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Impact of Sodium Humate Coating on Collector Surfaces on Deposition of Polymer-Coated Nanoiron Particles

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Abstract

The affinity between nanoscale zerovalent iron (nano-ZVI) and mineral surfaces hinders its mobility, and hence its delivery into contaminated aquifers. We have tested the hypothesis that the attachment of poly(acrylic acid)-coated nano-ZVI (PAA-nano-ZVI) to mineral surfaces could be limited by coating such surfaces with sodium (Na) humate prior to PAA-nano-ZVI injection. Na humate was expected to form a coating over favorable sites for PAA-nano-ZVI attachment and hence reduce the affinity of PAA-nano-ZVI for the collector surfaces through electrosteric repulsion between the two interpenetrating charged polymers. Column experiments demonstrated that a low concentration (10 mg/L) Na humate solution in synthetic water significantly improved the mobility of PAA-nano-ZVI within a standard sand medium. This effect was, however, reduced in more heterogeneous natural collector media from contaminated sites, as not an adequate amount of the collector sites favorable for PAA-nano-ZVI attachment within these media appear to have been screened by the Na humate. Na humate did not interact with the surfaces of acid-washed glass beads or standard Ottawa sand, which presented less surface heterogeneity. Important factors influencing the effectiveness of Na humate application in improving PAA-nano-ZVI mobility include the solution chemistry, the Na humate concentration, and the collector properties.

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ASSOCIATED CONTENT

Supporting Information

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Properties of U.S. EPA moderately hard synthetic standard water, SEC chromatograms of 10 and 100 mg/L Na humate solutions, chemical composition, scanning electron micrographs, and X-ray diffractograms of the collector materials, and breakthrough curves for 10 mg/L Na humate in glass beads, Ottawa sand, and in the collectors from field sites (PDF)

The authors declare no competing financial interest.

Graphical abstract

INTRODUCTION

The affinity between nanoparticles (NPs) used in groundwater remediation and mineral surfaces affects their mobility and delivery into contaminated aquifers, the formation of a reactive zone, and consequently, the overall effectiveness of the nanoremediation technology. The surfaces of naturally occurring granular porous media are chemically and physically heterogeneous, due to the presence of a variety of minerals, surface coatings, and crystal faces. These heterogeneities and the associated heterogeneous charge distributions are identified as having a major influence on the transport of colloidal particles in subsurface porous media.^{1–4}

Efforts to increase NP mobility have, to date, largely focused on increasing the suspension stability of NPs by altering their chemistry. This has been achieved by modifying NP surfaces with a polyelectrolyte, which results in electro (steric) stabilization that inhibits aggregation. Such an approach has been adopted for nanoscale zerovalent iron (nano-ZVI) particles, which are the NPs most commonly used in groundwater remediation.^{5,6} However, despite these modifications the affinity of nano-ZVI for granular porous media remains high and particle mobility is still limited.^{1,7}

A previous investigation by Lin et al.⁸ into polymer-coated silver NPs (AgNPs) revealed that although the polymeric particle coating hindered homoaggregation, it resulted in an increased deposition of AgNPs onto the uncoated surfaces of a silica collector. The authors explained this phenomenon by a shift in the contact frontier between AgNPs and silica grains, resulting in a weaker electric double layer interaction. When a polymer coating was allowed to preadsorb onto the surfaces of the silica collector, the attachment efficiency of the polymer-coated AgNPs was reduced as a result of electrosteric stabilization. Chen and Elimelech⁹ reported a similar phenomenon for fullerene NPs; they observed that precoating silica collector surfaces with humic acids resulted in steric and electrosteric stabilization of fullerene NPs. This earlier research has suggested the possibility of being able to hinder the attachment of nano-ZVI particles used in groundwater remediation onto a collector by precoating the collector surfaces with a polymer, which has not previously been investigated.

In this research we have therefore investigated a possible alternative strategy to limit the attachment of a commercially available polyelectrolyte-coated nano-ZVI, with a known

reactivity^{10,11} to the collector surfaces, by conditioning the latter with a polyelectrolyte prior to the nano-ZVI injection. Sodium (Na) humate, a water-soluble Na salt of humic acid derived from leonardite (an oxidation product of lignite), was chosen as the preconditioning polyelectrolyte. Na humate is a commercially available low cost material that is increasingly used in biological farming as a soil conditioner, and also to stimulate plant growth.^{12–14}

In aquatic systems humic substances readily adsorb to solid surfaces, thus affecting the aggregation and deposition of NPs,⁹ and Na humate was also expected to behave in a similar manner. We therefore hypothesized that the adsorption of this charged, high molecular weight (MW) compound onto collector surfaces would form a coating over the favorable sites for NP attachment, thus reducing the affinity of polyelectrolyte-coated nano-ZVI for the collector surfaces through electrosteric repulsion between the two interpenetrating charged polymers (on the particle and collector surfaces). The objective of this study was therefore to elucidate whether or not Na humate adsorbs to collector surfaces since, if it does it may present a valuable way to hinder the deposition of polymer-coated nano-ZVI, thus enhancing its mobility and increasing its effectiveness in groundwater remediation.

