

Transport of poly(acrylic acid) coated 2-line ferrihydrite nanoparticles in saturated aquifer sediments for environmental remediation

Aishuang Xiang · Sheng Zhou · Bruce E. Koel · Peter R. Jaffé

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Abstract Groundwater remediation using iron oxide and zero-valent iron nanoparticles (NPs) can be effective, but is limited in many applications due to the NP strong retention in groundwater-saturated porous media after injection, the passivation of the porous surface, and the high cost of nanomaterials versus macro scale iron. In this study, we investigated transport of bare and polymer-coated 2-line

ferrihydrite NPs (30–300 nm) in saturated aquifer sediments. The influence of poly(acrylic acid) (PAA) polymer coatings was studied on the colloidal stability and transport in sediments packed column tests simulating groundwater flow in saturated sediments. In addition, the influence of calcium cations was investigated by transport measurements using sediments with calcium concentrations in the aqueous phase ranging from 0.5 (typical for most sediments) to 2 mM. Measurements were also made of zeta potential, hydrodynamic diameter, polymer adsorption and desorption properties, and bio-availability of PAA-coated NPs. We found that NP transport through the saturated aquifer sediments was improved by PAA coating and that the transport properties could be tuned by adjusting the polymer concentration. We further discovered that PAA coatings enhanced NP transport, compared to bare NPs, in all calcium-containing experiments tested, however, the presence of calcium always exhibited a negative effect on NP transport. In tests of bioavailability, the iron reduction rate of the coated and bare NPs by *Geobacter sulfurreducens* was the same, which shows that the PAA coating does not significantly reduce NP Fe(III) bioavailability. Our results demonstrate that much improved transport of iron oxide NP can be achieved in saturated aquifer sediments by introducing negatively charged poly-electrolytes and optimizing polymer concentrations, and furthermore, these coated NPs retain their bio-availability that is needed for applications in bio-environmental remediation.

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Introduction

Iron and iron oxide nanoparticles (NPs) have been recently investigated for groundwater remediation. Especially, the latter has been reported to be effective in bioremediation of groundwater, e.g., removing arsenic from contaminated water (Zouboulis and Katsoyiannis 2005). In another application, uranium reduction and precipitation occur simultaneously with microbially mediated iron reduction, meaning that bioavailable iron oxides can enhance uranium remediation (Komlos et al. 2008). It was shown by Moon et al. (2010) that augmentation of aquifer sediments with goethite NPs, could significantly enhance the activity of iron reducing microorganisms. Anderson et al. (2003) have observed in field biostimulation studies that once bioavailable iron is depleted and sulfate reduction initiated, uranium bioprecipitation is terminated, although the reasons are not fully understood. Therefore, augmenting the subsurface with bioavailable iron is thought to have significant relevance for processes such as uranium bio immobilization. Of the many forms of iron oxide, poorly crystalline iron oxides such as ferrihydrite are highly reactive, binding with many contaminants and important nutrients in natural environments.

Groundwater-saturated sediments contain numerous ingredients leading to a negative surface charge on sediment particles and porous media and concomitant strong interactions with the positively charged surfaces of iron or iron oxide NPs (Tan 2011). Therefore, transport and delivery of iron or iron oxide NPs at distances greater than a few meters in groundwater-saturated sediments is a great challenge during practical use involving well injection of NPs. Surface engineering of zero-valent iron NPs (nZVI) for environmental remediation has been widely investigated with strategies utilizing polymer coatings (Schrick et al. 2004), emulsion (Quinn et al. 2005), and carbon supports (Choi et al. 2008). However, there are few investigations concerned with surface engineering

strategies for improving the transport of iron oxide NPs for environmental applications (Holsen et al. 1991; Ghosh et al. 2011). Surfactant coatings on ferrihydrite particle surfaces have been investigated to remove organic contaminants from water (Holsen et al. 1991), but there has been no report of improving the delivery distance of ferrihydrite NPs in groundwater-saturated sediments by using organic or polymer coatings.

