objective of this paper is to determine the removal efficiencies of two natural sediments for latex colloids. The experiments were conducted under controlled hydrochemical conditions. To describe an attachment efficiency at various chemical conditions an attachment parameter α was introduced to Happel's *Sphere-in-Cell Model* of the filtration theory. This parameter considers the dependence of the removal efficiency on the counterion and its concentration. To study the effects of a complex and heterogeneous matrix on colloid transport and deposition the experiments were conducted with natural sediments, a fine sand, and a sandy gravel.

Experimental Section

Apparatus. The column setup consists of a solution reservoir containing the background electrolyte solution, a pulsationless peristaltic pump controlling the steady-state flow rate, an injection loop, a PMMA (poly(methyl methacrylate)) column packed with the porous medium, and an online detection system connected to a PC for data acquisition. The column was 100 mm in diameter and 200 mm in length. Flow rates were determined by collecting the effluent over a given time period. The porous media consisted of soil aggregates with $d_C < 10$ mm. Except for the pump tubing that was made of Tygon all tubings and fittings were made of Teflon.

Column Experiments. Two types of electrolytes were used to investigate both the effects of the ionic strength and of the valence of the counterions on the particle deposition (Table 1). The electrolyte solutions were prepared by dissolving an appropriate amount of the salts in high quality purified water from a Milli-Q-plus system (Millipore, Eschborn, FRG). A second set of experiments was conducted with purified water.

After saturating the packed columns with the electrolyte solution, tracer breakthrough experiments were conducted to determine the pore volume. Electrolyte solutions containing 1 $mg{\cdot}L^{-1}$ NO_3^- as a conservative tracer were injected with a peak input, and the NO_3^- concentration in the effluent was monitored using a flow-through UV−vis detector (Beckman DU650, Mühlheim, FRG) at a wavelength of 220 nm. The average transport time of the tracer and the longitudinal dispersivity were calculated by fitting the one-dimensional convective-dispersive transport equation to the NO_3^- breakthrough data.

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TABLE 1: Characterization of the Chemical Composition of the Feed Solution Used for the Column Experiments

expt	salt	$[M^{n+}]$, $mmol{\cdot}L^{-1}$	ionic strength, $mmol{\cdot}L^{-1}$
1	NaCl	10.0	10.0
2	NaCl	1.0	1.0
3	$CaCl_2$	3.3	10.0
4	$CaCl_2$	0.33	1.0
5	H_2O_{dest}		

TABLE 2: Characterization of the Latex Particles Used for the Column Experiments

particle diameter, μm	λ_{ex}, nm	λ_{em}, nm	detection limit, $mg{\cdot}L^{-1}$	linear range, $mg{\cdot}L^{-1}$
0.053	521	611	2.0	2.0−100.0
0.161	520	578	0.3	0.3−50.0
0.302	520	574	0.5	0.5−40.0
0.503	519	587	1.0	1.0−50.0
0.691	519	582	0.5	0.5−40.0
1.01	520	575	0.9	0.9−50.0
1.96	519	574	0.6	0.6−40.0

The colloid breakthrough curves were obtained after injecting 1 mL pulses of well dispersed, diluted latex colloids at the column entrance under steady state, saturated flow conditions. The colloid concentrations in the effluents were monitored using a flow-through fluorescence detector (Perkin-Elmer LS50, Überlingen, FRG) with a cell volume of 750 μL. The fractions of colloids recovered at the column effluent were calculated by numerical integration of the breakthrough curves. Due to the small number of injected latex particles no changes of the hydrodynamics are expected as the result of the blockage of small pores by colloidal particles.

Latex Colloids. The breakthrough experiments were conducted with spherical and monodisperse surfactant-free latex colloids and labeled with a fluorescent dye (Polymer Standards Service, Mainz, FRG). The particle diameters of the injected colloids ranged from 0.053 to 1.93 μm. The experimetally determined optimum excitation and emission wavelengths of the individual sizes are given in Table 2. The density of the polystyrene particle is reported by the company to be 1.055 $g{\cdot}cm^{-3}$.

