



## Transport and deposition of ZnO nanoparticles in saturated porous media

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### ABSTRACT

The impact of ionic strength and cation valence on the transport and deposition kinetics of ZnO nanoparticles in saturated porous media was systematically investigated in this research. Packed column experiments were performed over a series of environmentally relevant ionic strength in both NaCl (ranging from 1 to 20 mM) and CaCl<sub>2</sub> (ranging from 0.1 to 1 mM) solutions. Solution chemistries (ionic strength and ion types) greatly affected the transport of ZnO nanoparticles in saturated quartz sand. Flat breakthrough plateaus were observed at relatively low ionic strength in both NaCl (1 and 5 mM) and CaCl<sub>2</sub> (0.1–0.5 mM) solutions, whereas, ripening was observed at high ionic strength (10 and 20 mM in NaCl, and 1 mM CaCl<sub>2</sub>) conditions. Deposition of nanoparticle increased with increasing solution ionic strength in both monovalent and divalent salt solutions. The presence of divalent ions in solutions increased nanoparticle deposition in quartz sand. Under all examined conditions, nanoparticles mainly retained at segments near the column inlet. The retained ZnO nanoparticle concentrations versus transport distance decreased faster than the theory prediction of log-linear decrease under all examined conditions. Our study found that concurrent aggregation of ZnO nanoparticles occurred during the transport process, which contributed to the hyper-exponential retained profiles.

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### 1. Introduction

Due to their enhanced physico-chemical properties relative to their bulk counterparts, nanoparticles have drawn great attentions in the fields of science and engineering in past several years [1]. Massive investment in nanotechnology has led to the rapid emerging of new nanoparticles such as metal oxide nanoparticles [2]. Although great application promise of nanoparticles has been demonstrated, understanding the transport and fate of these nanomaterials especially metal oxide nanoparticles in natural environment is still incomplete.

ZnO nanoparticles are one of the most popular metal oxide nanoparticles that have been wide applications in various industries, such as electronic engineering [3,4], environmental engineering [5,6] and cosmetics industry [2]. Recent studies have showed that ZnO nanoparticles were toxic to plants [7,8], bacteria [9,10], rodents [11], as well as human cell lines [12]. The potential risks of ZnO nanoparticles to the environmental and public health after released into natural environment have been found to be greatly correlated to their distributions of concentration and particle sizes in natural environment [13,14]. Understanding the transport and aggregation behaviors of ZnO nanoparticles under environmentally relevant conditions is therefore necessary.

A few studies have investigated the aggregation behavior of ZnO nanoparticles. Zhang et al. [15] examined the stability of ZnO nanoparticles at pH 8 and found particles were quickly aggregated after suspending in tap water. Zhang et al. [16] also showed that the addition of a relatively weak electrolyte concentration (0.01 M KCl) could result in the aggregation of ZnO nanoparticles in neutral water. By comparing the aggregation kinetics of two types of ZnO nanoparticles (spherical and irregular shaped ZnO) under various conditions, Zhou and Keller [17] found that the aggregation of the nearly spherical ZnO exhibited strong dependence on the solution ionic strength, while the influence of ionic strength on aggregation of the irregularly shaped ZnO was minimal. By dispersing ZnO nanoparticles in samples taken from eight different aqueous media associated with seawater, lagoon, river, and groundwater, Keller et al. [18] showed that the electrophoretic mobility of nanoparticles in a given aqueous media was controlled by ionic strength and the presence of natural organic matter.

Unlike the studies regarding the aggregation kinetics of ZnO nanoparticles, to date, very few investigations have directed toward understanding the deposition and transport behavior of ZnO nanoparticles under environmentally relevant conditions. By employing a quartz crystal microbalance with dissipation (QCM-D), our recent study [19] investigated the influence of ionic strength and salt composition on the deposition of ZnO nanoparticles on flat silica surface. This study showed that increasing solution ionic strength increased ZnO nanoparticle deposition and the deposition was more enhanced in the presence of divalent ions. Very

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recently, Ben-Moshe et al. [20] examined the transport behavior of ZnO nanoparticles in packed spherical porous media (glass beads). By comparing the breakthrough curves obtained under different ionic strength in NaCl solutions, these authors found increasing ionic strength enhanced the deposition of nanoparticles. However, retained profiles (the retained nanoparticle concentrations versus transport distance), a more important 'indicator' of nanoparticle transport behavior from which the mechanism(s) controlling the ZnO transport can be derived, have not been investigated in these studies. Moreover, the transport of ZnO nanoparticles in irregular porous media (quartz sand) that are more common in natural environment relative to spherical porous media (glass bead) has never been examined.

Hence, this study was performed to fully understand the mechanisms controlling the deposition and transport behaviors of ZnO nanoparticles in packed irregular porous media by monitoring both the breakthrough curves and the retained profiles. The transport experiments were performed under series of environmentally relevant ionic strengths in both monovalent and divalent solutions. Our study showed that solution chemistries had great influence on the transport behavior of ZnO nanoparticles. In all examined conditions both in monovalent and in divalent salt solutions, the retained nanoparticle profiles displayed hyper-exponential decreases with transport distance. Simultaneous aggregation of nanoparticles occurred in the packed porous media was found to drive the observed hyper-exponential retained profiles.