Our previous report on poly(acrylic acid) (PAA) as a water-soluble polyelectrolyte surface modifier demonstrated increased stability and transport properties of ferrihydrite NPs in water-saturated silica sand media (Xiang et al. 2013). NP stability was characterized by measurements of the zeta potential, a term derived from electric double layer theory (Hunter 1988). Transport properties were probed by using sand-packed column tests, in which we found a remarkable increase in the transport of PAA-treated ferrihydrite NPs that matched that of a sodium bromide (NaBr) tracer in some tests. This surface engineering approach offers exciting prospects for improving the delivery of iron oxide NPs in saturated porous media.

In this article, we further report on studies of the stability and sorption of PAA coated 2-line ferrihydrite NPs, with the goal of enhancing their transport and delivery in saturated aquifer sediments. As a new feature, we studied the influence of calcium, a groundwater constituent that affects the performance of PAA coatings, on the stability and transport of the NPs in groundwater-saturated sediments. In addition, the bio-availability of PAA-coated NPs was also tested using *Geobacter sulfurreducens*. Overall, our findings reveal that PAA coating can remarkably improve the transport distance of ferrihydrite NPs, not only through sand, but also through aquifer sediments. Furthermore, calcium, which has a negative influence on NP transport, is completely mitigated by PAA coatings at low calcium concentrations typical of most groundwater environments. Most importantly, the coated NPs show no reduced bioavailability compared with bare NPs in Fe(III) reduction by *G. sulfurreducens*. Such performance enhancements have not been reported previously, and our findings demonstrate a surface engineering strategy that can improve the delivery distance of iron oxide NPs in practical groundwater bioremediation applications.

Materials and methods

Materials

Sodium PAA polyelectrolyte with molecular weight of 6,000 was supplied by Polysciences as a white powder and was applied as the surface modifier. The wet sediment was collected from a field site at Rifle, CO, and was sealed and stored at 5 °C. The geochemical characterization of these sediments is described in detail by Komlos et al. (2008) and will be further given in “[Transport tests through sediment columns](#)” section. The silica sands were natural quartz ASTM sands supplied by Sigma-Aldrich (20–30 mesh), and were pretreated following a previous method (Xiang et al. 2013). Poly(acrylic acid)-graft-poly(ethyl glycol) (PAA-PEG, 59–61 % solids, 38 K M_w) was provided by Grace Construction Products as a superplasticizer. Ferric nitrite ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH), potassium hydroxide (KOH), NaBr, sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), hydrogen chloride (HCl), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), hydroxylamine hydrochloride ($\text{NH}_4\text{OH} \cdot \text{HCl}$), FerroZine[®] ion reagent, ferric citrate, ammonium chloride (NH_4Cl), sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), potassium chloride (KCl), and sodium acetate were purchased from Sigma-Aldrich and used as received. The *Geobacter sulfurreducens* seed was prepared and preserved following a previous report (Komlos et al. 2008) as well as the preparation of vitamin and mineral mixtures.

Synthesis of 2-line ferrihydrite NPs

Synthesis of 2-line ferrihydrite NPs was conducted using a slightly modified, quick method reported previously (Cornell and Schwertmann 2003). Briefly, 8 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 100 ml DI water, and 66 ml 1 M KOH was added to bring the pH to 7–8 while vigorously stirring with a magnetic stirrer. The last 6 ml of KOH was added dropwise while constantly checking the pH. The mixture was stirred vigorously overnight, transferred into dialysis tubing (molecular-weight cutoff 12,000) and then dialysed until free from electrolyte. The dialysis tubing was placed in DI water, and fresh DI water was replaced every 1 h during the first 5 h, and then three times a day for 3 days. The final

particles were dispersed in DI water with a solid content of 10 g/l, sonicated for 5 min, and stirred for 10 min, prior to storing at 5 °C for future use. The solid content was estimated from mass balance and using a pseudo-ferrihydrite formula of $\text{Fe}(\text{OH})_3$. Prior to each future use, the suspension was sonicated for 5 min, and stirred for 10 min to redisperse the suspension uniformly.