Column Material. The "Munich gravel", taken from the Munich gravel plain, is dominated by carbonatic matter. The material consists of 96.6% calcite and dolomite, 1.4% SiO_2, and 2% clay minerals. The "Sengenthal sand", taken from the "Neumarkter Becken" near Sengenthal, is dominated by silicates. The material consists of 96.1% SiO_2, 2.4% feldspar, and 1% clay minerals. The distributions of the grain size for both sediments are shown in Figure 1. The uniformity number U_N is approximately 4.7 for Sengenthal and 15.0 for Munich. The pore size distributions of the sediments, also shown in Figure 1, were calculated on the basis of the respective grain size distribution according to Silveira *(23)*. From this figure it is clear that the smallest pores are at least 2 orders of magnitude larger than the largest colloids. Thus, a limitation of the filtration by the blockage of small pores by colloidal particles is of negligible importance. Experimental parameters for both systems are listed in Table 3. All experiments with the same porous medium were performed on the same column.

Filtration Theory. The single collector removal efficiency, usually denoted as η, is calculated in the absence of the repulsive forces acting between the particle and the collector. In general, the dimensionless parameter η represents the ratio of the rate at which particles strike a collector to the rate at which particles approach a collector. It is calculated as the sum of the removal efficiencies of the individual filtration processes *(8)*.

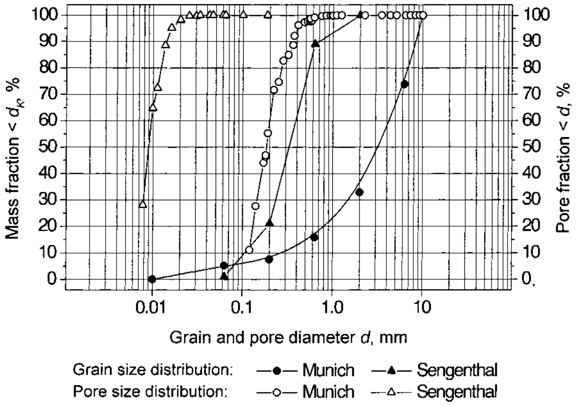

FIGURE 1. Size distribution of the grains and pores of the column material from the Munich gravel plain in Munich and the "Neumarkter Becken" in Sengenthal.

TABLE 3: Column Parameters for the Transport Experiments of Latex Colloids

	Munich	Sengenthal
porosity ϵ	0.18	0.26
uniformity number U_N	15.0	4.7
fluid velocity U, $mL{\cdot}min^{-1}$	2.5−2.7	2.3−2.5
fluid velocity U, $cm{\cdot}h^{-1}$	17.4−18.7	6.7−7.3
column length L, m	0.2	0.2
injected volume V, mL	1.0	1.0
Peclet number Pe	16.7	125.0

$$\eta = \eta_I + \eta_S + \eta_D \tag{1}$$

Here η_I, η_S, and η_D are theoretical values for the single collector efficiencies due to interception, sedimentation, and diffusion. Their definition is thoroughly described elsewhere *(10, 24)*.

In natural porous media the removal of colloidal particles occurs not at a single collector but along a filter bed of a specified length. Happel's *Sphere-in-Cell Model* describes natural porous media as a number of collectors, so-called unit bed elements (UBEs), connected in series *(10, 25)*. To distinguish the removal efficiencies of the different parts of a filter bed the indices η_{UBE} and η_{tot} will be introduced. The resulting unit removal efficiency, η_{UBE}, for each UBE of a filter bed is according to Tien *(10)*

$$\eta_{UBE} = 1.209\eta \tag{2}$$

The number N of UBEs is defined as

$$N = \frac{L}{l} \tag{3}$$

$$I = \left(\frac{\pi}{6{\cdot}(1-\epsilon)}\right)^{1/3}{\cdot}d_c \tag{4}$$

Here l is the effective thickness of a UBE and depends on d_c, ϵ is the porosity of the porous medium, and L is the length of the filter bed. The collector diameter d_c corresponds to an equivalent collector diameter and was set for both sediments to the value of d_{10} of each sediment. The value of d_{10} is known as the effective grain diameter for the description of hydraulic properties of sediments. Based on the column parameters given in Table 3 the theoretical values N and l were calculated using eqs 3 and 4. The results are listed in Table 4.

TABLE 4: Theoretical Parameters of *N* and *l* Calculated Using Eqs 6 and 7

parameter	Munich gravel	Sengenthal sand
collector diameter d_c, mm	0.25	0.10
UBE thickness *l*, m	2.1×10^{-4}	8.9×10^{-5}
number of UBEs *N*	954	2244

The overall removal efficiency η_{tot} of a filter bed can be expressed as

$$\eta_{tot} = 1 - \prod_{i=1}^{N}(1 - \eta_{UBE,i}) \tag{5}$$

where $\eta_{UBE,i}$ is the efficiency of the UBE number *i*. For identical UBEs eq 5 can be rewritten as

$$\eta_{tot} = 1 - (1 - \eta_{UBE})^N \tag{6}$$

An increasing removal efficiency for increasing filter height has been confirmed by a model system with latex particles *(17)*. Although these theories have been developed for considerably uniform porous granular media with pore size much greater than the size of colloids intercepted, some studies have confirmed that the filtration theory also can be applied to natural porous media. Furthermore, the pore size in the present study is much larger than the investigated latex particles.