The mobility of polymer-coated nano-ZVI was investigated in three different types of granular standardized silica collector with different heterogeneities, increasing from glass beads, through Ottawa sand to Dorsilit8 sand. In each case, the mobility was investigated both with and without preconditioning (or precoating) of the collector surfaces with Na humate. To also take into account the increased heterogeneity of natural environments, the porous media from two contaminated granular aquifers were also included. The breakthrough of nano-ZVI particles in pristine collectors is compared with that in collectors whose surfaces had been modified with Na humate, and the influence of Na humate on interactions between NPs and collector surfaces elucidated and discussed.

MATERIALS AND METHODS

Solution Chemistry

Moderately hard standard synthetic water was chosen for our investigations as being relevant to realistic scenarios for field applications, in which both NP suspensions and Na humate solutions are prepared with, for example, on site surface water or local tap water. This synthetic water, prepared following the protocol of the U.S. Environmental Protection Agency,¹⁵ had an ionic strength (IS) and divalent cation content characteristic of naturally occurring waters (Table S1).

Nano-ZVI Particles and Particle Suspension

The nano-ZVI particles that we used (NANO FER 25S; NANO IRON, s.r.o., Czech Republic) consisted of ZVI cores with magnetite shells, coated with poly(acrylic acid) (PAA); they are hereafter referred to as PAA-nano-ZVI particles. The particles were provided in an aqueous stock suspension containing 20 wt % of particles (manufacturer's specification). A PAA-nano-ZVI particle suspension with a total Fe concentration of 1 g/L was used as the feed suspension for column experiments; it was prepared by diluting the stock suspension with the synthetic water, followed by 15 min of homogenization in an

ultrasonic bath (SONOREX SUPER RK 106; BANDELIN Electronic GmbH & Co. KG, Germany). The PAA-nano-ZVI particles in this suspension were characterized in terms of their zeta (ζ) potential (calculated from the electrophoretic mobility, measured with a Nano ZS ZetaSizer from Malvern Instruments, U.K. and using the Smoluchowski relationship¹⁶), and the particle size distribution (determined by laser diffraction analysis, using a Mastersizer 2000 from Malvern Instruments, U.K.).

Na Humate Solutions

Na humate powder (HUMIN-S 775; HUMINTECH GmbH, Germany) was used to prepare 10 and 100 mg/L solutions in synthetic water which were then homogenized for 5 min in an ultrasonic bath (Sonorex RK 106, Ø 240 mm, 130 mm high, 120 W indicated power; BANDELIN Electronic GmbH & Co. KG, Germany). The Na humate solutions were characterized in terms of: (1) electrical conductivity (EC) and pH (both measured using standard electrodes, WTW GmbH, Germany), and IS (calculated from the EC after McCleskey et al.¹⁷); (2) dissolved organic carbon (DOC) content (measured with a TOC-L CPH TOC analyzer; Shimadzu, Japan); and (3) MW distributions determined by size-exclusion chromatography (SEC). In order to avoid clogging of the size-exclusion column by high MW moieties, Na humate solutions were first filtered through a 0.1 µm polyvinylidene fluoride membrane. The SEC was carried out using a liquid chromatography system (Agilent 1100 Series; Agilent Technologies, Japan) equipped with a microvacuum degasser, a 200 × 8 mm Toyopearl HW 55S size-exclusion column, and a 20 × 8 mm precolumn (Grace Davison Discovery Sciences products; Alltech Grom GmbH, Germany), following the protocol of Neubauer et al.¹⁸ The mobile phase was a solution of 25 mM ammonium carbonate and ammonium carbamate (1:1). The column was calibrated with polystyrenesulfonate sodium salt molecular mass standards (PSS, Polymer Standards Service GmbH; Mainz, Germany) of 1920, 3610, 10 600, and 32 900 g/mol. The column void volume and total permeation volume were determined using 145 000 g/mol PSS and acetone, respectively. The SEC was performed at a pH of 7.5, which corresponded to the pH of the Na humate solutions. Both Na humate solutions were used for the precoating of Dorsilit8 sand and on the basis of the results obtained, only the 10 mg/L solution was then used for the remaining collectors.

Collectors

The six types of granular collector used in these investigations were selected to take into account the physical and chemical heterogeneity of porous media, including variations in roughness and surface charge. The porous media selected were as follows: (i) acid-washed glass beads (approximately 1 mm), with impurities removed from the grain surfaces following the protocol of Yang et al.,¹⁹ (ii) acid-washed standard Ottawa sand, with well-sorted round grains (0.4–0.85 mm) of extra pure quartz (Fisher Scientific, U.K.), (iii) acid-washed Dorsilit8 sand, with moderately well-sorted angular grains (0.3–0.8 mm) of at least 95% quartz (Gebrüder Dorfner GmbH & Co. Kaolin- and Kristallquarzsand-Werke KG, Germany), (iv) unwashed Dorsilit8 sand, and finally, granular aquifer material (0.25–4 mm) from two contaminated sites envisioned for remediation, (v) Site 1 and (vi) Site 2. The collectors were characterized in terms of (1) grain size distribution (determined by wet sieving using mesh sizes of 0.063, 0.125, 0.25, 0.5, 1.0, 2.0, and 4.0 mm), (2) total organic