PAA coating and adsorption on NP, sediments, and sand surfaces

The stock solution of 2,000 or 4,000 mg/l PAA buffered with carbonate/bicarbonate was added to 125-ml Pyrex glass bottles to give a final polymer concentration from 0 to 550 mg/l. The carbonate/bicarbonate buffer was used to control the pH at 8 and the sodium ion concentration at 10 mM (Corning pH/ion analyzer model 350). The pH was achieved via titration of small amounts of 0.1 M NaOH and/or HCl solutions. A proper volume of the 10 g/l 2-line ferrihydrite NP stock solution was injected into the polymer solution slowly with a stirring speed of 500 rpm to give a solid content of 150 mg/l or less. The stock NP suspension was stirred 1 h, sonicated for 6 min, and remained well stirred before the injection. The coated NP samples were placed on a 15-spot stirring plate at room temperature and a stirring speed of 300 rpm for 12 h before the measurements of adsorption, particle size, and zeta potential. To prepare coated NP suspensions for the transport tests, the stock solution of 4,000 mg/l PAA was added to 2-l Pyrex glass bottles to give a final polymer concentration of 30, 500, or 1,000 mg/l. The final coated samples had a solid content of 150 mg/l and were equilibrated for 24 h at room temperature with a stirring speed of 300 rpm. The rest of the coating procedure was the same.

Adsorption of PAA on Rifle sediments and silica sand surfaces followed the same procedure given below. The carbonate/bicarbonate buffer at a sodium concentration of 10 mM and a pH of 8 was added to 20 ml scintillation vials, and was stirred at a speed of 500 rpm. The 2,000 mg/l PAA stock solution was added to give a polymer concentration from 0 to 200 mg/l. The pH was adjusted to 8 by titration of 0.1 M NaOH and HCl solutions before adding 1 g wet Rifle sediments or dry silica sand. The suspensions were equilibrated 24 h at

room temperature with a stirring speed of 300 rpm before adsorption measurements.

Adsorption measurements

PAA adsorption measurements were conducted on three surfaces: (1) 2-line ferrihydrite NPs; (2) sediments; and (3) silica sand. A 15 ml sample of the coated systems (“[PAA coating and adsorption on NP, sediments, and sand surfaces](#)” section) was centrifuged at 10,410g and 20 °C for 30 min (DuPont Sorvall RC-5B Refrigerated Superspeed Centrifuge). The polymer concentration in the supernatant was analyzed by a total organic carbon (TOC) analyzer (Shimadzu V-TOC/TN) in the non-purgeable organic carbon (NPOC) mode. The low-loading NPOC analysis was performed with 2 % 2 N HCl acid addition, 1.5 min sparge time, and 2–3 injections with a 50 µl injection volume. Other settings were kept as default values. Polymer concentration in the supernatant was corrected by background TOC of each centrifuged surface. Subtracting polymer concentration in the supernatant from the total concentration of polymer added initially provides the amount of adsorbed PAA. This value is then divided by the initial mass of the solids to determine the mass ratio of adsorbed PAA to the solids. Duplicate measurements were made for each sample.

Desorption dynamics

Desorption of the coated polymer from iron oxide NP surfaces was investigated in polymer-free water, which was prepared by adding a volume of 295 ml carbonate/bicarbonate buffer at a pH of 8 and a sodium ion concentration of 10 mM into a 500 ml flask and stirred at a speed of 500 rpm. In order to determine the desorption dynamics, 5 ml of the PAA-coated 2-line ferrihydrite NPs were quickly injected into the buffer to initiate desorption. Prior to injection, the coated NP suspension had a PAA content of 500 mg/l and a solid content of 150 mg/l (i.e., 3.33 mg PAA/mg NPs). Desorption dynamics were measured by taking a 15 ml sample of the dilute suspension as time increased, and these samples were centrifuged at 10,410g and 20 °C for 30 min (DuPont Sorvall RC-5B Refrigerated Superspeed Centrifuge). Polymer content in the supernatant was determined with NPOC

analysis. The amount of polymer that was desorbed (removed) from the particle surface with each passing time interval was calculated by mass balance. The desorption time included the 30 min centrifuging time. Duplicate samples were used for each NPOC analysis and this analysis was repeated three times for each sample.