Results and Discussion

Influence of Ionic Strength. The concentration of the latex colloids in the column effluent relative to the inlet concentration (C/C_0) is plotted in the figures as a function of the number of pore volumes. This number is the void volume of the column divided by the total volume of solution passed through the column up to that point (V/V_P). It should be pointed out that the loading of the collectors is much smaller than the maximum loading, so filtration caused by ripening can be excluded *(26)*. The same applies to the filtration due to the blockage of small pores by colloidal particles. This arises from the small amounts of particles injected compared to both the dimensions of the column and the pore size distribution (see Figure 1).

Typical breakthrough curves (BTC) obtained for particle diameters of $d_P = 0.691$ μm (Munich gravel) and $d_P = 0.503$ μm (Sengenthal sand) in the two sediments at various chemical conditions are presented in Figure 2. In the Munich gravel the shape of the colloid breakthrough curves are narrower than that of the conservative tracer. This difference is evident at the point at which the colloid pulse has completely moved through the column compared to that of the tracer. While the colloid breakthrough is completed after 3.5 pore volumes, the tracer breakthrough reaches the baseline after 6.5 pore volumes. The flow in the Munich gravel is characterized by a high dispersivity, resulting from the heterogeneous grain size distribution. The substantial tailing of the tracer is caused by hydrodynamic processes and not by sorption processes. The BTC represents the entire pore-system, whereas the BTCs of the colloids are somehow narrowed by filtration and size-exclusion-effects. The importance of the size-exclusion will be discussed in a later section. The differences in the shape of the breakthrough curves of both the colloids and the tracer are less pronounced in the Sengenthal sand. The pulses of the colloids and tracer have completely moved through the column after 1.8 pore volumes, and the shapes of the breakthrough curves were very similar.

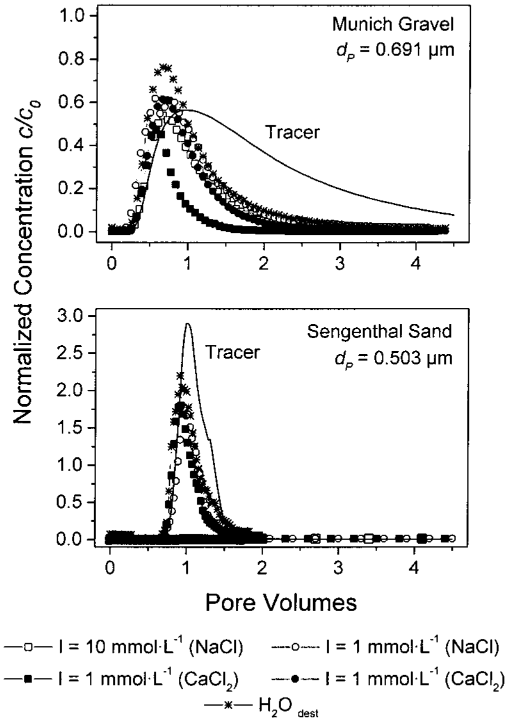

FIGURE 2. Influence of electrolyte concentration on the transport and deposition kinetics of latex colloids. Breakthrough curves resulting from short-pulse inputs of a conservative tracer (NO_3^-) and latex colloids for the Munich gravel ($d_P = 0.691$ μm) and Sengenthal sand ($d_P = 0.503$ μm).

The findings of the experiments are in qualitative agreement with the DLVO theory. With increasing electrolyte concentration the electric double layer repulsion decreases resulting in a decreasing mobility of the colloidal particles. At very low salt concentrations, electric double layer interactions are very large, and deposition is expected to decrease. This fact was observed for both systems and could be derived from the enhanced mobility obtained for purified water. Generally, compared to the Munich gravel the removal efficiency of the Sengenthal sand depends more upon the investigated electrolyte conditions listed in Table 1.

