Quantifying the influence of EDTA on polymer nanoparticle deposition and retention in an iron-oxide-coated sand column†

Xinyao Yang,*ab Dongxu Liangb and Shihuai Dengb

Received 19th February 2012, Accepted 29th May 2012
DOI: 10.1039/c2em30145h

Ethylene diaminetetraacetic acid (EDTA) occurring in groundwater aquifers complicates the prediction of nanoparticle movement in the porous medium. This paper demonstrates an approach combining Triple Pulse Experiments (TPEs) and numerical modelling to quantify the influence of EDTA on the deposition and retention of polymer nanoparticles in a water-saturated column packed with iron-oxide-coated sand. TPEs injecting three successive pulses in the order of nanoparticle, EDTA, nanoparticle permit nanoparticle deposition in the absence and the presence of EDTA to be compared. Random Sequential Adsorption (RSA) modelling of the nanoparticle breakthrough curves combining mass balance calculation allows the influence of EDTA to be quantified. TPE results demonstrate that the injected EDTA eluted the oxide coatings (favorable deposition sites) from the sand surface and the resulting decline in sites led to enhanced nanoparticle mobility in the subsequent pulse. Quantification results suggest that at the experimental time-scale and under the controlled conditions, elution of one deposition site requires injection of $2.4 \times 10^{11}$ EDTA molecules. In total, 75 gram EDTA needs to be injected to remove all the column sites.

1. Introduction

Today, the nano-market is growing fast and large quantities of nanomaterials are entering the broad environment. The large uncertainty surrounding the environmental risks that these materials may pose necessitates research on their migration and exposure in environmental media.1,2 Groundwater, as an important source of drinking water in many regions of the world, presents the most significant exposure for assessing environmental risks of engineered nanomaterials.3 Movement of nanomaterials in the groundwater environment is controlled by the physicochemical characteristics of the porous medium surface.4,5 The surface of porous medium in groundwater is often coated with patchy coatings and interstitial aggregates of minerals like ferric and aluminum oxyhydroxides, displaying positive charges under typical groundwater pH values rendering them attractive to a range of negatively charged nanoparticles.6–11

In many situations, the medium surface is also associated with organic matter, whose interaction with the oxide coatings may alter the medium surface property by various mechanisms.12–14 Large volume of studies focused on the effect of natural organic matter (NOM) such as humic acid,12,13,15–19 These studies show that NOM may cover (block) the oxide coatings (favorable sites) and inhibit nanoparticle deposition by electrostatic and/or steric repulsions. The site blocking effect has been quantified at laboratory column

Environmental impact

Aquifer environments present an important medium for assessing the environmental risks of nanoparticles. EDTA, a widely used anthropogenic organic ligand, may enter groundwater via river bank infiltration or intentional release for groundwater remediation. EDTA could elute the metal oxide coatings (often acting as favorable deposition sites for nanoparticles) from the porous medium surface and change its control on nanoparticle movement. This complicates prediction of nanoparticle deposition and retention in EDTA-impacted environment. The approach presented in this paper allows the number of sites eluted by EDTA to be quantified and thus makes it possible to estimate the deposition rate of nanoparticles in the presence of EDTA. The quantitative ability has implications to risk evaluation of nanomaterials in heterogeneous porous medium.
In comparison to the influence of natural organic matter, anthropogenic organic ligands have been noted to interact with the immobile solid phase by a different mechanism, i.e., mobilization of the oxide coatings. Since the nanoparticle deposition rate is proportional to the accessible number of sites, we expect that the decline in site may reduce the deposition rate of nanoparticles, and that an approach allowing the site elution effect to be quantified is critical for predicting the nanoparticle translocation in ligand-impacted environment.