Particle size and zeta potential

Measurements of dynamic light scattering (DLS) and electrophoretic light scattering (ELS) (Murdock et al. 2008) for zeta potential and particle size, respectively, for bare and coated 2-line ferrihydrite NPs were performed using a Malvern Zetasizer Nano instrument. The polymer coating on the 2-line ferrihydrite NPs was carried out 12 h before analysis, and the solid content in each sample was <150 mg/l. The samples for the DLS and ELS experiments were sonicated for 2 min and stirred continuously to make sure each sample uniformly dispersed prior to taking the measurements. All measurements in this study were taken at a temperature of 25 °C. Measurements were repeated three times on each sample and at least two independent samples were measured to check for repeatability.

Transport tests through sediment columns

After collection with a backhoe, the sediment was air dried, sieved (<2 mm), and stored at 4 °C until use. The sediment porosity was 0.19, the organic carbon content was 0.17 %, and the 0.5 N HCl extractable Fe(II) and Fe(III) concentrations were 7.2 and 23.6 µmol/g sediment, respectively (Moon et al. 2007).

Glass chromatography columns (Knotes Brand Chromaflex) with an inner diameter of 2.5 cm and a fixed length of 15 cm were used in the column transport experiments. Several identical setups were used, and Rifle sediment was wet packed into each column, following the same procedure. A spatula with a length of 15 cm, in order to reach the column bottom, was used to transfer the wet sediments into the glass column, and used to tap each scoop of sediments 10 times to minimize any layering or trapped air. To further minimize the potential of any air entrapment, the packed column was equilibrated by flushing the porous matrix with 20 pore volumes of the background

electrolyte at a speed of 0.1 ml/min prior to each transport experiment. The flushing conditions followed a previous method (Tiraferri and Sethi 2009).

The transport experiments were conducted using vertical columns by pumping a suspension of 2-line ferrihydrite NPs from the bottom to the top using a peristaltic pump (Ismatec[®] Low-speed Planetary Gear-Driven Digital Pump) at a pore water velocity of 1.315 m/day (10.3 pore volumes/day).

Samples of the 2-l influent suspension were prepared by injection of 10 g/l bare 2-line ferrihydrite NPs into a pretreated solution while stirring. The pretreated solution had a pH of 8 maintained by a carbonate/bicarbonate buffer, a sodium ion concentration of 10 mM, and various amounts of dissolved PAA polymer. The final 2-line ferrihydrite NP solid content was 150 mg/l. The suspension was stabilized for 24 h at room temperature with stirring and the pH readjusted to 8 using HCl or NaOH solutions prior to pumping into the column. In some samples, CaCl₂ was added into the equilibrated suspension to investigate the effect of calcium in groundwater on the transport distance of coated NPs. The suspension was constantly stirred at a speed of 300 rpm during the transport tests. The effluent at the column outlet was collected with a fraction collector (Spectra/Chrom[®] CF-2) at a frequency of a sample every 60 min, and were stored for iron and PAA detachment analysis.

A bromide breakthrough experiment was conducted using 0.5 mM NaBr to contrast the transport of a conservative tracer to that of the NPs. These tests followed the same procedure as the transport of the NPs.

Bio-availability test

Geobacter sulfurreducens is an obligate anaerobic bacteria capable of iron reduction with acetate or hydrogen as electron donors, and has been investigated as a model microorganism to reduce Fe(III) in a variety of subsurface environments. Preparation of growth culture followed a previously described method (Komlos and Jaffé 2004). 1 l of the growth culture contains 13.7 g ferric citrate, 10 ml vitamin mixture, 10 ml mineral mixture, 2.5 g NaHCO₃, 0.25 NH₄Cl, 0.6 g NaH₂PO₄·H₂O, and 0.1 g KCl. A 9 ml sample of growth culture was autoclaved, transferred to crimp-seal test tubes, and purged with CO₂/N₂ (20:80) gas. A 1 ml sample of a culture of *G.*

sulfurreducens that had been grown previously was inoculated into the test tubes followed by 0.1 ml of 1 M sodium acetate. The test tubes were sealed with a rubber stopper and incubated for 5 days at 30 °C (Fisher Low Temperature Incubator model 307).