carbon (TOC) content, determined following Mici et al.²⁰ using an RC-612 Carbon analyzer (LECO, U.S.), (3) chemical composition, determined by inductively coupled plasma optical emission spectrometry (ICP-OES Optima 5300; PerkinElmer, U.S.), (4) bulk sample and fine fraction mineralogical compositions, determined by X-ray powder diffraction (XRD PW 3040/60 X'Pert PRO XRD with Cu K α radiation; PANalytical, The Netherlands), (5) the morphology of mineral grains, determined by scanning electron microscope (SEM, Inspect S50; FEI, U.S.), with an Everhart–Thornley detector, operated at a high vacuum of 10 kV, (6) surface chemistry, determined by X-ray photoelectron spectroscopy (XPS, Axis Ultra; Kratos Analytical, U.K.), (7) ζ potential when the pristine and Na humate-coated collectors were saturated with synthetic water (determined using the Fairbrother-Mastin equation²¹ from the streaming potential, measured with a SurPASS Electrokinetic Analyzer (Anton Paar, Austria) following the protocol described in Laumann et al.¹), and (8) specific BET surface area (SA 3100 BET surface area and pore size analyzer; Beckman Coulter, U.S.), including the “ratio of surface areas”. The ratio of surface areas is defined as the ratio of the measured BET surface area to the theoretical BET surface area²² and was used as a measure of the surface roughness of collector grains, calculated using the median diameter (d_{50}) for the standard collectors and the sieve analysis for the collectors from the contaminated sites.

Column Experiments

Packed column experiments were conducted to assess the breakthrough of PAA-nano-ZVI particles in granular collectors. A glass column (inner diameter 2.5 cm, length 15 cm; Omnifit, Germany) was wet-packed with the collector material and the length of the packed column adjusted to 10 cm using a column adaptor (Omnifit, Germany). A nylon mesh (180 μ m pore size; EMD Millipore, U.S.) was placed at either end of the packed column to prevent material from being displaced into the tubing and adapters. The effective porosities of the collectors were determined using a NaBr tracer, analyzed by ion chromatography (Dionex ICS 1000; Thermo Fisher Scientific, U.S.). The column was then preconditioned with approximately 15 pore volumes of the synthetic water, delivered by a peristaltic pump (Ismatec, Germany) at an injection velocity of approximately 100 m/d. This was followed by the injection of approximately 10 pore volumes of a Na humate solution, using the same peristaltic pump and the same injection velocity. The column effluents were collected continuously and used to determine Na humate breakthrough (in duplicate for each collector) by UV–vis spectroscopy at a wavelength of 254 nm (LAMBDA 35; PerkinElmer, U.S.). This was then followed by the injection of approximately 20 pore volumes of a PAA-nano-ZVI suspension, containing approximately 1 g/L Fe_{tot} at the same injection velocity. The column effluents were again collected continuously and, after acid digestion, analyzed for Fe_{tot} (using ICP-OES), which served as a proxy for PAA-nano-ZVI particle concentration. Control column experiments with no Na humate injection were also carried out in order to evaluate the PAA-nano-ZVI particle breakthrough in pristine collectors. Each column experiment was replicated at least three times.

RESULTS AND DISCUSSION

Characterization of Particles in Suspension

The ζ potential of PAA-nano-ZVI particles in synthetic water was -24.2 ± 4.5 mV. The PAA-nano-ZVI particles appeared to be polydisperse and have a broad particle size distribution, as previously observed by Laumann et al.;¹ the particle size distribution in synthetic water was as follows: $d_{10}/d_{50}/d_{90} = 1.7/5.8/31.6$ μm . When this is compared with the particle size distribution in ultrapure water ($d_{10}/d_{50}/d_{90} = 1.2/2.6/9.5$ μm) it is clear that, as previously observed by Laumann et al.,²³ the larger particle size in synthetic water was due to aggregation as a result of reduced electrostatic repulsion between particles in the presence of divalent ions.

Characterization of Na Humate Solution

The 10 mg/L solution of Na humate in synthetic water had a pH of 7.3, an EC of 302 $\mu\text{S}/\text{cm}$, an IS of 4.8 mM, and a DOC content of 3.6 ± 0.1 mg/L. The DOC content remained unchanged when the solution was filtered through a 0.1 μm filter in preparation for SEC. The SEC retention time of Na humate solutions was compared to the retention times of MW standards. The SEC revealed three MW fractions within the 10 mg/L Na humate solution, with peaks at 3.6, 2.6, and 1.8 log Da, corresponding to approximately 3980, 400, and 63 Da (Figure S1). It should be noted that these are estimates of MWs, since molecule configuration and column interaction differences between the standards and the Na humate solution may introduce errors. The 100 mg/L solution of Na humate had a pH of 7.5, an EC of 314 $\mu\text{S}/\text{cm}$, an IS of 5.0 mM, and a DOC content of 29.8 ± 0.6 mg/L. Only 68.1% of the DOC content remained after the solution had been filtered with nearly one-third of the DOC being >0.1 μm . The SEC revealed only a single predominant MW fraction (3980 Da, Figure S1). As has been previously observed for humic acid and alginate,⁹ the presence of Ca^{2+} promotes the formation of larger aggregates at higher DOC concentrations.

