Effect of Adsorbed Polyelectrolytes on Nanoscale Zero Valent Iron Particle Attachment to Soil Surface Models

KEVIN M. SIRK,¹ NAVID B. SALEH,¹ TANAPON PHENRAT,¹ HYE-JIN KIM,¹ BRUNO DUFOUR,⁵ JEONGBIN OK,⁵ PATRICIA L. GOLAS,⁵ KRZYSZTOF MATYJASZEWSKI,⁵ GREGORY V. LOWRY,⁷ AND ROBERT D. TILTON*¹,¹

Center for Environmental Implications of Nanotechnology and Departments of Chemical Engineering, Civil and Environmental Engineering, Chemistry, and Biomedical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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Polyelectrolyte coatings significantly increase the mobility of nanoscale zerovalent iron (NZVI) in saturated porous media. The effect can be attributed to improved colloidal stability of NZVI suspensions, decreased adhesion to soil surfaces, or a combination of the two effects. This research explicitly examines how coatings control NZVI adhesion to model soil surfaces. NZVI was coated with three different polyelectrolyte block copolymers based on poly(methacrylic acid), poly(methyl methacrylate or butyl methacrylate), and poly(styrenesulfonate) or with a poly(styrenesulfonate) homopolymer. SiO₂ and a humic acid film served as model soil surfaces. The polyelectrolytes increased the magnitude of the electrophoretic mobility of NZVI over a broad pH range relative to unmodified NZVI and shifted the isoelectric point outside the typical groundwater pH range. Quartz crystal microgravimetry measurements indicated extensive adhesion of unmodified NZVI to SiO₂. Polyelectrolyte coatings decreased adhesion by approximately 3 orders of magnitude. Adding 50 mM NaCl to screen electrostatic repulsions did not significantly increase adhesion of modified NZVI. Coated NZVI did not adhere to humic acid films for either 1 mM NaHCO₃ or 1 mM NaHCO₃ + 50 mM NaCl. The lack of adhesion even in a high ionic strength medium was attributed to electrostatic repulsion, as opposed to electrostatic double layer repulsion, between the polyelectrolyte-coated NZVI and the negatively charged surfaces. The lack of significant adhesion on either model surface was observed for all polymer architectures investigated.

Introduction

Fe⁰ nanoparticles, or NZVI, are proposed as a groundwater remediation technology to immobilize toxic metals (1) and to dechlorinate dense, nonaqueous phase liquid (DNAPL) contaminants. NZVI oxidation in the presence of water reduces DNAPL contaminants to less toxic or immobile products (2–5). NZVI offers high reactivity mainly due to large specific surface areas (2). Because of the small particle size relative to subsurface pores, NZVI also offers the potential to be transported in groundwater, perhaps even to be targeted and emplaced in subsurface source zones. Yet, recent research has shown that unmodified NZVI suspensions transport poorly through water-saturated sand columns (6–11).

Several strategies have been proposed to promote NZVI transport, such as emulsifying NZVI in vegetable oil (12), or attaching NZVI to 50–200 nm hydrophilic, anionic carbon supports (8). Another approach is to directly modify the surfaces of individual NZVI particles to enhance their stability and transport (13). Adsorbed poly(acrylic acid) (8) and carboxymethylcellulose (7) have been shown to significantly enhance NZVI elution from sand columns.

We have used a novel triblock copolymer architecture as a surface modifier, poly(methacrylic acid)-block-(methyl methacrylate or butyl methacrylate)-block-(styrenesulfonate) (PMAA-PMMA-PSS or PMAA-PBMA-PSS), that can enhance NZVI dispersion stability (14, 15), increase mobility in porous media (9), and promote pollutant targetability (9, 14). The triblock copolymers were designed to incorporate multiple functions within a single polymer chain. Since carboxylic acids bind strongly to iron oxide surfaces (16, 17), the PMAA block is intended to strongly anchor the copolymer to the NZVI surface. The PMMA (or PBMA) block is hydrophobic and renders the polymer coating amphiphilic, so that it might anchor the particle to the water/DNAPL interface (9, 14). The PSS block has two functions. Highly water-soluble, it serves as a NZVI dispersant. Second, since most soil minerals, whether bare or coated by natural organic matter (NOM), are negatively charged, the anionic PSS block provides electrosteric repulsion between NZVI and groundwater solids. PSS is a strong polyelectrolyte, with ionization independent of pH. Adsorbed layers of such “quenched” polyelectrolytes provide electrostatic repulsions that are strong and robust, persisting to high ionic strengths where simple electrostatic double layer repulsions fail (18–20). The repulsion arises from increased osmotic pressure associated with polymer chain confinement and ion redistributions when the layer is compressed. We previously showed that adsorbed PMAA–PMAA–PSS triblock copolymers enabled >95% NZVI elution from saturated sand columns, compared to ∼1% for unmodified NZVI (9).

