

Sensing the Presence and Transport of Engineered Nanoparticles in Saturated Porous Media using Spectral Induced Polarization (SIP) Method

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Summary

Laboratory column experiments were conducted to investigate the sensitivity of the spectral induced polarization (SIP) measurements to the presence and transport of Silver (Ag) and Zero Valent Iron (ZVI) nanoparticles with particle diameters of 90-250 nm in saturated quartz sand packed column. SIP measurements were obtained between 0.1 to 10000 Hz using the dynamic signal analyzer (DSA) National Instruments (NI) – 4461. The impedance magnitude $|\sigma|$ and the phase shift ϕ of the sample were measured relative to a high-quality resistor. The real (σ') and imaginary (σ'') parts of the sample complex conductivity were calculated. The first experiment measured the SIP response to the mixture of one pore volume of the nanoparticle suspension with the porous medium. The same procedure was repeated with the two nanoparticles using different nanoparticle concentrations (0-20 mg/ml). At frequencies above 1 Hz, the magnitudes of the phase and imaginary conductivity increased with increasing concentration of the nanoparticle concentration. The magnitudes of the phase and imaginary conductivity of the ZVI were two times the magnitude of the Ag. The transport experiment was conducted using a 12 mg/mL concentration nanoparticle suspension. A peristaltic pump with flow at 1 mL/minute was used to introduce the suspension into the sand columns. Effluent samples of the suspensions from the sand columns and SIP measurements were collected every five minutes for 180 minutes. The optical density of the nanoparticles in the effluent samples were determined at 430 nm wavelength using a spectrophotometer and then converted into concentrations using relationships determined from the linear correlation between concentrations of nanoparticle suspensions and their measured optical densities. A breakthrough curve (BTC) was obtained by plotting the normalized outlet nanoparticle concentration as a function of time. A similar procedure was followed for the SIP parameters. The BTC of normalized outlet Ag was higher in magnitude compared to the BTC of the normalized ZVI, suggesting retention of ZVI in the sand column was higher than Ag. Higher retention of ZVI was reflected in higher magnitudes for the normalized phase and imaginary conductivity component. Interestingly, the trend of the BTC of the normalized imaginary conductivity component was similar to the BTC trends of normalized outlet nanoparticle concentration. These results demonstrate the sensitivity of the SIP technique to nanoparticles and their transport in saturated porous media.

Introduction

Nanomaterials are emerging into the global marketplace. Engineered Nanoparticles (NP), and other throwaway nanodevices may constitute a whole new class of non-biodegradable pollutants of which scientists have very little understanding. Therefore, the production of significant quantities of nanomaterials and their accidental introduction into the subsurface may pose a potential risk and hazard to the environment and public health which needs an urgent and exhaustive evaluation (Luque-Garcia et al. 2013). NPs are extensively used or tried for environmental remediation (Zhang et al. 2013), where information on their fate and impact is largely limited. Therefore, there is a demand to develop a technique that is sensitive to the presence and transport of these nanoparticles in the subsurface. Geophysical methods, specifically spectral induced polarization (SIP), have shown to be sensitive to the very small physiochemical changes that occur at the grain fluid interface and has been used to locate disseminated metallic mineral deposits (AbdelAal et al., 2014). The main objectives of the present study are to (1) investigate the sensitivity of SIP measurements to the presence of different concentrations of Ag and ZVI nanoparticles in saturated porous media and (2) assess the potential to use SIP measurements to monitor the transport of Ag and ZVI nanoparticles in the subsurface.

