Modelling the Effects of Water Velocity on TiO₂ Nanoparticles Transport in Saturated Porous Media.

Ivan Toloni, François Lehmann, Philippe Ackerer*

LHyGeS, UMR 7517 CNRS, Université de Strasbourg/EOST, 1 rue Blessig, 67084

STRASBOURG Cedex.

Submitted to Journal of Contaminant Hydrology

First submission: Monday, May 19, 2014

Revised manuscript submission: Wednesday, September 17, 2014

*Corresponding author email: ivan.toloni@etu.unistra.fr

Abstract

The transport of manufactured titanium dioxide (TiO_2 , rutile) nanoparticles (NP) in porous media was investigated under saturated conditions. Experiments were carried out with different fluid velocities, with values in the range of observed velocities in alluvial aquifers. As reported on the literature for different kinds of NPs, the amount of retained NPs decreased when the water velocity increased. Moreover, no retention was observed for ionic strength values smaller than 5 mM.

A transport model coupling convective-dispersive transport with a Langmuirian kinetic deposition was used to fit the BTCs. Empirical linear equations were developed to estimate the attachment rate k_a and the maximal solid phase concentration $s_{\max}$. Both parameters were found to be linearly depending on the collector efficiency (η_0). It was also observed that attachment efficiency (α) did not change with increase of water velocity under the given experimental conditions and that the model had a low sensitivity to α . Based on these estimates of the retention parameters, the classical dispersion-convection model coupled with a Langmuir type adsorption model was able to reproduce quite well the observed TiO_2 breakthrough curves for every fluid velocity used in the experiments.

Keywords: titanium dioxide; column experiments; retention; attachment efficiency; single collector efficiency; langmuirian kinetic.

1. Introduction

The nanotechnology industry constantly develops new applications of nanomaterials, exploiting their large spectrum of properties due to their nanometric size (Auffan et al., 2009). The majority of nanomaterials involve metal nanoparticles (NPs), metal oxide NPs or carbon-based NPs (Batley et al., 2011). NPs are present, inter alia, in sunscreens, coatings, paintings, sports clothing, alimentary packaging, solar cells and fuel cells. They are also involved in degradation processes for contaminants present in soil and water (Nowack and Bucheli, 2007). Inevitably, direct and indirect emissions in the environment occur, leading to a NP presence in air, water and soil (Brar et al., 2010). A better understanding of the NP life cycle could allow a better evaluation of their movements among ecosystems and the transformations that may occur. In this scenario, the environmental risk assessment of NPs is important to ultimately develop adequate regulations for nanoparticle applications (Auffan et al., 2009). NP ecotoxicology takes into account parameters such as the type of NP, size, surface properties and possible coatings (Kahru and Dubourguier, 2010). Focusing the analysis on the aquatic environment is quite difficult to evaluate the fate and environmental impact of NPs due to the number of transformations that NPs can be subject to, *e.g.*, coagulation, interactions with the humic fraction of natural organic matter (NOM), interactions with clays and natural colloids and many surface property modifications (Lowry et al., 2012, Lin et al., 2010). NP behavior in groundwater is of great importance due to the possible underground accumulation of NPs and the consequent risk of contamination of drinking water. TiO₂ NPs are among the most used manufactured NPs and, consequently, are among the most released in the environment.

Many studies, mainly conducted under simplified conditions with cleaned sand packed into columns, have investigated ionic strength (IS) and pH influences on the transport and retention