To transport effectively in groundwater, NZVI must resist aggregation and straining, as well as hydrodynamic and/or gravitational deposition into adhesive contact with solid surfaces (13). Here, we used the quartz crystal microgravimetry with dissipation (QCM-D) technique (21, 22) to monitor the direct adhesion of NZVI to bare silica surfaces and to humic acid films in order to simulate the surfaces of groundwater media for environmentally relevant solution ionic conditions (1–50 mM Na⁺). Since block copolymer architecture is well-known to control the conformation of adsorbed polymer layers and the resulting colloidal forces, we employed the family of PMAA–PMAA–PSS block copolymers described by Saleh and co-workers (9, 14) with systematically varied block content to develop design rules for the most effective elimination of adhesion to model groundwater solids. Surprisingly, all of the PSS-containing polymers prevent NZVI adhesion to both silica and humic acid films with equal effectiveness. This is attributed to the...
strong electrostatic repulsions imparted by PSS. Evidently, these repulsions are sufficiently strong to eliminate adhesion regardless of how the polymer architecture determines the conformation of the adsorbed layers. As a result, one may have considerable freedom in designing polymers for source-zone delivery, provided that it contains a strong anionic polyelectrolyte block.

**Experimental Section**

**Materials.** All samples were prepared using reverse osmosis water that was further purified to 18 MΩ·cm resistivity by an Easypure II system (Barnstead). NaHCO₃ (Sigma), NaCl (Fisher Chemicals), octadecyltrichlorosilane (OTS, Aldrich), concentrated HCl (trace metal grade, Fisher Chemicals), concentrated HNO₃ (trace metal grade, Fisher Chemicals), humic acid from coal tar (ACROS), and poly(sodium-4-styrenesulfonate) with M₉0 = 70 000 g/mol (Aldrich) were all used as received. Reactive nano-iron particles (RNIP) provided by Toda Kogyo (Onada, Japan) were used as the NZVI. RNIP has a Fe⁰ core with a predominantly Fe₃O₄ shell (²).

The specific surface area for these particles, measured using the BET method (Quantachrome, NOVAe), was 4.9 ± 0.4 m²/g. This is lower than the manufacturer reports, most likely because of the RNIP aging process described below. Further RNIP characterization information is published elsewhere (², ⁶).

Atom transfer radical polymerization (²³, ²⁴) was used to synthesize three different block copolymers: poly(methacrylic acid)-poly(styrenesulfonate) diblocks, and a poly(methacrylic acid)-poly(butyl methacrylate) diblock copolymer. Synthesis methods are described in the Supporting Information.

**Materials and Methods.** Sample Preparation. Adsorption isotherms for each polymer on RNIP were measured by the polymer adsorption isotherms for each polymer on RNIP. After centrifugation, supernatant aliquots were taken and diluted to measure the free polymer concentration in solution by its absorbance at 225 nm (Varian Cary 300), based on a separately determined calibration curve for each polymer. Lack of spectrophotometric interference from dissolved iron was verified by comparing the full supernatant spectrum to that of pure polyelectrolyte solutions in iron-free water. Subtracting the free polymer concentration from the original bulk concentration yielded the adsorbed amount. Surface concentrations were calculated from the measured RNIP concentration and 4.9 ± 0.4 m²/g specific surface area. All RNIP samples to be used for electrophoretic mobility or QCM-D experiments were centrifuged and washed four times to ensure complete removal of nonadsorbed polymers from solution, leaving only polymer irreversibly adsorbed on RNIP. Polymer adsorption is typically irreversible. Had polymer desorption been significant, it would have been evident by a resulting aggregation of the NZVI suspensions (⁶). This did not occur.

**Electrophoretic Mobility vs pH.** Several 25 mg/L suspensions of bare or polymer modified RNIP in 1 mM NaHCO₃ were made and small aliquots of either HCl or NaOH were added to adjust the pH to between ∼3.5 and 10. Five replicate electrophoretic mobility measurements were made with a Malvern Zetasizer 3000.