For the bioavailability tests of the PAA coated and bare NPs, cultures of *G. sulfurreducens* were used that had been transferred five times as described above. Then, 1 ml of this *G. sulfurreducens* culture was inoculated into test tubes containing 9 ml of an autoclaved growth culture, except that the 50 mM ferric citrate normally present in the growth culture was replaced with 500 mg/l of either PAA coated or bare NPs with a 150 mg/l solid content, followed by purging with CO₂/N₂ gas and addition of sodium acetate as before, and then the test tubes were sealed with a rubber stopper and dynamically incubated at 50 rpm (Fisher Low Temperature Incubator model 307).

Iron analysis

The column effluent was collected using a fractional collector, and its iron concentration was quantified using a previously reported spectrophotometric iron analysis method (Komlos and Jaffé 2004). In our procedure, 1 ml samples of effluent were added into 4 ml 0.65 N HCl in order to dissolve the iron NPs. After 1 h at room temperature, 0.2 ml of 6.25 N NH₄OH·HCl was added to reduce ferric ions into ferrous ions. This was kept overnight and purified by 0.2 µm syringe filter before transferring a 0.1 ml sample into 5 ml of 1 g/l ferrozine, which was buffered with 11.92 g/l HEPES. Absorbance was measured using a spectrophotometer (Spectronic[®] GenesysTM 2) at a wavelength of 562 nm. Absorbance of the sediment blank (effluent without NP or polymers) was measured using the same method, and the concentration of iron oxide NPs in the effluent was evaluated from the absorbance difference of the effluent and blank.

The Fe(II) concentration in the bacteria growth culture with the NPs was measured by removing a 0.1-ml sample and adding it to 5 ml of 0.65 N HCl. After 3 h at room temperature, 0.1 ml of this sample/HCl solution was added to 5 ml of ferrozine solution (Komlos and Jaffé 2004), mixed for 15 s, and analyzed within 30 min using the spectrophotometer. The total iron concentration was quantified similarly, except that

$\text{NH}_4\text{OH}\cdot\text{HCl}$ was added to the 0.65 N HCl solution to achieve a final concentration of 0.25 N $\text{NH}_4\text{OH}\cdot\text{HCl}$ about 2 h prior to the addition to ferrozine.

Ion chromatography

The bromide and calcium concentrations were measured using a Dionex DX500 ion chromatograph equipped with a CD25 conductivity detector and an ICS 3000 system. A Dionex IonPac AS22 column was used for the bromide anion analysis, and a Dionex IonPac CS16 column was for the calcium ion measurements. The mobile phase was a 4.5/1.4-mM sodium carbonate/bicarbonate solution, pumped at a speed of 1.2 ml/min at a temperature of 30 °C for the bromide analysis. The mobile phase for the calcium analysis was 30 mM sulfuric acid, pumped at a flow rate of 1.0 ml/min at a temperature of 40 °C. The injection volume of the sample was 25 μl , with three repeated measurements for each sample.

PAA detachment during the column experiments

The column effluent was collected using a fractional collector, and its PAA content was quantified using a TOC method similar to that in “[Adsorption measurements](#)” section. 12 ml 0.65 N HCl was added to 3 ml effluent samples in order to dissolve the iron oxide particles and to release PAA from the particle surface. The mixture was stirred for 1 h before filtered using a 0.2 μm membrane syringe. The liquid sample was used for the TOC analysis. The measured PAA content subtracted a background TOC of 5.2 mg/ml to give a final PAA content in the effluent. The final PAA content was then normalized to its iron oxide solids content and compared with that of the influent in order to determine the detachment of PAA through the columns.