Characterization of Collectors

The collectors exhibited a broad range of physical and chemical heterogeneity. Acid-washed glass beads and Ottawa sand differed in grain size, shape, surface roughness and morphology, as well as in BET surface area (Table 1 and Figure S2). Nevertheless, they were very similar with regard to surface chemistry and mineralogy, although traces of K-feldspar and illite were detected in the fine fraction of Ottawa sand (Figure S3). Both acid-washed and unwashed Dorsilit8 sand had the same surface grain morphology (Figure S2). Although the X-ray diffractograms of the two bulk pulverized Dorsilit8 collector materials had similar mineralogical compositions (Figure S4), the XRD analysis of the fine fraction clearly showed a higher content of kaolinite in the unwashed Dorsilit8 sand (Figure S3). This explains the recorded differences in surface and bulk chemistry between the acid-washed and unwashed Dorsilit8 sand (Tables 1 and S2), and indicates that a proportion of the clay and feldspar content (max. 5% of the bulk material, manufacturer's specifications) and the associated Al content was removed by the acid treatment. This is likely to have resulted in a slight change in the BET surface area and the corresponding ratio of surface areas (Table 1), all of which suggests that the acid-washing reduced both the chemical and physical heterogeneity. The collectors from Site 1 and Site 2 were undoubtedly the most

heterogeneous in terms of mineralogical and chemical composition, as well as in grain size distribution and surface roughness (Tables 1 and S2 and Figures S2 and S4).

The ζ potentials of the Ottawa sand and Dorsilit8 sand collectors in synthetic water were all close to -25 mV, with the glass beads recording a somewhat less negative ζ potential (Table 1). This was a consequence of the larger grain size of the glass beads and the higher permeability of this collector, with a resulting higher stream current, leading to a reduction in ζ potential at constant grain mineralogy, temperature, pH, and salt concentration, as was also previously observed by Abaza.²⁴ However, the ζ potential of the collectors from the field sites differed significantly, reflecting the mineralogical and chemical differences between these natural porous media and the standard collectors. Precoating the collectors with Na humate had no significant impact on the measured ζ potentials, despite an impact being expected if the charge heterogeneity was effectively screened by Na humate adsorption. This lack of any change in the ζ potentials is likely to be due to the fact that the measured ζ potential represents the bulk charge of the entire measured surface and therefore fails to take into account the local heterogeneity of mineral grains, as has been previously reported by Elimelech et al.⁴

Impact of Heterogeneity in the Standard Silica Collectors on PAA-nano-ZVI Mobility

The mobility of PAA-nano-ZVI was first compared between the pristine collectors, whose heterogeneity increased from acid-washed glass beads, through acid-washed Ottawa sand to acid-washed Dorsilit8 sand, and finally to unwashed Dorsilit8 sand. There was no difference in particle mobility between the acid-washed glass beads and the acid-washed Ottawa sand; in both of these collectors the normalized particle breakthrough reached a plateau of 0.5 ± 0.1 (for glass beads) and 0.6 ± 0.1 (for Ottawa sand) after 1.7 pore volumes (Figure 1). The almost identical particle breakthrough in these two collectors suggests that either their physical heterogeneities (as indicated by variations in grain size, grain morphology, BET surface area, and roughness) had no major effect on the mobility of PAA-nano-ZVI particles, or the effect of these individual heterogeneities has canceled one another. In contrast, the particle breakthrough in the more heterogeneous acid-washed Dorsilit8 sand was significantly different, with the normalized particle breakthrough reaching a lower plateau of approximately 0.4 after four pore volumes. Since the overall effect of the physical differences between the acid-washed glass beads and the acid-washed Ottawa sand had no influence on the PAA-nano-ZVI breakthrough, it is expected that the mineralogical compositions (i.e., the minor presence of clay minerals in the fine fraction of acid-washed Dorsilit8 sand, Figure S3) resulted in the increased attachment of PAA-nano-ZVI to acid-washed Dorsilit8 sand. The lowest PAA-nano-ZVI mobility was in unwashed Dorsilit8 sand, with the normalized particle breakthrough reaching a plateau of 0.1 ± 0.1 after approximately two pore volumes. This lower mobility is attributed to a greater heterogeneity in this collector than in the other collectors investigated, as reflected in the higher surface and bulk Si/Al ratios and the higher clay content in the fine fraction, as well as in the BET surface area and the ratio of surface areas (Table 1 and Figure S3). On the basis of these observations it would appear that the reductions in PAA-nano-ZVI mobility are due to small differences in mineralogy within the collectors, such that mobility reduces from acid-washed glass beads and acid-washed Ottawa sand to acid-washed Dorsilit8 sand, and then again to

unwashed Dorsilit8 sand. This interpretation is in accordance with the results obtained in previous investigations, which showed that even a small variation (approximately 2%) in the geochemical heterogeneity of porous media can have a significant effect on particle transport.^{4,25}

Impact of Different Na Humate Concentrations on PAA-nano-ZVI Mobility in Unwashed Standard Dorsilit8 Sand