This effect can be seen from the fraction of colloids recovered for the most mobile particle diameter $d_P = 0.691$ μm. The amount of colloids recovered in the column effluent of the Munich gravel decreased from approximately 71.9% (H_2O_{dest}) to 30.8% ($CaCl_2$, $I = 10$ mmol·L^{-1}). In contrast the fractions of colloids recovered in the Sengenthal sands were in the range of 88.8% (H_2O_{dest}) to < 0.1% ($CaCl_2$, $I = 10$ mmol·L^{-1}). In this context it should be noted that model simulations with PHREEQC *(27)* have shown that the dissolution of calcite in the Munich gravel in distilled water can be neglected. The concentration of Ca^{2+} at equilibrium conditions were in the range of 0.07 mmol·L^{-1} resulting in an overall ionic strength of 0.05 mmol·L^{-1}. Thus, the better particle removal due to “coagulation” of the latex particles by dissolved calcite in the Munich gravel compared to the Sengenthal sand with purified water can be neglected. The results of these experiments are summarized in Table 5 and are in agreement with those reported for the transport of colloids through natural porous media previously *(14, 19, 20, 22, 28)*.

Influence of the Valence of the Dominant Counterion. The solution chemistry of many natural soils and groundwaters is dominated by Na^+ or Ca^{2+}. Therefore, it is interesting to investigate the influence of the counterion valence on the transport of colloids.

TABLE 5: Influence of the Particle Diameter d_P on the Fraction Recovered in the Column Effluent at Various Chemical Conditions

electrolyte (ionic strength)	particle diameter d_P, μm 0.053	0.161	0.302	0.503	0.691	1.01	1.96
Munich Gravel							
NaCl (10 mmol·L^{-1})	0.095	0.448	0.519	0.537	0.509	0.468	0.253
NaCl (1 mmol·L^{-1})	0.276	0.472	0.572	0.638	0.656	0.631	0.345
$CaCl_2$ (10 mmol·L^{-1})	0.050	0.081	0.177	0.275	0.308	0.246	0.160
$CaCl_2$ (1 mmol·L^{-1})	0.157	0.210	0.375	0.393	0.494	0.445	0.225
H_2O_{dest}	0.411	0.557	0.607	0.697	0.719	0.637	0.319
Sengenthal Sand							
NaCl (10 mmol·L^{-1})	0.000	0.000	0.001	0.002	0.014	0.009	0.005
NaCl (1 mmol·L^{-1})	0.228	0.334	0.463	0.611	0.664	0.518	0.287
$CaCl_2$ (10 mmol·L^{-1})	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$CaCl_2$ (1 mmol·L^{-1})	0.384	0.385	0.466	0.553	0.642	0.540	0.464
H_2O_{dest}	0.731	0.769	0.797	0.844	0.888	0.876	0.713

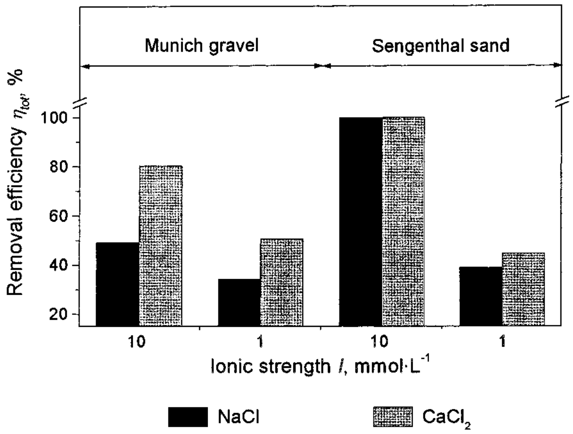

FIGURE 3. Influence of the counterion valence on removal efficiency *E* of the natural porous media of Munich ($d_P = 0.691$ μm) and Sengenthal ($d_P = 0.503$ μm).

The valence of the counterion has no impact on the shape of the breakthrough curves (Figure 2). The dependence of colloidal transport on the valence of the dominant counterion at constant ionic strength is presented in Figure 3 as removal efficiency for the most mobile colloids with particle diameters of $d_P = 0.691$ μm. Generally, at constant ionic strength the removal efficiency decreases if the solution is dominated by a monovalent cation. There was no colloid transport observed in the Sengenthal sand, if a $CaCl_2$ solution at an ionic strength of 10 mmol·L^{-1} was used. At the same hydrochemical conditions, all colloids were observed to be mobile in the Munich gravel. If Na^+ as dominant counterion was used, only the colloids with particle diameters between $d_P = 0.302$ μm and $d_P = 1.01$ μm were mobile in the Sengenthal sand, while all investigated sizes of injected colloids were detected in the Munich gravel. This dependence on the valence of the counterion is more pronounced in the Munich gravel. The replacement of Na^+ by Ca^{2+} increases the removal efficiency by a factor of 1.6, while in the Sengenthal sand the removal efficiency increases by a factor of 1.1. Despite the lower electrolyte concentration the higher removal efficiencies are measured for Ca^{2+} as dominant counterion at given ionic strength. Bivalent electrolytes such as $CaCl_2$ can interact more effectively with the surface of particles and collectors. These interactions cause a greater double layer compression resulting in an increased removal efficiency. Similar results were reported for the dependence of the transport of latex colloids through model systems *(21, 29)*.