**QCM-D.** To monitor RNIP adhesion to silica or humic acid films, we used the QCM-D instrument from QSense (D300, Göteborg, Sweden), which is described in detail elsewhere (¹⁸). In a QCM-D experiment, there are four separate resonance frequencies (overtones, n) for the driven oscillation of the shear wave through an AT cut quartz crystal, with the gold electrode coated with an overlay of SiO₂: 5 MHz (n = 1), 15 MHz (n = 3), 25 MHz (n = 5), and 35 MHz (n = 7). As mass is adsorbed from the bulk fluid to the crystal surface, each of the resonance frequencies decreases. If the adsorbed layer is uniformly distributed, rigidly attached, and small compared to the mass of the crystal, the change in frequency (Δf) can be related to the adsorbed mass per unit area (Δm) using the Sauerbrey relation (²⁵):

\[
\Delta m = -\frac{C\Delta f}{n}
\]

where C is an instrument constant related to the properties of the crystal (in our case C = 0.177 mg m⁻² Hz⁻¹). In all of the experiments, the data from the third overtone was used to calculate the adsorbed mass. The QCM-D “sensed” mass represents the mass of adherent particles plus the bound water in the adsorbed layer (²²).

Silica-coated crystals were purchased from Q-Sense and cleaned immediately before use as follows: crystals were placed in a UV-Ozone chamber (Jelight Co., Irving, CA) for 90 min and then immersed in Chromerge (Fisher Scientific) Cr₂O₃/H₂SO₄ cleaning solution for 30 min followed by copious rinsing with deionized water. Crystals were blown dry with N₂. All experiments were performed at 25 ± 0.1 °C.

Before injecting samples, a stable baseline was recorded for at least 2 min with the appropriate background solution (1 mM NaHCO₃ or 1 mM NaHCO₃ + 50 mM NaCl) in the cell. Then, 2 mL of RNIP suspension were injected through the
cell (corresponding to 25 cell volumes) to ensure complete displacement of the background solution. Any subsequent adhesion was monitored for at least one hour. The RNIP concentration was 0.2 wt% in all adhesion measurements. This concentration is in the typical range appropriate for groundwater remediation (6, 13).

For the humic acid studies, cleaned crystals were immersed in a 3 mM solution of OTS in a 90:10 hexadecane-chloroform mixture for 45 min to produce an uncharged, hydrophobic alkane monolayer (26). Crystals were then rinsed with excess chloroform and blown dry with N₂. This hydrophobization step was necessary to deposit a stable humic acid film on the crystals. Humic acid solutions of initial concentration 0.4 mg/mL were filtered with a 0.45 µm filter prior to use. After mounting the hydrophobized crystal in the QCM-D, a 1 mM NaHC0₃ solution was injected to collect the baseline, after which 2 mL of the humic acid solution was injected and allowed to adsorb for at least one hour. Then fresh NaHC0₃ solution was injected to remove any free humic acid from the system. This deposition and rinse procedure was repeated twice before injecting RNIP suspensions.

**Results and Discussion**

**Electrophoretic Mobility and Adsorption Isotherms of Polymer Modified RNIP**. Figure 1 presents the electrophoretic mobility of bare RNIP, PMAA₁₅-PBMA₄₃-PSS₈₁₁, PMAA₁₅-PSS₈₁₁, PMMA₄₅-PSS₆₀₉, and PSS₃₃₉ modified RNIP as a function of pH (subscripts denote the degree of polymerization for each block). The isoelectric point for the bare particles was slightly below pH 6. Adsorption of any of the polyelectrolytes increased the negative electrophoretic mobility and shifted the isoelectric point to below pH 3 (beyond the pH range investigated). Thus, any of the polyelectrolyte modifiers should enhance the electrostatic repulsion between RNIP and other similarly charged surfaces, for any pH likely to be found in typical groundwater.

Adsorption isotherms are plotted in Figure 2 for PMAA₁₅-PBMA₄₃-PSS₈₁₁ and PMAA₁₅-PSS₈₁₁ on RNIP in 1 mM NaHC0₃. The maximum attained surface excess concentrations for PMAA₁₅-PBMA₄₃-PSS₈₁₁ triblocks and PMAA₁₅-PSS₈₁₁ diblocks are 1.6 ± 0.3 mg/m² and 0.34 ± 0.1 mg/m², respectively. The presence of the hydrophobic PBMA block, with otherwise identical PMAA (anchor) and PSS (stabilizing) blocks, promotes a 5-fold increase in adsorbed mass. Hydrophobic attractions among the adsorbed PBMA blocks evidently create a higher areal density of chains on the surface that would lead to greater PSS chain extension. This effect would promote stronger, longer ranged electrostatic repulsions (15).