Precoating the collector surfaces with Na humate to reduce PAA-nano-ZVI attachment and improve its mobility was investigated in unwashed Dorsilit8 sand. Two different concentrations of Na humate solution were used: 10 and 100 mg/L. After precoating the collector surfaces with a 10 mg/L Na humate solution the mean particle breakthrough increased approximately 4-fold (Figure 2, left), indicating a significant improvement in PAA-nano-ZVI mobility. In contrast, precoating the collector surfaces with a 100 mg/L Na humate had no effect at all on the PAA-nano-ZVI mobility (Figure 2, left). While the more concentrated solution was fully eluted from the column after approximately 3 pore volumes, indicating that there was little interaction with the collector surfaces (Figure 2, right), the less concentrated solution gradually approached a breakthrough of approximately 0.75 for the duration of the Na humate injection. The observed difference in the interaction of these two solutions with the collector can be explained by the different components of the Na humate solutions, as revealed by the SEC and DOC analyses. In the more concentrated solution where approximately 30% of the DOC was in the $>0.1 \mu\text{m}$ fraction, the $<0.1 \mu\text{m}$ fraction was dominated by MWs of in the region of 3980 Da. In contrast, the entire DOC in the 10 mg/L solution was in the $<0.1 \mu\text{m}$ fraction, with one proportion of this fraction having MWs in the region of 3980 Da, and two other proportions with similar abundances having MWs of approximately 400 and 63 Da (Figure S1). The difference in Na humate breakthrough between these two solutions suggests that only that fraction of the Na humate with MWs < 3980 Da (approximately 400 and 63 Da) sufficiently interacted with the collector surfaces and effectively screened the chemical heterogeneity within the unwashed Dorsilit8 sand, while the Na humate fraction with larger MWs eluted from the column after only minimal interaction with the collector surfaces.

The different interactions of the two Na humate solutions with unwashed Dorsilit8 sand were expected to lead to differences in the TOC loading of the collector, following Na humate precoating. This was tested in a separate set of column experiments, in which the collector material precoated with either 10 or 100 mg/L Na humate was collected and air-dried. The TOC remaining on the collector surfaces was then extracted for 16 h with the solution of 0.1 M NaOH in a reciprocating shaker (GLF 3018, Germany) followed by 30 min of centrifugation at 1000g (Jouan CR4.22, Canada), and then measured using a TOC-L CPH TOC analyzer (Shimadzu, Japan). The resulting TOC content was significantly higher in the collector precoated with the 10 mg/L Na humate solution (6.4 ± 0.4 mg/kg) than in the collector precoated with the 100 mg/L solution ($<1.1 \pm 0.2$ mg/kg). These findings confirm that the less concentrated Na humate solution interacted to a significantly greater degree with the collector surfaces than the more concentrated solution. Nevertheless, the overall mass concentration of low MW fractions is still expected to be higher in the 100 mg/L Na humate solution compared to the 10 mg/L Na humate solution. The lack of interaction of the

small MW fractions with the collector surfaces in the more concentrated solution can be explained by the limited presence of 400 and 63 Da fractions, but also the presence of large aggregates (approximately 30% of DOC > 0.1 μm), which prevent the sorption of low MW fractions. A better mechanistic understanding of Na humate interactions with collector surfaces is clearly needed, but from the above observations it seems very likely that the high MW fractions within Na humate tend to remain within the solution and are then eluted from the column, while those with lower MWs are able to interact with the collector surfaces and screen the charge heterogeneity, thus significantly improving PAA-nano-ZVI mobility.

The polydispersity of macromolecules or polymers that interact with NPs is known to influence the adsorption of the macromolecules or polymers and affect the stability of NPs and their resistance to aggregation.²⁶ The influence of Na humate polydispersity was also observed in its interaction with the collector surfaces. High MW fractions contain more hydrophobic moieties in natural organic matter (NOM), and since divalent cations (present in the synthetic water) bind preferentially with these hydrophobic moieties (ref 27 and references therein), the complexation or cation-bridging between Ca^{2+} or Mg^{2+} and these moieties is likely to neutralize the negative charges of NOM molecules²⁸ and result in the formation of even larger fractions. Since the precoating of the collector with the higher concentrated Na humate solution containing significantly more high MW fractions shows no effects on PAA-nano-ZVI mobility, we conclude that the low MW fractions of Na humate are able to effectively screen charge heterogeneities within the collector. This conclusion is in line with the study of Joo et al.,²⁹ who have shown that the lower MW fractions of NOM are preferentially adsorbed onto metal (hydr)oxide-coated sands, leaving the higher MW fractions in solution.²⁹ This corresponds with the findings of Golas et al.,³⁰ who observed that low MW molecules can diffuse more quickly onto NP surfaces and occupy surface sites, thus preventing bridging by slow-diffusing, high MW components. As reported by Joo et al.,²⁹ the adsorption of heterogeneous NOM onto metal (hydr)oxide-coated sands represents a combination of two adsorption mechanisms: rapid ligand exchange with lower MW fractions and slow hydrophobic interaction with higher MW fractions. Nevertheless, as the low MW fractions are strongly binding and are not readily replaced with higher MW fractions from solution, the lower MW fractions result in greater adsorption even after a longer reaction time (4 h). As the Na humate injection lasted for a much shorter time, (approximately 15 min), a significant exchange between the adsorbed low MW fractions with high MW fractions was not expected.