Size Dependent Transport. Concerning the breakthrough behavior of latex colloids, which was discussed in a previous section for a single particle diameter, the results can be qualitatively transferred to all investigated particle diameters. The BTCs of the colloidal particles are characterized by a more narrow shape of the BTC and the slightly higher transport velocities compared to the tracer. These differences can be explained by the size-exclusion-effect that causes the exclusion of colloids from small pores *(26, 30, 31)*. It is obvious that this effect is more significant for larger particles. The size-exclusion-effect is more pronounced in heterogeneous materials with a wide grain size distribution. This fact can be seen at the greater differences between the BTCs of colloidal particles and tracer in the Munich gravel compared to the Sengenthal sand.

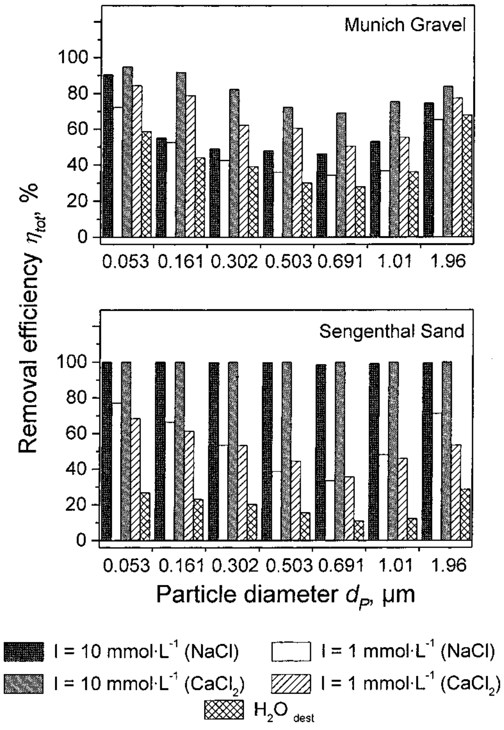

FIGURE 4. Removal efficiencies of the sediments from Munich and Sengenthal at various chemical conditions depending on the particle diameter d_P of the injected latex colloids.

According to the filtration theory the removal efficiency of a porous media depends on the particle diameter, if all other parameters are kept constant. The size-exclusion-effects are negligible in the case of Munich gravel and Sengenthal sand, since 95% of the pores are at least 2 orders of magnitude larger than the colloids (see Figure 1). The removal efficiencies of the investigated sediments for the different chemical conditions in Figure 4 are shown as the function of the diameter of latex particles.

The theoretical predictions of the filtration theory were qualitatively confirmed by the transport experiments. A suspended particle size with a minimum probability for removal is observed to exist. The magnitude of this critical particle diameter (in the range of $d_P = 0.691$ μm) is in good agreement with the predictions. Furthermore, the removal efficiency increases for particles with $d_P < 0.691$ μm due to filtration by diffusion as well as for particles with $d_P > 0.691$ μm due to removal by sedimentation and/or interception as predicted by theory.

Introduction of the Attachment Parameter α. It is well-known that the influence of both electrolyte concentration and type of natural porous media on the removal efficiency of colloids with particle diameters between 1 nm and 10 μm cannot be described quantitatively. Specifically, the predictions based on the DLVO theory show great discrepancies to the experimental data *(13, 29)*. To compare the removal

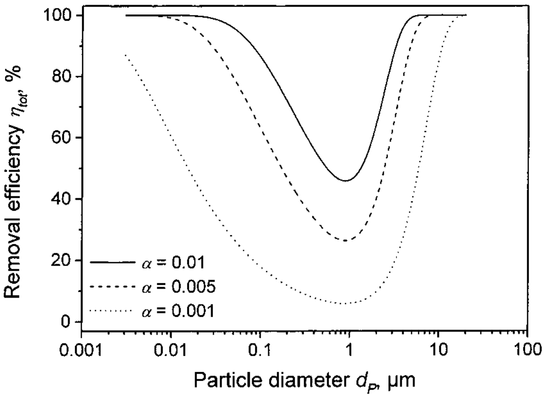

FIGURE 5. Schematic diagram of the influence of α on the removal efficiency *E* of a filter bed.