of TiO₂ NPs in saturated porous media. Chemical parameters are fundamental to the understanding of retention mechanisms because they influence the nanoparticles' surface charge and, consequently, their electrostatic interactions with porous media. Experimental results show that TiO₂ deposition in sand-packed columns is favored by an acidic or neutral pH, which gives NPs a positive or slightly negative surface charge (Chowdhury et al., 2012, Chowdhury et al., 2011, Fang et al., 2013, Godinez and Darnault, 2011, Liang et al., 2013b, Solovitch et al., 2010, Wang et al., 2012). Deposition is also enhanced by increased IS, the effects of which depend on the type of ions in solution (Chowdhury et al., 2012, Chowdhury et al., 2011, Fang et al., 2013, Godinez and Darnault, 2011, Liang et al., 2013b, Solovitch et al., 2010, Wang et al., 2012, Godinez et al., 2013, Chen et al., 2011, Chen et al., 2012). Other parameters, such as concentration, porous media grain size and pore water velocity, modify the probability that NPs will come into contact with collector grains, affecting the deposition rate. Specifically, NP retention increases with a decrease in NP solution concentration and pore water velocity (Chowdhury et al., 2011, Godinez and Darnault, 2011, Liang et al., 2013b). According to previous studies, the presence of surfactants, natural organic matter and bacteria can modify the interactions between NP and porous media, resulting in a reduction of NP retention (Chowdhury et al., 2012, Godinez and Darnault, 2011, Wang et al., 2012, Godinez et al., 2013, Chen et al., 2012). For more complex porous media, columns of soil (Liang et al., 2013a, Cornelis et al., 2013, Fang et al., 2009) and sand with reactive coatings (Wang et al., 2012, El Badawy et al., 2013) have been used. It was found that TiO₂ NPs are more retained in soils with a high clay content and strong salinity. According to Chrysikopoulos and Syngouna (2014), dense NP transport could be influenced by water flow modifications due to gravity effects.

One way to evaluate retention mechanism effects is to apply filtration theory (El Badawy et al., 2013, Petosa et al., 2012, Li et al., 2011), which takes into account physicochemical conditions and describes the frequency of collisions between nanoparticles and collector grains. The parameters of filtration theory offer a simple description of deposition dynamics but can be quite imprecise in some cases. Deviations between predictions and experimental observations are mainly due to repulsive interactions related to the presence of collector surface heterogeneity and of the secondary minima expected by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Tufenkji and Elimelech, 2005a).

Many studies (Fang et al., 2013, Liang et al., 2013b, El Badawy et al., 2013, Li et al., 2011) have fitted NP breakthrough curves (BTCs) to models based on convection-dispersion transport and deposition kinetics, which can simulate different retention mechanisms, such as blocking and straining (Bradford et al., 2011, Bradford et al., 2006). Optimization of the model parameters permits the researcher to better understand the role of the different retention mechanisms and their relevance under different experimental conditions.

The objective of this work was to investigate in greater depth how TiO_2 NP retention mechanisms depend on pore water velocity by conducting column experiments and fitting BTCs. In fact, few publications have been concerned with the effect of water velocity on TiO_2 NP transport (Chowdhury et al., 2011, Godinez and Darnault, 2011), and none have developed a model with a unique set of parameters to simulate the measured BTC. Moreover, to date, the transport models based on convection, dispersion and retention have never been coupled with filtration theory to study the retention mechanisms of TiO_2 nanoparticles. This coupling approach was adopted to investigate the relationship between transport model parameters, filtration theory and experimental conditions. This coupling allows the development of model to

predict the effect of transport model parameters on the function of the experimental conditions and thus to predict NP transport regardless of the pore water velocity.

2. Materials and Methods

2.1 Characterization of Manufactured TiO₂ Nanoparticles

Aqueous suspensions of TiO₂ were prepared by diluting commercial anatase dispersion (NanoAmor 7012WJWR, 15 wt%, 5-30 nm) with deionized (DI) water and setting ionic strength (IS) and pH values with KCl and KOH. In agreement with manufacturer's statement, a primary particle size of 5 nm was determined through transmission electron microscopy. The zeta potential (ζ) of the NPs was measured as a function of pH under different IS values (Figure 1), by means of a Malvern ZetaSizer Nano ZS, yielding an isoelectric point (IEP) around pH 6.

A TiO₂ solution with a concentration of 50 mg L⁻¹, pH 10 and IS of 5 mM was prepared for the experiments, resulting in a Z-average NP size between 70 and 100 nm, measured with the ZetaSizer (Figure S3). The solution pH was chosen to minimize NP deposition. A large NP surface charge ($|\zeta_{\text{nano}}|$) was adopted to make a stable colloidal solution. As reported in the literature, the ζ potential of quartz is around -50 mV at pH 10 (Liang et al., 2013b, Solovitch et al., 2010, Yukselen-Aksoy and Kaya, 2011); therefore, electrostatic repulsion ($|\zeta_{\text{nano}} - \zeta_{\text{sand}}|^{-1}$) between the quartz and NP surfaces was maximized. IS, which increases NP retention, was then chosen to have a measurable retention, since, for IS values smaller than 5 mM, no retention was observed. Complete characterization of the NPs is provided in the support information (SI), including ultraviolet spectra, calibration curves and suspension stability analysis.