Results and discussion

Effect of the PAA polymer coating on NP transport

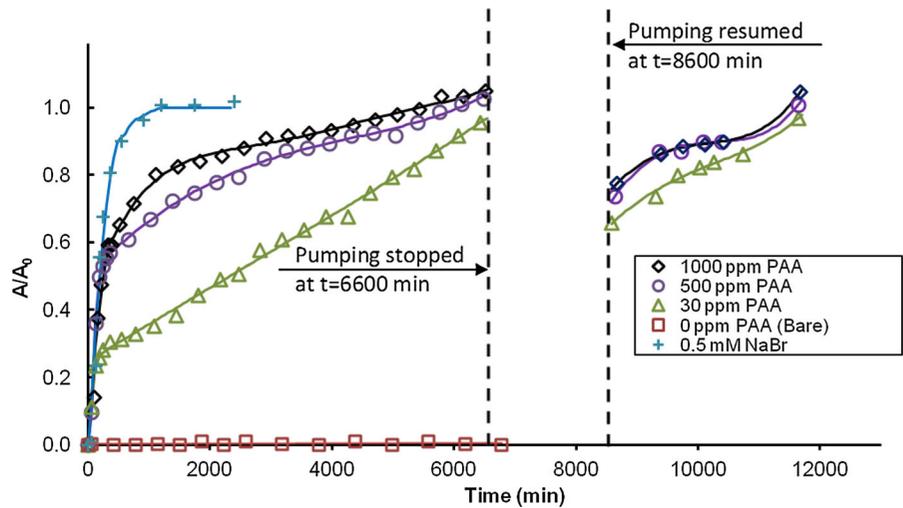
Our previous study reported that the transport of 2-line ferrihydrite NPs in sand columns was improved by PAA coating and that the transport properties could be tuned by adjusting the polymer concentration in sand-

packed porous media (Xiang et al. 2013). In this study, we further investigated the transport of the bare and coated NPs in the porous media of the saturated aquifer sediments and observed very different transport properties from the previous study using sand porous media. Figure 1 shows that PAA coatings improve the transport of NPs in the porous media of the aquifer sediments. The effluent in the test using bare NPs (0 ppm PAA) shows a constant and near zero iron concentration indicating that the NPs were not transported through the sediment column on this time scale. The data for PAA-coated NPs show “breakthrough” indicating a high transport rate. These curves show a very fast initial stage transport followed by a reduced rate at later stages. Higher PAA coating concentrations resulted in shorter times required to reach 100 % transport of the NP through the sediment column. The NPs with the highest PAA coating concentration were transported through the sediment column not too differently from the bromide tracer. We note that the bromide tracer broke through the sediment column much earlier than through the silica sand column (Xiang et al. 2013), implying that the packed sediments in this study has a lower porosity than the sand.

Breakthrough curves for the sediment-packed columns as shown in Fig. 1 have a different form from those through the sand-packed columns (Xiang et al. 2013). In sediments, there is a fast initial, but incomplete breakthrough followed by a slowly increasing breakthrough rate, as shown in Fig. 1. In sand, the breakthrough curves nearly matched the bromide tracer (Xiang et al. 2013). In order to help explain this difference, pumping of the PAA-coated NPs into the sediment columns was interrupted for more than 24 h, and then started again. The breakthrough curves dropped to lower iron concentration levels and then increased to the high levels attained before the interruption, which indicates that there are zones within the porous medium where the transport of the PAA-coated NPs in sediment is diffusion-controlled (Schrick et al. 2004).

A key factor in determining the transport distance of the NPs is the stability of their PAA polymer coating as the coated NPs pass through the saturated aquifer sediment. The amount of transported PAA polymer was monitored with the collected column test samples. Figure S.1 in supplementary materials illustrates the amount of polymer coating lost from the NPs

Fig. 1 Transport of 2-line ferrihydrite NPs, with and without PAA coatings, through packed sediment. Data obtained using a bromide tracer is also shown. The *solid curves* are trend lines to the experimental data. 10.3 pore volumes = 1 day



collected in the effluent of the column test for the NPs coated with 30 mg/l PAA. The decrease of PAA coatings on the NP surface in the effluent of the column test implies that the interplay between the coated NPs and the sediments affects the stability of the PAA coating, and a minimum PAA coating to maintain the stability could be determined by quantifying this interplay. However, in this study, zeta potential measurements of those effluent samples showed nearly constant values in a range of -34.5 to -35.5 mV and were the same as in the influent (-35.0 mV), and particle size measurements also showed nearly constant values in a range of 390–430 nm and were close to the influent of about 400 nm. These two measurements indicate that the NPs collected in the column tests maintained their stability even though they lost some polymer coating during the transport through the sediment column. This can be explained by the measurements shown in Fig. S.2, which illustrates that the zeta potential is nearly constant as the PAA concentration is changed in the region of 30 mg/l PAA. Figure S.2 also shows a slightly more negative charge of the coated NPs at a PAA concentration of 500 mg/l, and the shift of the curve from 0 to a very negative zeta potential is between the 0 and 30 mg/l PAAs. Since zeta potential reflects surface charge of NPs, the approximately constant zeta potential means that introducing more PAAs do not increase the surface charge to a significant degree. More information on the kinetics of PAA desorption from the coated NPs is shown in Fig. 4, which follows the polymer loss in an infinitely

dilute solution. This data will assist theoretical modeling of the transport of PAA-coated NPs in groundwater.