Materials and Method

A schematic representation of the SIP setup used in this study is shown in Figure 1. The SIP measurements were obtained using a dynamic signal analyzer (DSA) (National Instruments (NI) – 4461) between 0.1 Hz to 10000 Hz at 16 equal logarithmic intervals (sensitivity of 0.1 mrad over this frequency range). The conductivity magnitude $|\sigma|$ and phase shift ϕ of the samples were measured relative to a high-quality resistor at 1000 Ohms. Once measured, the complex sample conductivity which includes the real ($\sigma' = |\sigma| \cos \phi$) and imaginary ($\sigma'' = |\sigma| \sin \phi$) conductivity components was calculated. The porous media (Ottawa sands) used to fill the column consisted of fine silica sand (U.S. Silica Company). The Ag nanoparticles and the nano ZVI were in a powder form (90-250 nm) of 99% purity (Nanostructured and Amorphous Materials Incorporated, Inc). The surface area (m^2/g) ranges from 2.4-4.4 and 3-7 for Ag and ZVI, respectively. The fluid used to prepare the nanoparticles suspensions was artificial groundwater (AGW) similar to that used by Abdel Aal et al., (2009).

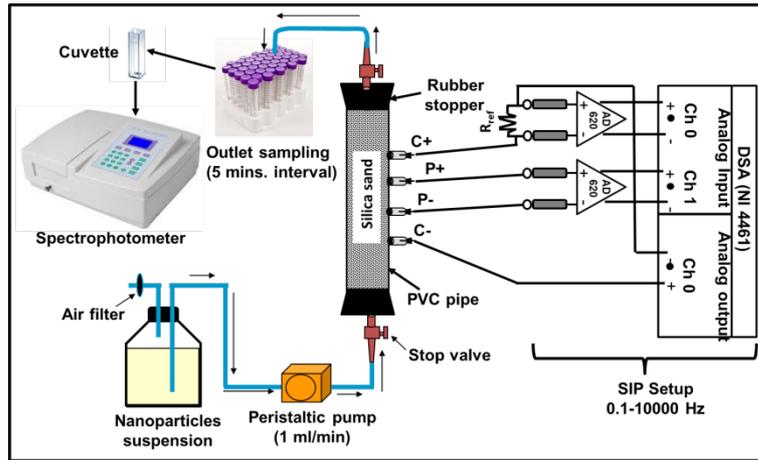


Figure 1. Schematic of column setup and instrumentation used in SIP measurements.

The first experiment measured the SIP response to the mixture of one pore volume of the nanoparticle suspension with the porous medium. The same procedure was repeated with the two nanoparticles using different nanoparticle concentrations (0-20 mg/ml). The transport experiment was conducted using a 12 mg/mL concentration nanoparticle suspension. A peristaltic pump with flow at 1 mL/minute was used to introduce the suspension into the sand columns. Effluent samples of the suspensions from the sand columns and complex conductivity measurements were collected every five minutes for 180 minutes. The optical density of the nanoparticles in the effluent samples were determined at 430 nm wavelength using a spectrophotometer and then converted into concentrations using relationships determined from the linear correlation between concentrations of nanoparticle suspensions and their measured optical densities. A breakthrough curve (BTC) was obtained by plotting the normalized outlet nanoparticle concentration as a function of time. A similar procedure was followed for the SIP parameters.

Results and Discussion

Figure 2 shows the SIP results of different concentrations of Ag and ZVI nanoparticles (NPs) in saturated sand. The magnitude of the phase shift (φ) (figure 2a) and imaginary conductivity (σ'') (figure 2b) increases with increasing nanoparticle concentration as shown in figure 2a and b, respectively. The real conductivity component (σ') shows insignificant changes with increasing nanoparticles concentrations (figure 2c). Conduction and polarization at the grain-fluid interface are a function of surface area, surface-charge density, surface ionic mobility, and interfacial geometry (Revil and Glover, 1998; Lesmes and Frye, 2001). Relationships between the magnitude of the SIP effect and the percentages of metallic minerals are well documented (Bigalke and Junge, 1999). The magnitudes of the phase and imaginary conductivity of the ZVI are two times the magnitude of the Ag as shown in figure 2 a and b, respectively. This can be explained by the high surface area of ZVI compared to Ag nanoparticles which considered a major control on the magnitude of SIP response of metallic minerals. These results indicate that both the phase shift and imaginary conductivity are more sensitive to the presence of metallic nanoparticles compared to the real conductivity component.