Adsorption isotherms for the same two polymers adsorbed at a higher ionic strength, 1 mM NaHCO₃ + 50 mM NaCl, yielded maximum surface excess concentrations of 2.8 ± 0.6 mg/m² and 0.7 ± 0.2 mg/m² for the triblock and diblock polymers, respectively (Data in the Supporting Information). Increasing ionic strength more effectively screens interchain electrostatic repulsions and allows the polymers to pack closer together. We also adsorbed PSS₃₃₉ homopolymer and PMMA₄₅-PSS₆₀₉ diblock copolymer to RNIP in 1 mM NaHCO₃ and found the maximum surface excess concentrations to be 0.26 ± 0.03 mg/m² and 1.3 ± 0.4 mg/m² respectively (Data in the Supporting Information). Noting that the adsorbed amount of polyelectrolyte homopolymers is typically independent of molecular weight (27, 28), the similar adsorbed amounts attained for PMAA₁₅-PSS₈₁₁ (0.34 ± 0.1 mg/m²) and PSS₃₃₉ (0.26 ± 0.03 mg/m²) indicate that the PMAA block had little influence on the adsorption. In the case of the amphiphilic PMMA₄₅-PSS₆₀₉ diblock copolymer, the hydrophobic PMMA block was able to displace adsorbed PSS segments from the surface, forcing them to adopt a more extended conformation stretching away from the surface, and thereby allowing the greater adsorbed amount for the diblock relative to the homopolymer. In the case of the hydrophobic PMAA₁₅-PSS₈₁₁ diblock copolymer, the affinity of the PMAA block for the iron oxide surface was not sufficient to displace PSS segments, and the entire chain lay relatively flat on the surface, resulting in an indistinguishable amount of adsorption relative to the PSS homopolymer that would also lay in a relatively flat conformation.

Although these results show that the PMAA block had little effect on the adsorbed amount, such a block does appear to help promote triblock copolymer-modified RNIP attachment to the water/TCE interface as noted by Saleh et al. (14). Previously, Somtum and co-workers (29) measured PSS homopolymer adsorption on positively charged iron oxide particles at pH 4 and estimated the surface excess concentration to be 26 mg/m². They attributed the unusually high adsorbed amount to multilayer adsorption. On the negatively charged RNIP surfaces, the measured adsorbed amounts we obtained indicate monolayer adsorption for PSS. In summary, the adsorption isotherm measurements indicate that amphiphilic diblock and triblock copolymers containing PSS adopt a more extended conformation on the surface, while hydrophobic PMAA-PSS diblock and PSS homopolymers adopt a flatter conformation on the surface. Differences in adsorbed polyelectrolyte surface excess concentration and conformation are known to control the strength and range of electrostatic repulsion forces (16–20), leading one to anticipate differences in the adhesion resistance of RNIP modified by these different polyelectrolytes.
An increase in polyelectrolyte-modified RNIP adhesion to silica would be expected due to the additional charge screening provided by the 50 mM NaCl, had simple electrostatic double layer repulsion been responsible for the adhesion resistance. Whereas the Debye screening length (30) is 9.6 nm for the 1 mM ionic strength, it decreases to only 1.4 nm for 50 mM ionic strength. Since the elevated ionic strength had no significant effect on adhesion, it is more likely that electrosteric repulsion is the source of this lack of adhesion. This can explain the enhanced mobility of triblock copolymer-modified RNIP recently reported in saturated porous media at high salt concentration (13). Electrosteric repulsions, which can operate either between two opposing polyelectrolyte layers on interacting surfaces, or between one polyelectrolyte layer and an opposing bare, but charged, surface, are known to remain strong even at elevated ionic strengths (18–20). The presence of the polyelectrolyte surface modifier on RNIP drastically reduces the amount of particle adhesion compared with the unmodified RNIP sample over a broad range of ionic strengths due to the robustness of electrosteric forces, rather than simple electrostatic forces.

