

LABORATORY ASSESSMENT OF NANO-SILVER TRANSPORT IN SAND COLUMNS USING COMPLEX CONDUCTIVITY MEASUREMENTS

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Abstract

Nano-materials are emerging into the global marketplace. Nano-particles, and other throwaway nano-devices may constitute a whole new class of non-biodegradable pollutants of which scientists have very little understanding. Therefore, the production of significant quantities of nano-materials will inevitably result in the introduction of these materials to the environment with important implications for both environmental and human health. Currently there are many unanswered questions related to the release of nano-materials, their fate, transport, and transformation in the environment, and their potential toxic effects (Wiesner, 2007; Grassian, 2008; Sellers, 2009). Due to their desirable chemical–physical, electronic, and optical properties, metal nano-particles have attracted much attention and demonstrated a wide range of applications (Kamat, 2002; Oliveira et al., 2005). Among metal nano-particles, silver nano-particles possess many superior properties, such as increased electrical conductivity, antimicrobial activity, catalytic effect, etc. (Kabashin et al., 2003).

In the present study, a flow through experiment was conducted to investigate the sensitivity of complex conductivity measurements (e.g., imaginary conductivity component) to the mobility and transport of three different concentrations (100, 500, 1000 mg/l) of nano-silver (90-210 nm) in laboratory sand columns. Stabilized aqueous suspensions of the different concentrations of the nano-silver particles were prepared following the procedure of Bihari et al. (2008), with fluid conductivity (0.08 S/m) and pH (7.2) values kept constant. Three identical columns constructed from polyvinyl chloride (PVC) pipe and dry filled with clean quartz sands were prepared (Figure 1). Each of the stabilized nano-silver dispersions was further kept homogenized by using a magnetic stirrer and a Teflon-coated stir bar.

Current (Ag) electrodes were positioned at the influent and effluent ends of the flow cell, while potential (non-polarizable Ag-AgCl) electrodes were installed equidistant along the side of the sand columns, in a modified wenner array (Slater and Glaser, 2003). A two channel dynamic signal analyzer (DSA) based around a National Instruments (NI) 4551 was used to perform the complex conductivity measurements between 1 to 1000 Hz at 30 equal logarithmic intervals (Slater and Lesmes, 2002). The impedance magnitude $|\sigma|$ and the phase shift ϕ (between a measured voltage sinusoid and an impressed current sinusoid) of the sample were measured relative to a high-quality resistor. The real ($\sigma' = |\sigma| \cos \phi$) and imaginary ($\sigma'' = |\sigma| \sin \phi$) parts of the sample complex conductivity were then calculated. The real conductivity is an energy loss term that contains an electrolytic (σ_{el}) and interfacial (σ'_{surf}) component (e.g., Lesmes and Frye, 2001). The σ'_{surf} results from surface conduction via the formation of an electrical double layer (EDL) at the grain-fluid interface (Revil and Glover, 1998). The σ'' is an energy storage or polarization term, which at low frequencies (<1000 Hz) results primarily from the polarization of ions in the EDL at the mineral-fluid interface in the absence of metallic minerals (Lesmes and Frye, 2001).