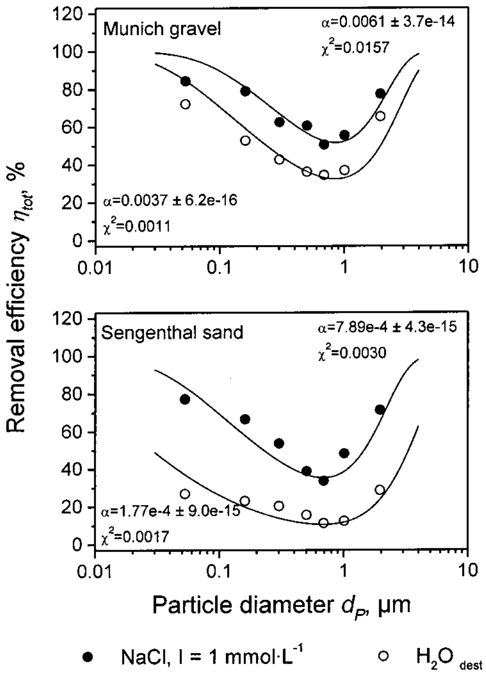

FIGURE 6. Comparison of experimental (symbols) and fitted (solid line) data for removal efficiencies *E* of Munich gravel and Sengenthal sand.

efficiencies of different systems, a set of easy measurable parameters must be defined at first. As mentioned above, Happel's *Sphere-in-Cell Model* was developed to adapt the filtration theory from a single collector to a filter bed. The additional introduced parameter is the total number *N* of unit bed elements UBEs. Every UBE is composed of single collectors. This parameter was calculated for the investigated porous media. According to eq 6 and in contrast to experimental data no colloid breakthrough should be observable for the used systems and conditions (Table 4). The differences between theoretical predictions and experimental data prove once again the influence of electrolyte, i.e., the repulsive double layer interactions on filtration efficiency cannot be neglected. While the transport of colloidal particles to a stationary surface is dominated by convection and diffusion, the attachment of these particles is controlled by colloidal interaction forces which operate at short distances of separation. Thus, not each collision between a colloid and the matrix results in an attachment. To consider solution chemistry Elimelech et al. defined an attachment efficiency that can be calculated from the data of breakthrough experiments and characteristic parameters of the filter bed *(13, 14)*. With increasing electrolyte concentration an increasing attachment efficiency was observed. This finding was explained by the reduced energy barrier between matrix grain and colloid resulting in an increasing fraction of colloids that are "successfully" attached. In analogy to the attachment efficiency of Elimelech et al. a similar parameter will be considered in order to reflect the influence of ionic strength on removal efficiency. Thus, eq 6 can be rewritten as follows:

$$\eta_{tot} = 1 - (1 - \alpha \cdot \eta_{UBE})^N \tag{7}$$

Herein α is the attachment parameter that describes the success of a collision between a colloid and the matrix grains of a UBE. With increasing ionic strength the electrostatic double layer interactions decreases and α is expected to increase. The effect of α on removal efficiency is presented in Figure 5. The shape of the filtration curve is qualitatively determined by d_C and *N*. The position of the minimum removal efficiency is independent of α, while the exact value of η_{tot} increases with increasing α.

To evaluate eq 7 this equation was fitted against the experimental removal efficiencies by varying α and using the parameters of Tables 3 and 4. For each sediment the fitted and experimental removal efficiencies are plotted in Figure 6. As it can been seen in the corresponding charts from the statistical data the experimental data can be described by the exclusive variation of α quite well. In addition, the good agreement of experimental and fitted data confirm the reliability of d_{10} as equivalent collector diameter d_C. This parameter was apart from the porosity the only input parameter that is characteristic for each sediment. Thus, the removal efficiencies of natural porous media can be described without explicit consideration of repulsive double layer interactions by the additional parameter α in Happel's *Sphere-in-Cell Model*. In addition, the value of d_{10} is the only parameter of the sediment which is needed to describe the dependence of the removal efficiency on the sediment.