For field applications, the injection of 10 mg/L Na humate solution into aquifers has a number of advantages. First, it avoids any risk of remobilizing groundwater contaminants (by enhancing their dissolution), as this concentration is at least 2 orders of magnitude lower than the concentration of humic substances known to enhance dissolution of, for example, hydrocarbons;³¹ concentrations up to 10 mg/L DOC are also found to occur naturally in groundwater.³² Moreover, such a low Na humate concentration is not expected to have any adverse effects on indigenous bacteria within aquifers.³³ Finally, use of the lower concentration of Na humate in field applications will obviously result in lower material costs.

The 10 mg/L Na humate solution was therefore selected for further investigation into its effect on PAA-nano-ZVI mobility in more homogeneous collectors (namely, acid-washed glass beads and acid-washed Ottawa sand), as well as in heterogeneous collectors from contaminated sites.

Impact of Na Humate Preinjection on PAA-nano-ZVI Mobility in Acid-Washed Standard Silica Collectors

Preinjection of 10 mg/L Na humate into acid-washed glass beads and acid-washed Ottawa sand was found to have no effect on PAA-nano-ZVI mobility (Figure 3). Differences between the particle breakthroughs for pristine collectors and those precoated with Na humate were within the range of the standard deviation. It is apparent from the Na humate breakthrough curves for these two collectors that there were insufficient interactions between this polyelectrolyte and the collector surfaces, with the Na humate solution eluting fully from the columns after approximately 3 pore volumes (Figure S5).

There are two possible explanations for the lack of Na humate adsorption onto the surfaces of these two acid-washed standard silica collectors in contrast to unwashed Dorsilit8 sand surfaces. The ratio of surface areas for acid-washed glass beads and acid-washed Ottawa sand (0.005 and 0.065, respectively) was smaller than that of unwashed Dorsilit8 sand (Table 1), indicating a greater surface roughness for the unwashed Dorsilit8 sand. The increase in surface roughness was also seen in the high magnification scanning electron micrographs of these three collectors (Figure S6). It therefore appears plausible that Na humate attaches onto the rougher surfaces of unwashed Dorsilit8 sand, but not onto the smoother acid-washed surfaces of glass beads and Ottawa sand. The total interaction energy as sum of the van der Waals and electrical double layer forces between colloids and glass bead collectors³⁴ and rough rock surfaces³⁵ has previously been shown to decrease with increasing collector roughness, with colloids being attached preferentially by sorption onto surfaces with a high density of small protuberances. Similarly, the attachment of Na humate to the surfaces of relatively smooth glass beads and Ottawa sand was also expected to be less than to the rougher surfaces of unwashed Dorsilit8 sand. Moreover, the scarcity of chemical heterogeneities on the surfaces of acid-washed glass beads and Ottawa sand compared to those of unwashed Dorsilit8 sand, as revealed by the surface Si/Al ratio (Table 1) and the differences in clay content (Figure S3), may also have contributed to the lack of Na humate adsorption onto the acid-washed collector surfaces. Both physical and chemical heterogeneities may therefore have contributed to the differences in Na humate interactions between acid-washed glass beads and Ottawa sand on the one hand, and unwashed Dorsilit8 sand on the other.

Impact of Na Humate Preinjection on PAA-nano-ZVI Mobility in Collectors from Contaminated Sites

Precoating the surfaces of the collectors from contaminated sites with 10 mg/L Na humate achieved only a slight improvement in PAA-nano-ZVI mobility. The particle breakthrough increased by a factor of 2 in the collector from Site 1, and by a factor of 1.25 in the collector from site 2 (Figure 4).

Normalized Na humate breakthrough curves for these two porous media reached only approximately 0.6 (Figure S7). This suggests that the period of Na humate injection may have been too short for all of the available adsorption sites to be coated. Differences observed between the kinetics of Na humate coating of collector surfaces in the field site collectors and pristine Dorsilit8 sand and also differences observed between the effects of Na humate coating onto mobility of PAA-nano-ZVI, may relate to differences in the number and nature of favorable sites available, as well as to differences in permeability between these collectors. The Dorsilit8 sand is expected to have higher permeability because of its higher porosity and better sorting (Table 1 and Figure S2). It is reasonable to expect a greater improvement in PAA-nano-ZVI mobility in natural collectors, such as those from our field sites, if Na humate is allowed to interact with the collector surfaces over a prolonged period of time.

The results of our investigations demonstrate that Na humate conditioning of porous media can be expected to improve the mobility of PAA-nano-ZVI, but that the Na humate concentration and water composition will have a strong influence on aggregation and complexation of Na humate, and on its interaction with the collector surfaces. Moreover, the properties of the collector, such as its physical and chemical heterogeneity and its permeability, need to be taken into account to determine the duration of Na humate injection required and to predict the effects that Na humate coating will have on the granular porous media. Since our results have been obtained under laboratory conditions, upscaling or computational modeling will be required to obtain an improved evaluation of the effect of Na humate coating on a scale relevant to field application, and of the feasibility of using collector preconditioning to improve nano-ZVI dispersal in the nanoremediation of contaminated groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Laumann S, Mici V, Lowry GV, Hofmann T. Carbonate minerals in porous media decrease mobility of polyacrylic acid modified zero-valent iron nanoparticles used for groundwater remediation. *Environ. Pollut.* 2013; 179:53–60. [PubMed: 23644276]
2. Ryan JN, Elimelech M, Ard RA, Harvey RW, Johnson PR. Bacteriophage PRD1 and silica colloid transport and recovery in an iron oxide-coated sand aquifer. *Environ. Sci. Technol.* 1999; 33(1):63–73.