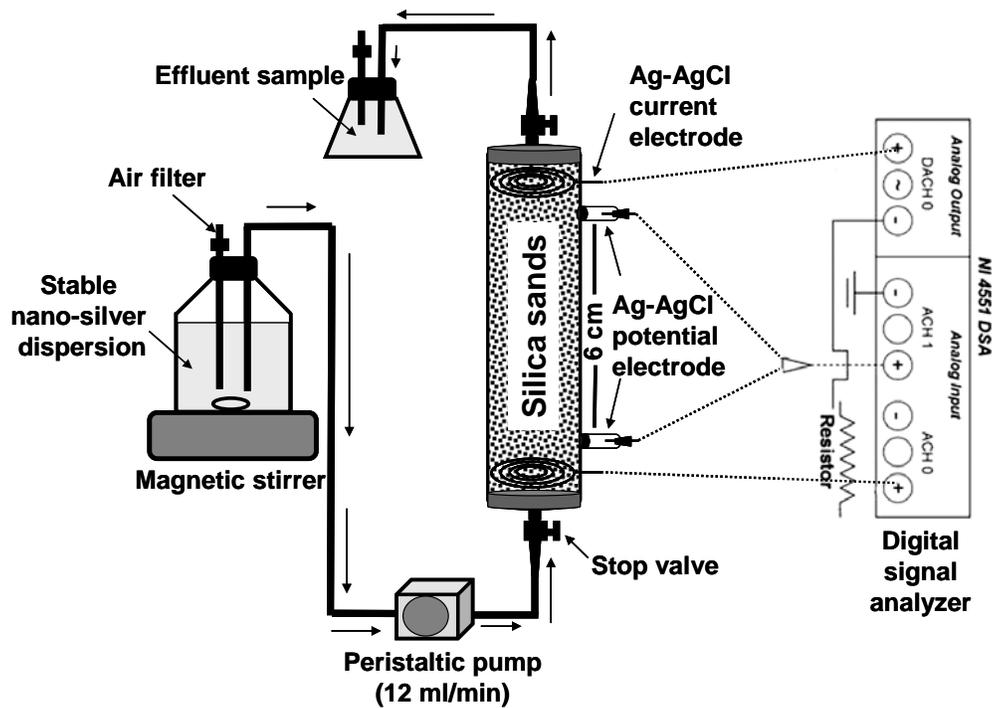


Figure 1: Schematic diagram of the experimental setup.

Prior to the start of the experiment, the three sand packed columns were flushed with 100 pore volumes of background solution similar to that used to prepare the stabilized nano-silver dispersions until the fluid conductivity and pH of the inlet and outlet fluids were the same. Thereafter, experimental columns were calibrated by performing low frequency electrical measurements to make sure that all columns have the same geophysical response as background. In addition, a tracer test was conducted to check the transport properties of the three sand columns prior to the start of the experiment. The tracer test was conducted using phenol red (Fisher Scientific) in which the absorbance at 3 minutes time interval (A) to the initial absorbance at time zero (A_0) using 600 nm wave length were plotted as a function of time and breakthrough curves (BTC) were obtained. The break through curves obtained from the dye tracer test using phenol red exhibit identical trend and shape (Figure 2) which indicate a great similarity in transport properties between the three packed sand columns used in this experiment.

A peristaltic pump was used to introduce the stabilized suspensions of nano-silver into the sand columns with flow rate of 12 ml/minute. Effluent samples of the nano-silver suspensions from the sand columns and complex conductivity measurements were collected every one minute. The optical density of the nano-silver in the effluent samples were determined at 600 nm wavelength using spectrophotometer and then converted into concentrations using the following equation (concentration (mg/l) = $1109 \times$ optical density) which was previously determined from the linear correlation between different concentrations of nano-silver suspensions and their measured optical densities. During the course of the experiment, the concentration of the nano-silver introduced to the column, C_0 , and the concentrations exiting the column, C , were monitored to obtain a breakthrough curve of C/C_0 as a function of the number of pore volumes passing through the porous medium. Similarly the imaginary

conductivity component (σ'') obtained from the complex conductivity measurements every one minute were normalized to initial imaginary conductivity value σ''_0 and plotted as a function of pore volume.

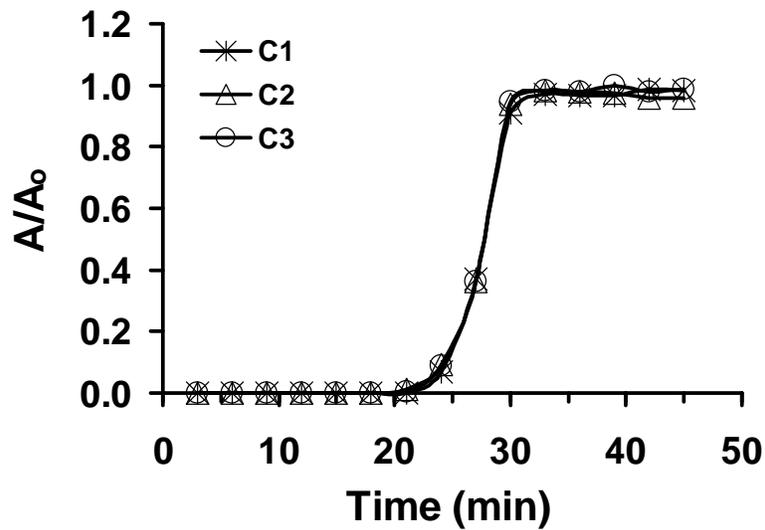


Figure 2: Break through curves (BTC's) from tracer tests using phenol red conducted prior to the start of the experiment for the three sand packed columns used in the experiment.

The break through curves (BTC's) obtained from the three normalized concentrations (100, 500, and 1000 mg/l) of the nano-silver effluent reached a plateau after two pore volumes (Figure 3). The three BTC's were also separated after two pore volumes upward towards the lower concentration of nano-silver suspension (100 mg/l). This indicates that the lower concentration of the nano-silver suspension has more mobility compared to the other two higher concentrations (500 and 1000 mg/l). In addition, previous studies show that at higher concentrations and pH values, nano particles tend to aggregate (Baalousha, 2009). Therefore, the possible aggregation of the nano-silver dispersion at higher concentrations (> 100 mg/l) may result in lowering the mobility of nano-silver and surface area as well as resulting in greater retention as shown in figure 3.