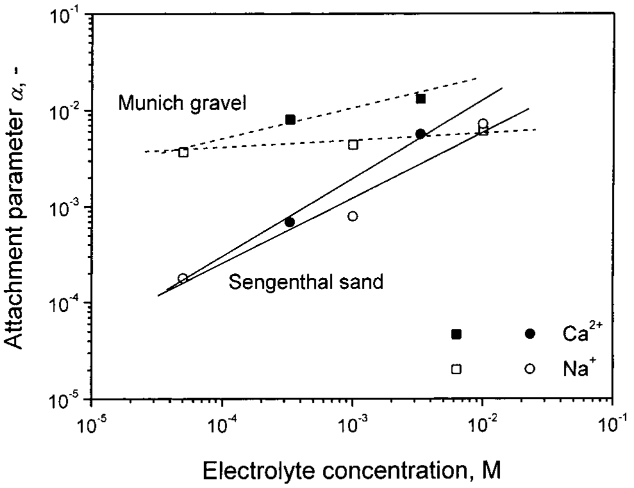

FIGURE 7. Influence of electrolyte concentration on the attachment parameter α for the removal of latex colloids in the Munich gravel and Sengenthal sand.

The influence of electrolyte concentration and valence of counterion on the attachment parameter α is illustrated in Figure 7. The electrolyte concentration of the solution in the effluent was $5 \cdot 10^{-5}$ mol·L^{-1}, if pure water as feed solution has been used. As expected the attachment parameter increases with increasing electrolyte concentration and is higher for Ca^{2+} than for Na^{+} at the same ionic strength. These results are comparable to those of Elimelech et al. *(13)*. The effect of electrolyte concentration on α is greater for Sengenthal sand than for Munich gravel. This observation is in agreement with the dependence of the removal efficiencies at various electrolyte concentrations (see Figure 4).

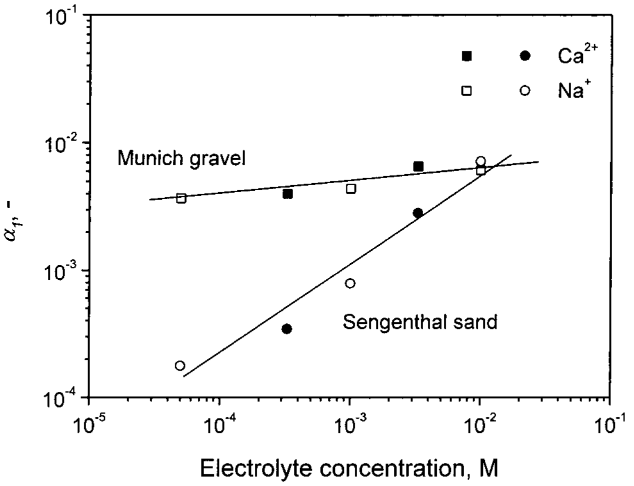

FIGURE 8. Attachment parameter k_1 determined from breakthrough experiments and normalized by the valence z of counterion for the Munich gravel and Sengenthal sand.

As illustrated in Figure 7 α depends on the electrolyte concentration, the valence of counterion, and the physicochemical properties of the sediment. To compare the removal efficiencies independent of the hydrochemistry, a parameter has to be defined which includes the dependence on the electrolyte solution. The influence of the electrolyte concentration but not the valence z of the counterion is partly considered by the attachment parameter α. To get a parameter which describes the removal efficiency η_{tot} at various hydrochemical conditions, α has been normalized by z (eq 8).

$$\alpha_1 = \frac{\alpha}{z} \tag{8}$$

The dependence of the normalized parameter α_1 on the electrolyte concentration is plotted in a log−log-scale as shown in Figure 8. The calculation of α_1 results in a linear relationship between α_1 and the electrolyte concentration. Thus, α_1 becomes independent of the counterion of the electrolyte.

Compared to the studies on model systems the experiments of this study were conducted with two natural porous media. They demonstrate the dependence of the removal efficiency of a filter bed not only on the particle diameter of the injected colloidal particles but also on the solution chemistry and the physico-chemical properties of the sediment. The data suggest that colloids are expected to be very mobile when the ionic strength decreases and the particle diameter d_P is in the range of 0.5−1.0 μm. The determined removal efficiencies are in qualitative agreement with the filtration theory for the removal of colloids at a single collector. The dependency of removal efficiency on the electrolyte concentration was described by an attachment parameter α. This parameter was introduced into the so-called Happel's *Sphere-in-Cell Model* that describes the removal of particles at a filter bed. The normalization of α by the valence of the counterion results in a linear relationship between the electrolyte concentration and α_1. Thus, the removal efficiency becomes independent of the electrolyte. However, the prediction of removal efficiencies is still limited to a certain aquifer material and kind of colloid. A better understanding of the interactions between colloidal particle and matrix grain is essential in order to predict removal efficiencies independent of both type of colloid and sediment.