These results are in good agreement with transport studies of bare RNIP in sand columns that show little elution of unmodified RNIP at comparable particle concentrations but extensive elution of polyelectrolyte-modified RNIP (9, 13). Unmodified RNIP elution is hindered by aggregation due to strong magnetic forces (6). Aggregates may grow in suspension to the point where they clog the porous medium (9). In addition, individual particles or small aggregates that adhere to the sand grains can continue to collect additional nanoparticles from suspension, and as those aggregates grow in size to fill pores, they can strain additional nanoparticles from the flowing suspension. Eliminating adhesion will weaken these tendencies.

**Adhesion to Humic Acid Coated Surfaces.** Natural organic matter (NOM), including humic acid, presents complex surface chemistry that could confound efforts to minimize RNIP adhesion in the subsurface. We used humic acid as a model for NOM to judge the effectiveness of the polyelectrolyte coatings under high organic content conditions. There has been previous research reported on the effects of humic acid on particle transport. When coated on mobile colloids, including hematite (31), kaolinite (32), and polymer latex (33), humic acid enhances colloidal transport through packed sand columns. In these three cases, humic acid was present in the bulk solution as well as adsorbed onto the colloidal particles. These studies show that humic acid is an effective surface modifier to enhance colloidal transport. Here we consider how humic acid coatings on the immobile surface influence particle adhesion.

Our first attempt to immobilize a humic acid layer was to merely adsorb it to the bare silica-coated QCM crystal, but it failed because all humic acid washed off during the rinse step. Given the negative charge on humic acid, a preadsorbed cationic polyelectrolyte layer on the silica surface could conceivably be used to bind humic acid. We chose not to use this strategy, since any exposed cationic sites could potentially cause adsorption of the anionic polyelectrolyte modified particles to the surface in a manner that would not be representative of humic acid interaction with polyelectrolyte modified RNIP. Instead we chose to first covalently bond a monolayer of electrically neutral, hydrophobic octadecyl chains to the silica crystal surface before exposing the surface to humic acids. This succeeded in creating an irreversibly bound humic acid coating, as shown in Figure 4. The stable humic acid surface concentration achieved here, ∼1.5 mg/m², is typical of saturated polymer or surfactant layers (15, 26), but it is not known with certainty that no methyl termini of the underlying OTS monolayer are exposed. Nevertheless,
TABLE 1. Summary of Adsorption Isotherms and QCM-D Adhesion Results for Polymer Modified RNIP on SiO$_2$ for Two Ionic Strengths

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer Surface Excess Concentration (mg/m$^2$) for 1 mM NaHCO$_3$</th>
<th>Polymer Surface Excess Concentration (mg/m$^2$) for 1 mM NaHCO$_3$ + 50 mM NaCl</th>
<th>Adhered Mass (mg/m$^2$) on silica for 1 mM NaHCO$_3$</th>
<th>Adhered Mass (mg/m$^2$) on silica for 1 mM NaHCO$_3$ + 50 mM NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified RNIP</td>
<td>NA</td>
<td>NA</td>
<td>80–180</td>
<td>NA</td>
</tr>
<tr>
<td>PMAA$<em>{15}$-PBMA$</em>{43}$-PSS$_{811}$</td>
<td>1.6 ± 0.3</td>
<td>2.8 ± 0.6</td>
<td>-0.32 ± 0.23*</td>
<td>0.47 ± 0.30</td>
</tr>
<tr>
<td>PMAA$<em>{15}$-PSS$</em>{811}$</td>
<td>0.34 ± 0.1</td>
<td>0.7 ± 0.2</td>
<td>-0.35 ± 0.23*</td>
<td>-0.35 ± 0.27*</td>
</tr>
<tr>
<td>PMMA$<em>{42}$-PSS$</em>{609}$</td>
<td>1.3 ± 0.4</td>
<td>NA</td>
<td>0.21 ± 0.28</td>
<td>0.09 ± 0.1</td>
</tr>
<tr>
<td>PSS$_{339}$</td>
<td>0.26 ± 0.03</td>
<td>1.37 ± 0.3</td>
<td>0.25 ± 0.01</td>
<td>0.33 ± 0.1</td>
</tr>
</tbody>
</table>

(*) Samples with negative masses should not be thought of as “desorbed” amounts. The drift measured for a clean SiO$_2$ crystal was found to be ± 2.8 Hz or ± 0.5 mg/m$^2$ over the same time period as the experiments. Error bars are standard deviations of replicate experiments.

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Supporting Information Available
Adsorption isotherms, block copolymer synthesis, and NMR spectra of sulfonated polymers are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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