The influence of these transport tests of PAA-coated NPs on the sediment structure was investigated by running another bromide tracer at the end of the column tests. The breakthrough curves of the two bromide tests were identical, which demonstrates that the detached PAA polymer and retained NPs do not significantly alter the pore structure of the sediments. Adsorption isotherms of PAA on the NPs, sediments, and sand demonstrate that the PAA polymer is strongly preferentially adsorbed on the NP surface compared to sediments or sand, as shown in Fig. S.3.

Effect of calcium

Calcium ions are common constituents in groundwater, especially in calcareous formations. Calculation using Visual MINTEQ, for example, taking calcite as an infinite solid phase, and atmospheric carbon dioxide concentrations, gives a dissolved calcium ion concentration of about 0.5 mM, although much higher calcium concentrations can be observed in more groundwater with a more complex geochemistry. The results of column transport studies of the 500 mg/l PAA-coated NP in the presence of 0, 0.5, and 2 mM calcium in the influent water are shown in Fig. 2. Calcium cations at a concentration of 0.5 mM strongly delayed the breakthrough of PAA-coated NPs, and severely reduced transport at a concentration of 2 mM. While demonstrating a strong influence of

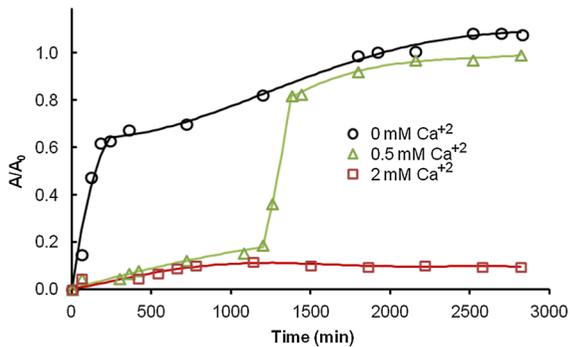


Fig. 2 Influence of calcium ions on the transport of 500 mg/l PAA-coated 2-line ferrihydrite NPs through packed sediments

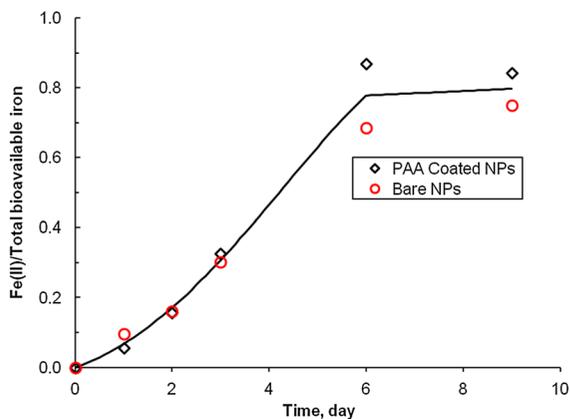


Fig. 3 Generation of Fe(II) by *Geobacter sulfurreducens* from bare and 500 mg/l PAA-coated 2-line ferrihydrite cultures

calcium on PAA-coated NP transport, these results show that the PAA coating strategy will work for most groundwater-saturated sediments to improve the delivery distance of the 2-line ferrihydrite NPs.