2.2 Porous Medium

The porous medium was composed of quartz sand (from Kaltenhouse, France) with an average size of $d_{50} = 490 \mu\text{m}$, a coefficient of uniformity $C_u = 1.595$ and orthoclase and variscite traces. To remove metal oxides, impurities and colloidal particles, the sand was cleaned through three cycles of 0.5 M HCl, 0.5 M KOH and DI water washings, then oven-dried at 60°C (Solovitch et al., 2010).

2.3 Column Experiments

A Plexiglas flow cell from Soil Measurement Systems, Tucson USA (3.75 cm in diameter and 15.2 cm in length) was wet-packed as uniformly as possible with cleaned sand, adding 1 cm of sand at a time, gently tapping the column from time to time and maintaining the water level 1 cm

Figure 1: Zeta potential (ζ) measurements as a function of pH under different ionic strength solution values (0 mM, 3 mM and 5 mM).

over the sand level throughout the process. The water velocity was ensured by a peristaltic pump (average pore velocity $v = 0.002\text{-}0.012\text{-}0.07 \text{ cm s}^{-1}$) and verified by a digital balance. Water flux was imposed from the bottom to the top of the column, to avoid air trapping. As regards conductivity, pH and ultraviolet absorption ($\lambda = 280 \text{ nm}$), values were measured automatically throughout the experiments for both inlet and outlet flows by means of on-line sensors. Before each NP injection, the column was equilibrated at the desired IS and pH with approximately 20 pore volumes (PV) of electrolyte solution. Moreover, a tracer injection of 3 PV (KCl) was effectuated to control the repeatability of the hydrodynamic parameters (porosity $\phi = 0.39 \pm 0.005$; longitudinal dispersivity $\alpha_L = 0.069 \pm 0.006 \text{ cm}$). Each experiment resulted in a 3 PV injection of the NP suspension, followed by an injection of the electrolyte solution until a complete breakthrough curve (BTC) was attained (approximately 2 PV more). After each NP injection, the tracer experiment was repeated to check whether hydrodynamic parameters were affected by NP deposition. All column experiments were conducted, in duplicate or additional replicates, at a room temperature of $22 \text{ }^\circ\text{C}$.

2.4 Retention Model

The transport and retention of NP through the porous media was simulated using the convection-dispersion equation model coupled with a kinetic retention term:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial c}{\partial x} \right) - \frac{\partial q_D c}{\partial x}, \quad q_D = \phi v \quad (1)$$

$$\rho \frac{\partial s}{\partial t} = \theta k_a \Psi c \quad (2)$$

$$\Psi = 1 - \frac{s}{s_{\max}} \quad (3)$$

where $\theta [-]$ is the volumetric water content, $c [\text{M L}^{-3}]$ is the NP aqueous phase concentration, $\rho [\text{M L}^{-3}]$ is the bulk density of the porous media, $s [\text{M M}^{-1}]$ is the NP solid phase concentration, t is time $[\text{T}]$, $x [\text{L}]$ is the distance from the column inlet, $D [\text{L}^2 \text{T}^{-1}]$ is the hydrodynamic dispersion coefficient, $q_D [\text{L T}^{-1}]$ is the Darcy velocity, $v [\text{L T}^{-1}]$ is the pore velocity, $\phi [-]$ is the porosity, $k_a [\text{T}^{-1}]$ is the attachment coefficient, $\Psi [-]$ is a retention function and $s_{\max} [\text{M M}^{-1}]$ the maximal solid phase concentration. Assuming that the porous media is saturated, the volumetric water content θ coincides with porosity in equation 1.

NP retention was assumed to be irreversible and time- and concentration-dependent. Accordingly, in equation 2, k_a is multiplied by Ψ , which decreases over time and with an increasing amount of retained NPs (El Badawy et al., 2013, Bradford et al., 2011, Adamczyk et al., 1994). Such a retention function is associated with blocking, a retention mechanism related to the filling of porous media attachment sites. Adopting this model, NPs were supposed to interact with a limited amount of attachment sites ($s_{\max}$) in porous media, such as metal oxide surfaces or roughness of the collector surface (Bradford, 2006). Therefore, as the number of occupied sites is increasing throughout an experiment, the probability of a NP encountering a free site decreases (Ryan and Elimelech, 1996).