Acknowledgments

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Literature Cited

(1) McCarthy, J. F.; Zachara, J. M. *Environ. Sci. Technol.* **1989**, *23*, 496−502.
(2) Grolimund, D.; Borkovec, M.; Barmettler, K.; Sticher, H. *Environ. Sci. Technol.* **1996**, *30*, 3118−3123.
(3) Roy, S. B.; Dzombak, D. A. *Environ. Sci. Technol.* **1997**, *31*, 656−664.
(4) Ryan, J. N.; Elimelech, M. *Colloids Surf. A* **1996**, *107*, 1−56.
(5) Gschwend, P. M.; Reynolds, M. D. *J. Contam. Hydrol.* **1987**, *1*, 309−327.
(6) O'Melia, C. R. *Environ. Sci. Technol.* **1980**, *14*, 1052−1060.
(7) Neumann, B. Ph.D. Thesis, Universität Karlsruhe, 1983.
(8) Yao, K. M.; Habibian, M. T.; O'Melia, C. R. *Environ. Sci. Technol.* **1971**, *11*, 1105−1112.
(9) Rajagopalan, R.; Tien, C. *AIChE J.* **1976**, *22*, 523−533.
(10) Tien, C. *Granular Filtration of Aerosols and Hydrosols*; Butterworth Publishers: Boston, MA, 1989.
(11) O'Melia, C. R. In *Aquatic Chemical Kinetics*; Stumm, W., Ed.; Wiley & Sons: New York, 1987; pp 447−474.
(12) Derjaguin, B. V.; Landau, L. D. *Acta Physicochim. URSS* **1941**, *14*, 733−762.
(13) Elimelech, M.; O'Melia, C. R. *Langmuir* **1990**, *6*, 1153−1163.
(14) Elimelech, M.; O'Melia, C. R. *Environ. Sci. Technol.* **1990**, *24*, 1528−1536.
(15) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1995.
(16) Swanton, S. W. *Adv. Colloid Interface Sci.* **1995**, *54*, 129−208.
(17) Fitzpatrick, J. A.; Spielman, L. A. *J. Colloid Interface Sci.* **1973**, *43*, 350−369.
(18) Elimelech, M. *Proc. Manipulation Groundwater Colloids Environ. Restor., Los Angeles* **1993**, 219−224.
(19) Kretzschmar, R.; Barmettler, K.; Grolimund, D.; Yan, Y.-D.; Borkovec, M.; Sticher, H. *Water Resour. Res.* **1997**, *33*, 1129−1137.
(20) Rodier, E.; Dodds, J. *Colloids Surf. A* **1995**, *105*, 221−231.
(21) Seaman, J. C.; Bertsch, P. M.; Miller, W. P. *Environ. Sci. Technol.* **1995**, *29*, 1808−1815.
(22) Nocito-Gobel, J.; Tobiason, J. E. *Colloids Surf. A* **1995**, *107*, 223−231.
(23) Silveira, A. *Proc. 6th Internat. Conf. SMFE* **1965**, 213−222.
(24) Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. A. *Particle Deposition and Aggregation. Measurement, Modelling and Simulation*; Butterworth-Heinemann: Woburn, 1998.
(25) Happel, J. *AIChE J.* **1958**, *4*, 197−201.
(26) Kretzschmar, R.; Sticher, H. *Phys. Chem. Earth* **1998**, *23*, 133−139.
(27) Parkhurst, D. L. *User's Guide to Phreeqc − A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations, Water-Resources Investigations Report 95-4227*; U.S. Geological Survey: Lakewood, 1995.
(28) Johnson, P. R.; Sun, N.; Elimelech, M. *Environ. Sci. Technol.* **1996**, *30*, 3284−3293.
(29) Liu, D.; Johnson, P. R.; Elimelech, M. *Environ. Sci. Technol.* **1995**, *29*, 2963−2973.
(30) Enfield, C. G.; Bengtsson, G. *Ground Water* **1988**, *26*, 64−70.
(31) Higgo, J. J.; Williams, G. M.; Harrison, I.; Warwick, P.; Gardiner, M. P.; Longworth, G. *Colloids Surf. A* **1993**, *73*, 179−200.

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