3. Song LF, Johnson PR, Elimelech M. Kinetics of colloid deposition onto heterogeneously charged surfaces in porous media. *Environ. Sci. Technol.* 1994; 28(6):1164–1171. [PubMed: 22176246]
4. Elimelech M, Nagai M, Ko CH, Ryan JN. Relative insignificance of mineral grain zeta potential to colloid transport in geochemically heterogeneous porous media. *Environ. Sci. Technol.* 2000; 34(11):2143–2148.
5. Phenrat T, Saleh N, Sirk K, Kim HJ, Tilton RD, Lowry GV. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J. Nanopart. Res.* 2008; 10(5):795–814.
6. Tiraferri A, Sethi R. Enhanced transport of zerovalent iron nanoparticles in saturated porous media by guar gum. *J. Nanopart. Res.* 2009; 11(3):635–645.
7. Basnet M, Tommaso CD, Ghoshal S, Tufenkji N. Reduced transport potential of a palladium-doped zero valent iron nanoparticle in a water saturated loamy sand. *Water Res.* 2015; 68:354–363. [PubMed: 25462742]
8. Lin SH, Cheng YW, Liu J, Wiesner MR. Polymeric coatings on silver nanoparticles hinder autoaggregation but enhance attachment to uncoated surfaces. *Langmuir.* 2012; 28(9):4178–4186. [PubMed: 22242766]
9. Chen KL, Elimelech M. Interaction of fullerene (C-60) nanoparticles with humic acid and alginate coated silica surfaces: measurements, mechanisms, and environmental implications. *Environ. Sci. Technol.* 2008; 42(20):7607–7614. [PubMed: 18983082]
10. Velimirovic M, Larsson PO, Simons Q, Bastiaens L. Reactivity screening of microscale zerovalent irons and iron sulfides towards different CAHs under standardized experimental conditions. *J. Hazard. Mater.* 2013;252–253. 204. [PubMed: 23611806]
11. Schmid D, Mici V, Laumann S, Hofmann T. Measuring the reactivity of commercially available zero-valent iron nanoparticles used for environmental remediation with iopromide. *J. Contam. Hydrol.* 2015; 181:36–45. [PubMed: 25708601]
12. Hashish KI, Fatma El-Quesni EM, Azza MM. Influence of potassium humate on growth and chemical constituents of *Jatropha Curcus L.* *Int. J. Chem. Technol. Res.* 2015; 8(9):279–283.
13. Olivares FL, Aguiar NO, Rosa RCC, Canellas LP. Substrate biofortification in combination with foliar sprays of plant growth promoting bacteria and humic substances boosts production of organic tomatoes. *Sci. Hortic.* 2015; 183(1):100–108.
14. Abobaker AM, Bound SA, Swarts N, Close DC. Effect of humic based soil conditioner, effective microbes and fertiliser on growth and flowering of sunflower (*Helianthus annus L.* 'Dwarf Sunsation'). *Acta Hortic.* 2016; 1112:291–298.
15. U.S EPA. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. 5. EPA-821-R-02-012; U.S. Environmental Protection Agency. Office of Water (4303T); Washington, DC: 2002.
16. Hunter, RJ. Zeta Potential in Colloid Science. Principles and Applications. Academic Press; London, England: 1988.
17. McCleskey RB, Nordstrom DK, Ryan JN. Comparison of electrical conductivity calculation methods for natural waters. *Limnol. Oceanogr.: Methods.* 2012; 10:952–967.
18. Neubauer E, v d Kammer F, Hofmann T. Using FLOWFFF and HPSEC to determine trace metal-colloid associations in wetland runoff. *Water Res.* 2013; 47(8):2757–2769. [PubMed: 23528782]
19. Yang X, Flynn R, von der Kammer F, Hofmann T. Quantifying the influence of humic acid adsorption on colloidal microsphere deposition onto iron-oxide-coated sand. *Environ. Pollut.* 2010; 158(12):3498–3506. [PubMed: 20382456]
20. Mici V, Krüge MA, Hofmann T. Variations of common riverine contaminants in reservoir sediments. *Sci. Total Environ.* 2013; 458–460:90–100.
21. Fairbrother F, Mastin H. Studies in electroendosmosis. Part I. *J. Chem. Soc., Trans.* 1924; 125:2319–2330.
22. Guven O, Ozdemir O, Karaagaciloglu IE, Celik MS. Surface morphologies and floatability of sand-blasted quartz particles. *Miner. Eng.* 2015; 70:1–7.