In the simulations, hydrodynamic parameters obtained from tracer experiments were prescribed, while k_a and $s_{\max}$ values were optimized to fit the BTC. HYDRUS-1D (Šimunek et al., 2008) (version 4.16) was used to solve both direct and inverse problems, applying the Levenberg-Marquardt algorithm for parameter optimization (Bradford et al., 2003). Equation 1 was solved by prescribing the Darcy flux and applying boundary conditions corresponding to the measured inlet concentration (bottom of the column). A zero-concentration gradient condition was applied at the outlet (top of the column).

2.5 Filtration Theory

According to classic filtration theory, the attachment coefficient k_a is related to the attachment efficiency α [-] and the single collector efficiency η_0 [-] (Ma et al., 2009):

$$k_a = \frac{3(1-\phi)q_D}{2d_{50}\phi} \alpha \eta_0 \quad (4)$$

where d_{50} [L] is the diameter of a spherical collector. The single collector efficiency η_0 represents the fraction of approaching particles that collide with collector grains, while the attachment efficiency α is the fraction of collisions that result in attachment. The product of α and η_0 gives the single collector removal efficiency η [-] (Ryan and Elimelech, 1996). The value of η_0 (Table 1) was calculated based on the model of Tufenkji and Elimelech (2004), presented in the SI. The value of α was calculated (Table 1) from optimized k_a values and η_0 values using Equation 4.

2.6 DLVO Theory

The classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to estimate the particle-collector and particle-particle interaction energy profiles. The total interaction energy is the sum of van der Waals attraction potential (V_{vdW}) and electric double layer repulsion potential (V_{edl}). Retarded van der Waals equations from Gregory (Gregory, 1981) were adopted for V_{vdW} together with V_{edl} equations from Hogg *et al.* (Hogg et al., 1966). DLVO energy calculations give an estimate of V_{edl} because the equations were adopted for ζ values near a small surface potential limit ($\zeta < 50$ -60 mV) (Hogg et al., 1966). Extended calculations and adopted parameters are provided in the SI.

3. Results and Discussion

3.1 Water Velocity Effect

Column experiments were performed under three pore water velocities (see BTC in Figure 2). The results show a decrease in the NP mass retained by the porous media when water velocity increases (Table 1), according to classic filtration theory (Zamani and Mainibrownian, 2009, Yao et al., 1971). The shapes of the elution curves are typical of blocking behavior, associated with a decrease of NP retention in time (Chen et al., 2012). This retention mechanism, resulting in an increase of NP concentration over time in the elution, consists in the progressive saturation of the attachment sites. The occurrence of retention, despite the unfavorable attachment conditions, could be explicated by secondary energy minima (see section 3.2) and by roughness and inhomogeneity of the sand surface. Recent studies emphasized that the presence of roughness can modify the torque balance, increasing the adhesive torque that the NPs experience and decreasing the hydrodynamic drag (Shen et al., 2014; Bradford et al., 2013). Furthermore, straining can be excluded because the ratio of NP to average grain size (0.0004) is significantly smaller than the 0.005 guideline available in the literature (Bradford et al., 2006).

3.2 Retention Model Parameters

The adopted retention model (Equations 1, 2 and 3), together with optimized parameters, provides a good description of the BTC ($R^2 > 0.94$, Table 1). It should be noted that the parameters at $v = 0.002 \text{ cm s}^{-1}$, unlike at other velocities, are strongly correlated (-0.94). This large correlation value is attributable to the BTC's poor signal variation nonmonotonic shape, which cannot be properly described by the model (Liang et al., 2013b).