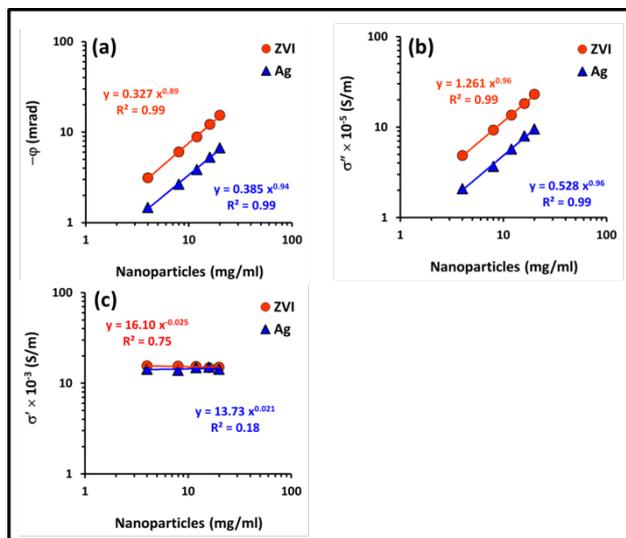


Figure 2. Results of SIP measurements at 1 HZ; (a) phase shift (φ), (b) imaginary conductivity (σ''), and (c) real conductivity (σ') of different concentration (0-20 mg/ml) of silver (Ag) and Zero Valent Iron (ZVI) nanoparticles in saturated sand.

Figure 3 shows the normalized outlet concentrations of the nanoparticles (Ag and ZVI) and the measured SIP parameters. The BTC of normalized outlet Ag is higher in magnitude compared to the BTC of the normalized ZVI which indicates higher retention of ZVI in sand column than AgNPs (Figure 3a). The higher retention of ZVI reflected in higher magnitudes for the normalized phase shift (φ) and imaginary conductivity (σ'') as shown in figure 3b and c, respectively. Again, no significant changes are observed for the BTC of the normalized real conductivity (σ') of Ag and ZVI nanoparticles (Figure 3d). Figure 4 shows a comparison between the BTC of the normalized outlet concentrations of Ag and ZVI nanoparticles and their normalized imaginary conductivity (σ''). The trend of the BTC of the normalized imaginary conductivity component is similar to the BTC trend of normalized outlet nanoparticle concentration for both Ag (Figure 4a) and ZVI (Figure 4b).