Other polymers may have an improved resistance to such a calcium influence. Therefore, an alternative polymer, PAA-PEG was also investigated, comparing NPs coated with PAA-PEG to those coated with PAA for calcium adsorption, particle size, and zeta potential. Fig. S.4 shows in the polymer-coated NP suspensions the relationship of the free calcium cation concentration in solution to the concentration of added calcium cations. If no adsorption of calcium by the polymer coating occurred, this would be a 1:1 relationship. Polymer adsorption of calcium lowers the amount of free calcium measured in solution. Figure S.4 also shows that the PAA-PEG coating take up more calcium from solution than PAA, indicating

PAA-PEG would be more negatively affected by calcium than PAA. Figures S.5 and S.6 give consistent results for the stronger effect of calcium on PAA-PEG coatings as measured by the particle size and zeta potential of the coated NPs for calcium cation concentrations ranging from 0 to 2 mM. Figure S.5 illustrates that calcium increased the particle size for PAA-PEG-coated NPs while the particle size for PAA-coated NPs was not altered significantly, perhaps even decreasing in the presence of calcium. Figure S.6 showed that the zeta potentials of the PAA-PEG coated NPs decreased more with calcium addition than that for the PAA-coated NPs. This indicates that PAA-coated NPs lead to a more stable suspension in the calcium solution, and should have a better performance in improving the delivery distance in groundwater-saturated sediments.

Bio-availability of the PAA-coated NPs

A key aspect to using PAA-coated NPs for bioremediation is the bioavailability of these NPs to the bacteria in the bioremediation process. *Geobacter sulfurreducens* is a model bacteria for ferric iron reduction, and the Fe(III) reduction mechanism in the *Geobacter* culture has been reported elsewhere (Straub et al. 2001). Figure 3 provides the results of Fe(III) reduction, measured via the generation of Fe(II) in PAA-coated and bare 2-line ferrihydrite NP anaerobic incubation experiments, augmented with acetate and seeded with *G. sulfurreducens*. These results demonstrate that the Fe(III) reduction rate in the PAA-coated NP culture is the same as that in the bare NP culture. This indicates that polymer coatings of PAA on the NPs do not lead to significantly reduced bio-availability of the NPs to the bacteria.

Conclusions

We report on a surface engineering strategy to improve the delivery distance of iron oxide NPs in groundwater for bioremediation. This strategy was demonstrated using PAA coatings on 2-line ferrihydrite. We found that PAA coating can achieve stable iron oxide NP suspension and reduce the interaction between the NPs and the aquifer sediments. The delivery distance of the iron oxide NPs in groundwater was dependent on the amount of coated PAA polymer,

and this dependence was reduced at a high PAA coating concentration.

We also provide a strategy in investigating the effect of calcium on the transport of PAA-coated NPs through the porous media of the aquifer sediments. We introduced calcium ions in the PAA-coated suspension, and observed decreased transport distance of the NPs. This study indicates calcium cations in groundwater will interact with the PAA polymer and slow the transport of PAA-coated NPs. However, this negative effect may be reduced by increasing the amount of the polymer coating.

Our work presented here also indicates that the PAA coating does not decrease the bioavailability of the iron oxide NPs. Therefore, the metabolism of Fe(III) reduction by *G. sulfurreducens* in PAA-coated NP suspensions can be studied further to elucidate the roles of the polymer in the bioremediation environment.

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Appendix

Desorption dynamics of PAA from 2-line ferrihydrite NP surfaces in a dilute solution

Data shown in Fig. 4 were used to determine a desorption rate of 47.73 mg PPA/g NP/h for 8 mg/l PAA-coated 2-line ferrihydrite NPs in an infinitely dilute solution containing a carbonate/bicarbonate

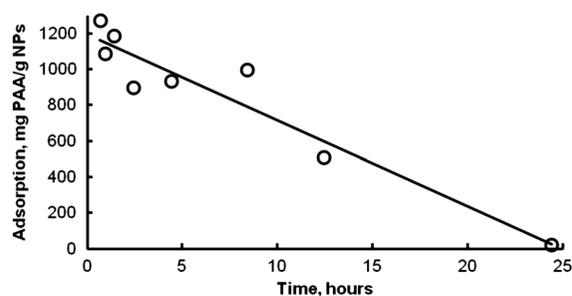


Fig. 4 Desorption dynamics of 8 mg/l PAA-coated 2-line ferrihydrite NPs in an infinitely dilute solution containing a carbonate/bicarbonate buffer at pH 8

buffer at pH 8. This demonstrates that PAA will detach from the NPs and be lost into the groundwater when the coated NPs are contacted with fresh groundwater.

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