The optimized parameters (Table 1) show a strong correlation with water velocity. Increases in q_D are accompanied by an attachment coefficient k_a increase and a maximal solid phase concentration s_{max} decrease. Thus, higher retention is not associated with a larger attachment

kinetics (k_a is a frequency). In contrast, higher retention is related to smaller kinetics, resulting from a longer resident time. Resident time, determined by the pore water velocity and column length, is therefore a key parameter for NP retention. Considering s_{max} as the number of attachment sites accessible to NPs, this behavior could be interpreted as a reduction in the number of sites “seen” by NPs when the water velocity increases. However, if the kinetic energy of a particle becomes larger, stronger energy bonds are needed to retain the particle after collision. Consequently, the sites that do not have sufficient attractive energy will not interact with the particle, and the s_{max} value decreases. According to our DLVO calculations (Figure S4), a very weak ($-0.13 k_B T$) secondary minimum is expected in the particle-collector energy profile. A relation between s_{max} and this secondary energy minimum could occur, being the secondary energy minima considered responsible for retention under unfavorable conditions (Liang et al., 2013b, Tufenkji and Elimelech, 2005b).

3.3 Filtration Theory Parameters

The fraction of NPs that collide with sand grains, the single collector efficiency η_0 , becomes smaller when water velocity increases (Table 1), in agreement with the trend of retained mass. In fact, for NPs, because their size makes them Brownian particles, diffusion is the most relevant transport mechanism involved in deposition (Zamani and Mainibrownian, 2009). Hence, when convection transport increases, it perturbs diffusive transport, also affecting the deposition mechanisms.

The α values obtained under different water velocities are very similar, suggesting that α is a parameter independent of water velocity in the range of adopted velocities. In the literature, the dependence of α on hydrodynamic factors is still a controversial topic. In previous studies, α was assumed to be unaffected by water velocity (Elimelech, 1992), while, elsewhere, a decrease

(Anders et al., 2005, Lecoanet et al., 2004) or an increase (Kim and Lee, 2014) of α was observed when the water velocity increases. Other studies reported the existence of a critical flow velocity (Shen et al., 2010; He et al., 2009). According to Shen et al. (2010), the attachment efficiency does not change with the increase of water velocity until a critical value is attained. This critical value is not reached under our experimental conditions and therefore, the attachment efficiency is independent of hydrodynamics.

Table 1: Experimental parameters, optimized parameters and calculated parameters for column experiments*.

v	M	η_0	s_{max}/C_0	k_a	Corr	R^2	α	k_{cal}	R^2
(cm s ⁻¹)	(%)	(-)	(cm ³ g ⁻¹)	($\times 10^{-4}$ s ⁻¹)				($\times 10^{-4}$ s ⁻¹)	
0.002	95	0.14	1.2 ± 0.1	5.5 ± 0.4	-0.94	0.94	0.106	6.2	0.94
0.012	45	0.04	0.31 ± 0.01	13 ± 1	-0.07	0.98	0.153	10.35	0.96
0.07	13	0.01	0.113 ± 0.008	15.0 ± 1	-0.28	0.98	0.103	17.0	0.98

*Errors represent the 95% confidence interval. v , average pore velocity; M, retained mass percentage; η_0 , calculated single collector efficiency; s_{max}/C_0 , maximal solid phase concentration; k_a , optimized attachment coefficient; Corr, correlation between optimized parameters s_{max} and k_a ; R^2 , Pearson's correlation coefficient for parameter optimization; α , calculated attachment efficiency; k_{cal} , attachment coefficient calculated with $\alpha = \alpha_{av} = 0.12$; R^2 , Pearson's correlation coefficient for new model fit.

3.4 A Predictive Transfer Model

To find tendencies that could help in modeling retention mechanisms, the mutual correlation between retention model parameters and filtration parameters was studied. Linear relations were found for both s_{max} and k_a as a function of η_0 (Figure 3):

$$k_a = a_1 \eta_0 + a_2 \quad (5)$$

$$s_{max} = a_3 \eta_0 \quad (6)$$

where the empirical parameters a_1 [T^{-1}], a_2 [T^{-1}], a_3 [$L^3 M^{-1}$] are equal to $(-9.06 \pm 0.01) \times 10^{-4} s^{-1}$, $(16.00 \pm 0.01) \times 10^{-4} s^{-1}$ and $8 \pm 0.1 cm^3 g^{-1}$. These linear equations accurately describe experimental BTCs and predict NP behavior for any pore water velocity in the studied range, at least under the experimental conditions. Gravity effects are not taken into account since the NP size is smaller than 500 nm (Lazouskaya et al., 2011). Retention mechanisms other than blocking are not considered in the model. Moreover, given the similarity of α values for different water velocities, the attachment efficiency was assumed to be independent of the fluid velocities as discussed in Section 3.3 and its arithmetic average value ($\alpha_{av} = 0.12 \pm 0.3$) was used in the following. Using this new parameter, k_a was subsequently recalculated through Equation 4:

$$k_{cal} = \frac{3(1-\phi)q_D}{2d_{50}\phi} \alpha_{av} \eta_0 \quad (7)$$

where k_{cal} is an expression for k_a that does not depend on BTC shape. Recalculated values deviate by 13-22% from optimized values, without a definite trend (Figure 3). Transport simulations of TiO_2 NP were then repeated with $k_a = k_{cal}$, obtaining good fits (Figure 2, Table 1). These results imply that Equations 6 and 7 give a sufficiently good prediction of the optimized parameters. We can also observe that the model is weakly sensitive to the attachment efficiency, the results for α and α_{av} being very similar, and that a rough estimation of this value could be

sufficient to obtain a good estimation of NP behavior. A similar lack of sensitivity to attachment efficiency has been also reported in the literature (Quirk et al., 2014; Praetorius et al., 2012).

Figure 2: BTC and model predictions under different pore water velocities (IS = 3 mM, pH 10). Maximal solid phase concentration s_{max} and attachment coefficient k_a obtained through Equations 6 and 7.

Figure 3: Model parameters as a function of collector efficiency. Maximal solid phase concentration s_{max} and attachment coefficient k_a are optimized, k_{cal} is calculated. k_a and s_{max} are linearly fitted through Equation 5 and 6. Error bars represent the 95% confidence interval.

4. Conclusion

A linear behavior as a function of the collector efficiency was observed for retention parameters (attachment rate and the maximal solid phase concentration) of the model that describes TiO₂ NP mobility in a saturated porous medium under different fluid velocities. We also found that attachment efficiency does not change with water velocity in the range of studied velocities. Based on empirical relationships between the transport model parameters and the filtration theory parameters, the retention model presented in our study, allows the simulation of TiO₂ NPs transport for any pore water velocity in the studied range and, at least, under the experimental conditions described in this article.

The dependence of the parameters involved in the relationships between the transport model parameters and the filtration theory parameters on one hand, and other physical-chemical parameters on the other hand, should be investigated, especially in relation to ionic strength. Moreover, the model should be tested with another type of NP to assess whether the observed behavior is related exclusively to the surface properties of the employed NP and porous material.

Supporting Information

Information as noted in the text.

Acknowledgments

This work was founded by the French National Research Agency under the program MESONNET. The authors gratefully thank Jérôme Labille, Mireille Del Nero and Catherine Galindo for discussions and help in Zetasizer measurements.

References

Adamczyk, Z., Siwek, B., Zembala, M., Belouschek, P., 1994. Kinetics of localized adsorption of colloid particles. *Advances in Colloid and Interface Science* 48, 151 – 280.

Anders, R., Chrysikopoulos, C.V., 2005. Virus fate and transport during artificial recharge with recycled water. *Water Resources Research* 41(10), W10415.

Auffan, M., Rose, J., Wiesner, M.R., Bottero, J.-Y., 2009. Chemical stability of metallic nanoparticles: A parameter controlling their potential cellular toxicity in vitro. *Environmental Pollution* 157(4), 1127–1133.

Batley, G.E., Kirby, J.K., McLaughlin, M.J., 2011. Fate and risks of nanomaterials in aquatic and terrestrial environments. *Accounts of Chemical Research* 46(3), 854–862.

Beydoun, H., Lehmann, F., 2006. Drainage experiments and parameter estimation in unsaturated porous media. *Comptes Rendus – Geoscience* 338, 180-187.

Bradford, S.A., Simunek, J., Bettahar, M., Van Genuchten, M.T., Yates, S.R., 2003. Modeling colloid attachment, straining, and exclusion in saturated porous media. *Environmental Science & Technology* 37(10), 2242–2250.

Bradford, S. A., Simunek, J., Bettahar, M., van Genuchten, M. T., Yates, S. R., 2006. Significance of straining in colloid deposition: Evidence and implications. *Water Resources Research* 42(12), W12S15.

Bradford, S., Torkzaban, S., Shapiro, A., 2013. A theoretical analysis of colloid attachment and straining in chemically heterogeneous porous media. *Langmuir*, 29(23), 6944-6952.