## 2. Materials and methods

### 2.1. Nanoparticle suspension preparation

ZnO nanoparticle stock suspension ( $100 \text{ mg L}^{-1}$ ) was prepared by suspending nanopowders ( $20 \pm 5 \text{ nm}$  in diameter, purity greater than 99.5%, Zhejiang Hongsheng Material Technology Co., China) in Milli-Q water (Q-Gard1, Millipore Inc., MA) and sonicated for 30 min with a sonicating probe (Ningboxinzi Biotechnology LTD., China) [19]. Nanoparticle suspensions ( $5 \text{ mg L}^{-1}$ ) were made by diluting stock suspension into salt solutions (NaCl or  $\text{CaCl}_2$ ) at pH  $8.0 \pm 0.1$  (adjusted with 0.1 M NaOH). After preparation, nanoparticle suspensions were stirred at 200 rpm for 3 h and then vigorously shaken using a vortex mixer at high speed for 15 min prior to each transport experiment. It should be noted that to ensure the pH of nanoparticle suspension stabilized at 8.0 during the transport experiment, nanoparticle suspension required continuously slight adjustment with 0.1 M NaOH within 2 h after preparation until the final pH of 8.0 was obtained and not changed afterwards. The stock suspension was freshly prepared each time before column experiment.

The detailed characterization of ZnO nanoparticles has been described in our latest published study [19] and also provided in the [Supplementary Information](#). The corresponding zeta potentials and particle sizes of ZnO nanoparticle suspension ( $5 \text{ mg L}^{-1}$ ) were measured in both NaCl and  $\text{CaCl}_2$  solutions with Zetasizer Nano ZS90 (Malvern Instruments, UK). Measurements were performed right before and after the column experiments and repeated 30–40 times at room temperature ( $25^\circ\text{C}$ ). The results for zeta potentials and particle sizes of ZnO nanoparticles at different ionic strength conditions in both NaCl and  $\text{CaCl}_2$  solution were depicted in [Figs. S1 and S2](#), respectively.

### 2.2. Porous media

The porous media used for ZnO nanoparticle transport experiments was irregular quartz sand (ultrapure with 99.80%  $\text{SiO}_2$ ) (Hebeizhensheng Mining LTD., China) with sizes ranging from 417

to  $600 \mu\text{m}$  (the median diameter of  $510 \mu\text{m}$ ). The procedure used for cleaning the quartz sand was provided in the previous publication [21], as well as in the [Supplementary Information](#). The zeta potentials of the crushed quartz sand were also measured in both NaCl and  $\text{CaCl}_2$  solutions under the experimental conditions and repeated 9–12 times.

### 2.3. Porous media experiments

ZnO nanoparticle transport experiments in porous media were performed at ionic strength ranged from 1 to 20 mM and from 0.1 to 1 mM in NaCl and  $\text{CaCl}_2$  solutions, respectively. These series of solution chemistries examined in this study can be commonly found in groundwater [22]. The cylindrical Plexiglass columns (20 cm in length and 4.0 cm in inner diameter) were wet-packed with cleaned quartz sand, and detailed information for this packing procedure has been described in Tong et al. [21], which was also provided in the [Supplementary Information](#). The porosity of packed column was approximately 0.42.

After packing, the columns were pre-equilibrated with at least 10 pore volumes of nanoparticle-free salt solutions at desired ionic strength and pH. Following pre-equilibration, 3 pore volumes of ZnO nanoparticle suspension were injected into the column, followed by elution with 5 pore volumes of salt solution at the same ionic strength and pH. The suspensions and solutions were injected into the columns in up-flow mode using a syringe pump (Harvard PHD 2000, Harvard Apparatus Inc., Holliston, MA). The influent concentration of ZnO nanoparticle suspension was  $5 \text{ mg L}^{-1}$ , which was determined by measuring the zinc concentration via coupled plasma mass spectrometry (ICP-MS) (XSeries II, Thermo Scientific) after acid digestion by dissolving in 5%  $\text{HNO}_3$  and diluting by a factor of 10. At this pH ( $\text{pH} < 1$ ), the release of  $\text{Zn}^{2+}$  from ZnO nanoparticles was above 92% [23,24]. The calibration curve of ZnO nanoparticle suspensions was provided in the [Supplementary Information](#) ([Fig. S3](#)). The pore water velocity of all experiments was set to be  $8 \text{ m day}^{-1}$  ( $2.93 \text{ mL min}^{-1}$ ) to represent fluid velocities in coarse aquifer sediments, forced-gradient conditions, or engineered filtration systems.

Samples from the column effluent were collected continuously ( $\sim 5 \text{ mL}$ ) in 10 mL sterile centrifuge tubes. Following the transport experiment, the sand was excluded from column under gravity and dissected into 10 segments (each 2 cm long). Specific volumes of Milli-Q water were added into each segment. The effluent samples and supernatant samples from recovery of retained nanoparticles were analyzed by measuring the zinc concentration via ICP-MS after dissolving in 5%  $\text{HNO}_3$  and diluting by a factor of 10. The area under the breakthrough–elution curve was integrated to yield the percentage of ZnO nanoparticles that exited the column. The percentage of ZnO nanoparticles recovered from the sediment was determined by summing the ZnO nanoparticles recovered from all segments of the sediment and dividing by total number (concentration) injected. Summing the percentages of both retained and exited nanoparticles resulted in the overall recovery (mass balance) of the ZnO nanoparticles ([Table 1](#)).

### 2.4. Particle tracking model

The transport and retention of nanoparticles was modeled using an advection–dispersion equation that includes removal from and re-entrainment to the aqueous phase

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - k_f C + \frac{\rho_b}{\theta} k_r S_r \quad (1)$$

where  $C$  is the concentration of nanoparticles in the aqueous phase (nanoparticles per unit volume of fluid),  $t$  is the travel time,  $x$  is the travel distance,  $v$  is the flow velocity,  $D$  is the dispersion coefficient

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