23. Laumann S, Mici V, Hofmann T. Mobility enhancement of nanoscale zero-valent iron in carbonate porous media through co-injection of polyelectrolytes. *Water Res.* 2014; 50:70–79. [PubMed: 24361704]
24. Abaza, MMI. Ph.D. Thesis. Utah State University; Logan, Utah, U.S: 1966. Streaming current and streaming potential induced by water flow through porous media.
25. Johnson PR, Sun N, Elimelech M. Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environ. Sci. Technol.* 1996; 30(11):3284–3293.
26. Louie SM, Tilton RD, Lowry GV. Critical review: impacts of macromolecular coatings on critical physicochemical processes controlling environmental fate of nanomaterials. *Environ. Sci.: Nano.* 2016; 3(2):283–310.
27. Shen MH, Yin YG, Booth A, Liu JF. Effects of molecular weight-dependent physicochemical heterogeneity of natural organic matter on the aggregation of fullerene nanoparticles in mono- and divalent electrolyte solutions. *Water Res.* 2015; 71:11–20. [PubMed: 25577691]
28. Li QL, Elimelech M. Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms. *Environ. Sci. Technol.* 2004; 38(17):4683–4693. [PubMed: 15461180]
29. Joo JC, Shackelford CD, Reardon KF. Association of humic acid with metal (hydr)oxide-coated sands at solid-water interfaces. *J. Colloid Interface Sci.* 2008; 317(2):424–433. [PubMed: 17963778]
30. Golas PL, Louie S, Lowry GV, Matyjaszewski K, Tilton RD. Comparative study of polymeric stabilizers for magnetite nanoparticles using ATRP. *Langmuir.* 2010; 26(22):16890–16900. [PubMed: 20945936]
31. Lesage S, Brown S, Millar K, Novakowski K. Humic acids enhanced removal of aromatic hydrocarbons from contaminated aquifers: Developing a sustainable technology. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* 2001; 36(8):1515–1533.
32. Thurman, EM. *Organic Geochemistry of Natural Waters*. Vol. 2. Martinus Nijhoff/Dr W. Junk Publishers; Dordrecht: 1985. p. 497
33. Mici V, Hofmann T. DL 4.2: Stability, Mobility, Delivery and Fate of optimized NPs under Field Relevant Conditions. <http://www.nanorem.eu/Deliverables.aspx>
34. Elimelech M, O'Melia CR. Effect of particle size on collision efficiency in the deposition of Brownian particles with electrostatic energy barriers. *Langmuir.* 1990; 6(6):1153–1163.
35. Darbha GK, Fischer C, Luetzenkirchen J, Schafer T. Site-specific retention of colloids at rough rock surfaces. *Environ. Sci. Technol.* 2012; 46(17):9378–9387. [PubMed: 22861645]

Figure 1.

Mean experimental breakthrough curves for PAA-nano-ZVI and the NaBr tracer in standard collectors with an increasing degree of heterogeneity. Error bars represent the standard deviation of n replicates.

Figure 2. Mean experimental breakthrough curves for PAA-nano-ZVI and the NaBr tracer in unwashed Dorsilit8 sand (left); error bars represent the standard deviation of n replicates. Duplicate breakthrough curves for Na humate at different concentrations in the same collector (right).

Figure 3. Mean experimental breakthrough curves for PAA-nano-ZVI and the NaBr tracer in acid-washed glass beads (left) and acid-washed Ottawa sand (right). Error bars represent the standard deviation of n replicates.

Figure 4. Mean experimental breakthrough curves for PAA-nano-ZVI and the NaBr tracer in the collectors from site 1 (left) and site 2 (right). Error bars represent the standard deviation of n replicates.

Table 1

Physical and Chemical Properties of Collectors^a

collector	$d_{10}/d_{50}/d_{90}$ (mm)	effective porosity (%)	BET surface area (m ² /g)	ratio of surface areas (-)	mineralogical composition	surface Si/ Al (-)	surface Si/ Ca (-)	surface Si/Fe (-)	bulk Si/ Al (-)	ζ potential (mV)	ζ potential after coating with 10 mg/L Na humate (mV)
(i) Glass beads a.w.	approximately 1/1/1	39.9 ± 1.1	0.005	3.1	quartz					-18.1 ± 2.8	-17.2 ± 0.3
(ii) Ottawa sand a.w.	0.40/0.67/0.85	37.8 ± 0.8	0.065	19.2	quartz, feldspar ^b , clay ^b					-25.9 ± 1.7	-24.8 ± 0.5
(iii) Dorsilit8 sand a.w.	0.34/0.65/0.88	39.6 ± 1.2	0.088	26.0	quartz, feldspar ^b , clay ^b	5.4 ± 1.3			129.1	-25.1 ± 1.9	-25.4 ± 0.5
(iv) Dorsilit8 sand	0.34/0.65/0.88	41.6 ± 2.8	0.095	28.7	quartz, feldspar ^b , clay ^b	2.3 ± 0.3			107.0	-24.3 ± 1.5	-24.7 ± 1.6/ -21.7 ^c ± 1.4
(v) site 1	0.14/0.48/2.3	28.3 ± 1.1	1.130	412	quartz, calcite, dolomite, feldspar	2.5 ± 0.3	3.8 ± 0.5	55.7 ± 24.5	6.9	-18.0 ± 2.7	-17.1 ± 1.0
(vi) site 2	0.26/0.80/2.85	26.6 ± 0.8	5.133	1473	quartz, feldspar, muscovite	1.9 ± 0.7	14.0 ± 7.5	38.1 ± 5.1	3.4	-14.1 ± 1.9	-13.2 ± 0.7

^a
a.w. = acid-washed.^b
Only detectable in the fine fraction, not in the bulk sample.^c
After coating with 100 mg/L Na humate.