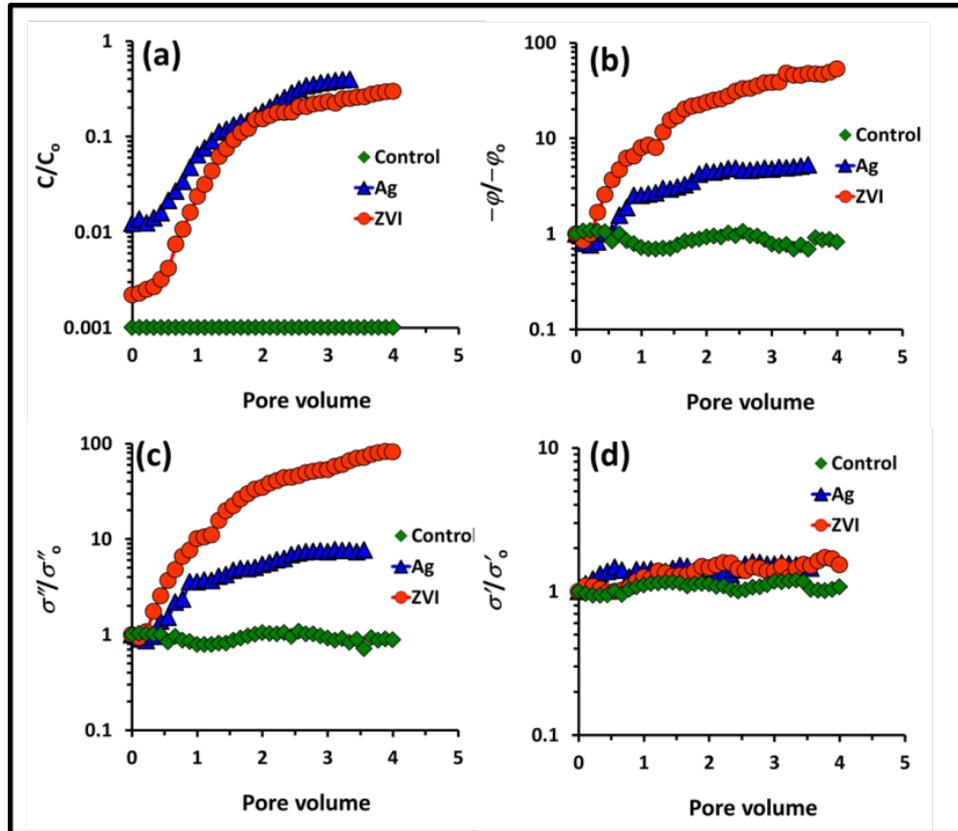


Figure 3. The break through curves (BTCs) of normalized (a) outlet concentrations, (b) phase shift (φ), (c) imaginary conductivity (σ''), and (d) real conductivity (σ') of control (no nanoparticles), Ag and ZVI nanoparticles (12 mg/ml).

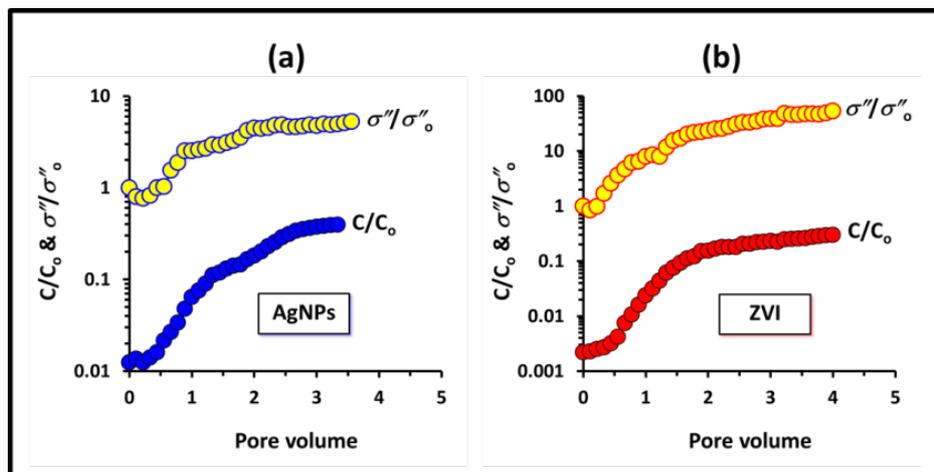


Figure 4. Comparison between the BTCs of the normalized outlet concentrations and imaginary conductivity (σ'') for (a) Ag and (b) ZVI nanoparticles (12 mg/ml).

Conclusions

The results from this study demonstrated the sensitivity of SIP measurements, specifically the imaginary conductivity (σ'') component, to the fate and transport of engineered nanoparticles (Ag and ZVI) in the subsurface saturated porous media. Breakthrough curves obtained from normalized imaginary conductivity component showed a similar trend and shape to those obtained from normalized concentrations of nanosilver dispersions. This suggests that geophysical measurements can be used to monitor the presence and transport of nanoparticles in the subsurface. However, further studies are needed to investigate the effect of pH, ionic strength, natural organic matter, and surface chemistry of nanoparticles and porous media on the transport of nanoparticles in the subsurface environment and their associated geophysical signatures.

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