Similar observations were obtained from the BTC's of the normalized imaginary conductivity values. The BTC's reached a plateau after two pore volumes and exhibit a separation upward towards the lower concentration of nano-silver suspension (Figure 4). Surface conductivity (e.g., imaginary conductivity) is primarily controlled by the product of surface area, surface charge density and surface ionic mobility (Lesmes and Frye, 2001; Slater and Lesmes, 2002; Slater and Glaser, 2003). Nano-particles have a large surface area relative to their mass. However, the possible aggregation of the nano-silver at higher concentrations will result in reduction of the surface area. This explains the shift upward in the normalized imaginary conductivity component towards the lower concentration of nano-silver dispersion. However, scanning electron microscopy images are needed to examine the surfaces of the sand grains and possible aggregation of the nano-silver particularly at higher concentrations.

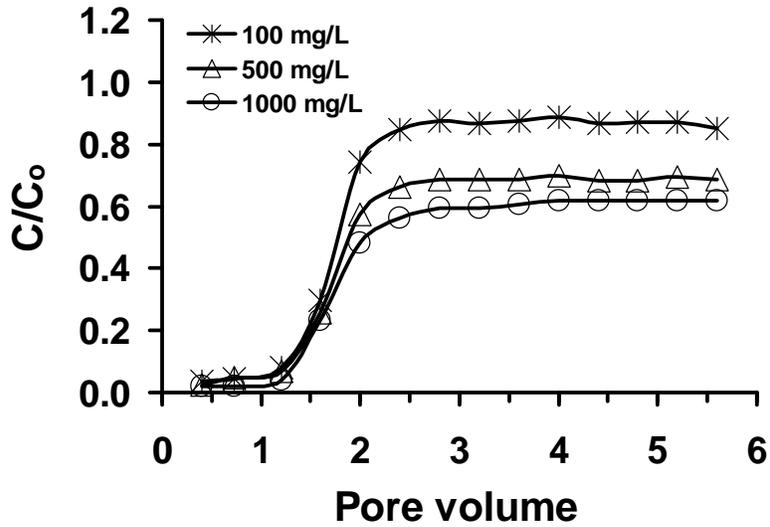


Figure 3: Breakthrough curves of nano-silver dispersions, showing the change in normalized effluent nano-particle concentration (C/C_0) as a function of pore volume.

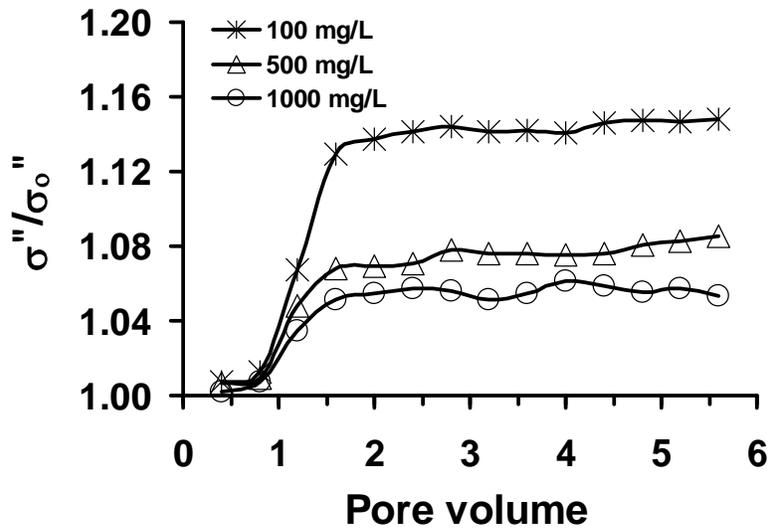


Figure 4: Breakthrough curves of nano-silver dispersions, showing the change in normalized imaginary conductivity values at 10 Hz (σ''/σ_0'') as a function of pore volume.

Conclusion

The results from this study demonstrated the sensitivity of complex conductivity measurements, specifically the imaginary conductivity (σ'') component, to the fate and transport of different concentrations of nano-silver in porous media. Breakthrough curves obtained from normalized imaginary conductivity component showed a similar trend and shape to those obtained from normalized concentrations of nano-silver dispersions. This suggests that geophysical measurements can be used to monitor the presence and transport of nano-particles in the subsurface. However, further studies are

needed to investigate the effect of pH, ionic strength, and surface chemistry of nano-particles and porous media on the transport of nano-particles in the subsurface environment and their associated geophysical signatures.

Acknowledgments

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