Bradford, S.A., Torkzaban, S., Simunek, J., 2011. Modeling colloid transport and retention in saturated porous media under unfavorable attachment conditions. *Water Resources Research* 47(10), W10503.

Brar, S.K., Verma, M., Tyagi, R.D., Surampalli, R.Y., 2010. Engineered nanoparticles in wastewater and wastewater sludge - Evidence and impacts. *Waste Management* 30(3), 504–520.

Chen, G., Liu, X., Su, C., 2011. Transport and retention of TiO₂ rutile nanoparticles in saturated porous media under low-ionic-strength conditions: measurements and mechanisms. *Langmuir* 27(9), 5393–5402.

Chen, G., Liu, X., Su, C., 2012. Distinct Effects of Humic Acid on Transport and Retention of TiO₂ Rutile Nanoparticles in Saturated Sand Columns. *Environmental Science & Technology* 46(13), 7142–7150.

Chowdhury, I., Hong, Y., Honda, R.J., Walker, S.L., 2011. Mechanisms of TiO₂ nanoparticle transport in porous media: Role of solution chemistry, nanoparticle concentration, and flowrate. *Journal of Colloid Interface Science* 360(2), 548–555.

Chowdhury, I., Cwiertny, D.M., Walker, S.L., 2012. Combined factors influencing the aggregation and deposition of nano-TiO₂ in the presence of humic acid and bacteria. *Environmental Science & Technology* 46(13), 6968–6976.

Chrysikopoulos, C.V., Syngouna, V.I., 2014. Effect of gravity on colloid transport through water-saturated columns packed with glass beads: modeling and experiments, *Environmental Science & Technology*, 48(12), 6805-6813.

Cornelis, G., Pang, L., Doolette, C., Kirby, J.K., McLaughlin, M.J., 2013. Transport of silver nanoparticles in saturated columns of natural soils. *Science of The Total Environment*, 463-464, 120 – 130.

El Badawy, A.M., Aly Hassan, A., Scheckel, K.G., Suidan, M.T., Tolaymat, T.M., 2013. Key factors controlling the transport of silver nanoparticles in porous media. *Environmental Science & Technology* 47(9), 4039–4045.

Elimelech, M., 1992. Predicting collision efficiencies of colloidal particles in porous media. *Water Research* 26(1), 1-8.

Fang, J., Shan, X.Q., Wen, B., Lin, J.M., Owens, G., 2009. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environmental Pollution* 157(4), 1101 – 1109.

Fang, J., Xu, M.J., Wang, D.J., Wen, B., Han, J.Y., 2013. Modeling the transport of TiO₂ nanoparticle aggregates in saturated and unsaturated granular media: effects of ionic strength and pH. *Water Research* 47(3), 1399 – 1408.

Godinez, I.G., Darnault, C.J.G., 2011. Aggregation and transport of nano-TiO₂ in saturated porous media: effects of pH, surfactants and flow velocity. *Water Research* 45(2), 839–851.

Godinez, I.G., Darnault, C.J.G., Khodadoust, A.P., Bogdan, D., 2013. Deposition and release kinetics of nano-TiO₂ in saturated porous media: effects of solution ionic strength and surfactants. *Environmental Pollution* 174, 106 – 113.

Gregory, J., 1981. Approximate expressions for retarded van der Waals interaction. *Journal of Colloid and Interface Science* 83(1), 138 – 145.

He, F., Zhang, M., Qian, T., Zhao, D., 2009. Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: Column experiments and modeling. *Journal of Colloid Interface Science* 334(1), 96–102.

Hogg, R., Healy, T.W., Fuerstenau, D.W., 1966. Mutual coagulation of colloidal dispersions. *Transactions of the Faraday Society* 62, 1638–1651.

Kahru, A., Dubourguier, H.C., 2010. From ecotoxicology to nanoecotoxicology. *Toxicology* 269, 105 – 119.

Kim, C., Lee, S., 2014. Effect of seepage velocity on the attachment efficiency of TiO₂ nanoparticles in porous media. *Journal of Hazardous Materials* 279, 163 – 168.

Lazouskaya, V., Wang, L.-P., Gao, H., Shi, X., Czymmek, K., Jin, Y., 2011. Pore-scale investigation of colloid retention and mobilization in the presence of a moving air-water interface. *Vadose Zone Journal*, 10(4), 1250-1260.

Li, Z., Sahle-Demessie, E., Hassan, A.A., Sorial, G.A., 2011. Transport and deposition of CeO₂ nanoparticles in water-saturated porous media. *Water Research* 45(15), 4409–4418.

Liang, Y., Bradford, S.A., Simunek, J., Heggen, M., Vereecken, H., Klumpp, E., 2013a. Retention and remobilization of stabilized silver nanoparticles in an undisturbed loamy sand soil. *Environmental Science & Technology* 47(21), 12229–12237.

Liang, Y., Bradford, S.A., Simunek, J., Vereecken, H., Klumpp, E., 2013b. Sensitivity of the transport and retention of stabilized silver nanoparticles to physicochemical factors. *Water Research* 47(7), 2572 – 2582.

Lin, D., Tian, X., Wu, F., Xing, B., 2010. Fate and transport of engineered nanomaterials in the environment. *Journal of Environmental Quality* 39(6), 1896–1908.

Lowry, G.V., Gregory, K.B., Apte, S.C., Lead, J. R., 2012. Transformations of Nanomaterials in the Environment. *Environmental Science & Technology* 46(13), 6893–6899.

Ma, H., Pedel, J., Fife, P., Johnson, W.P., 2009. Hemispheres-in-cell geometry to predict colloid deposition in porous media. *Environmental Science & Technology* 43(22), 8573–8579.

Nowack, B., Bucheli, T.D., 2007. Occurrence, behavior and effects of nanoparticles in the environment. *Environmental Pollution* 150(1), 5 – 22.

Petosa, A.R., Brennan, S.J., Rajput, F., Tufenkji, N., 2012. Transport of two metal oxide nanoparticles in saturated granular porous media: role of water chemistry and particle coating. *Water Research* 46(4), 1273–1285.

Praetorius, A., Scheringer, M., Hungerbühler, K., 2012. Development of environmental fate models for engineered nanoparticles - A case study of TiO₂ nanoparticles in the Rhine river. *Environmental Science & Technology* 46, 6705-6713.

Quik, J., Velzeboer, I., Wouterse, M., Koelmans, A., van de Meent, D., 2014. Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Water Research* 48, 269 – 279.

Ryan, J.N, Elimelech, M., 1996. Colloid mobilization and transport in groundwater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 107, 1 – 56.

Šimunek, J., van Genuchten, M.Th., Šejna, M., 2008. Development and Applications of the HYDRUS and STANMOD Software Packages and Related Codes. *Vadose Zone Journal* 7(2), 587–600.

Solovitch, N., Labille, J., Rose, J., Chaurand, P., Borschneck, D., Wiesner, M.R., Bottero, J.-Y., 2010. Concurrent aggregation and deposition of TiO₂ nanoparticles in a sandy porous media. *Environmental Science & Technology* 44(13), 4897–4902.

Tufenkji, N., Elimelech, M., 2004. Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical Filtration in Saturated Porous Media. *Environmental Science & Technology* 38(2), 529–536.

Tufenkji, N., Elimelech, M., 2005a. Breakdown of colloid filtration theory: role of the secondary energy minimum and surface charge heterogeneities. *Langmuir* 21(3), 841–852.

Tufenkji, N., Elimelech, M., 2005b. Reply to comment on breakdown of colloid filtration theory: role of the secondary energy minimum and surface charge heterogeneities. *Langmuir* 21(23), 10896–10897.

Wang, C., Bobba, A.D., Attinti, R., Shen, C., Lazouskaya, V., Wang, L.-P., Jin, Y., 2012. Retention and transport of silica nanoparticles in saturated porous media: effect of concentration and particle size. *Environmental Science & Technology* 46(13), 7151–7158.

Yao, K.-M., Habibian, M.T., O'Melia, C.R., 1971. Water and waste water filtration: concepts and applications. *Environmental Science & Technology* 5(11), 1105–1112.

Yukselen-Aksoy, Y., Kaya, A., 2011. A study of factors affecting on the zeta potential of kaolinite and quartz powder. *Environmental Earth Sciences* 62(4), 697–705.

Zamani, A., Mainibrownian, B., 2009. Flow of dispersed particles through porous media: deep bed filtration. *Journal of Petroleum Science and Engineering* 69(1-2), 71 – 88.