This study used EDTA (ethylenediaminetetraacetic acid) and polystyrene latex microspheres as models of organic ligand and polymer nanoparticles, respectively, as they have strong environmental implications. EDTA is an anthropogenic organic ligand capable of mobilizing strongly adsorbing metal ions in groundwater. Being widely used in industries and households, the organic ligand has been found in highest proportions in European waters. It may enter groundwater through river bank infiltration or intentional release for soil and groundwater remediation, with the reported levels in natural water bodies varying across a wide range, from 10 nM to 0.1 M. Like EDTA, polymer nanoparticles have also gained widespread interests. They are widely used for drug delivery and for soil and groundwater remediation. In a recent NanoImpactNet workshop held in Zurich, polystyrene microspheres have been confirmed as a major test material for environmental impact studies.

The paper presents an approach combining triple pulse experiments (TPEs) with numerical modelling to quantify the influence of EDTA on polymer nanoparticle deposition in an iron-oxide-coated porous medium. Study results confirm that EDTA could elute the favorable deposition sites (iron-oxide coatings) and enhance mobility of the nanoparticles. Modelling of the nanoparticle breakthrough curves integrated with mass balance calculations permits the quantification of sites eluted by EDTA.

2. Materials and methods

2.1. Triple pulse column experiments

Porous media. Iron-oxide-coated quartz sand acted as the porous medium for all experiments. Pure quartz sand (40-150 mesh, Sigma-Aldrich, Dorset, England) was processed and coated with iron-oxide following the procedure described in Yang et al. The 125 μm grain size fraction of the sand was used as column-filling materials. Examination of both coated and uncoated sand by scanning electron microscope revealed relatively uniform rounded to sub-angular grains with localised rough surfaces and cracking on individual grains. At higher magnification abundant submicro-sized clusters were noted on coated grain surfaces, which were observed to be absent on the uncoated sand (ESI, Fig. S1† contains the SEM images).

Solutions. All solutions were prepared using ultrapure water. Tris (tris(hydroxymethyl)aminomethane) (Fisher Scientific, Loughborough, UK) and hydrochloric acid (Sigma-Aldrich, Vienna, Austria) were added to all solutions and pH was maintained at 7.6 ± 0.1. This value is typical of common neutral pH conditions in groundwater. Ionic strength was controlled at 20 ± 1 mM for all solutions with sodium chloride salt (Acros Organics, Geel, Belgium).

Nanoparticle. Fluoresbrite® yellow-green fluorescent stained polystyrene latex microspheres with carboxylic functional groups and nominal diameter of 200 nm (Polyscience Inc., Eppelheim, Germany) were used as model nanoparticles in all experiments. This size is in the range employed by other studies investigating the transport of nanoparticles in porous media. The nanoparticle injection concentration was 10.4 ppm (2.5 × 10^9 particles per ml). Levels in column effluent were continuously monitored on-line using an HPLC fluorescence detector (FLD, Agilent 1200 Series, Waldbronn, Germany). Optimum conditions were determined by measuring an excitation/emission matrix. At excitation/emission wavelengths of 415/490 nm the nanoparticle detection limit was taken as three times the standard deviation of the blank noise signal (corresponding to 0.26 ppm). Preliminary experiments injecting solutions containing nanoparticles only and those containing a mixture of nanoparticles (in the same amount as those in the pure nanoparticle solution), EDTA, and iron oxide, into the flow cell of the FLD generated comparable optical responses, suggesting that EDTA and iron oxide could not be detected by FLD and their presence may not influence the nanoparticle level measurement by FLD.

Particle electrophoretic mobility measurements were performed with a Zetasizer (Model Nano ZS, Malvern Instruments Ltd, Worcestershire, UK). A zeta potential of −66 ± 2 mV was determined for the nanoparticle suspension employed for column experiments. Dynamic light scattering (DLS) measurements of hydrodynamic diameter, performed with the same instrument, suggested a particle size of 221.7 ± 6.0 nm, in close correspondence to the manufacturer’s stated size. All the measurements were conducted at least three times to allow the variability to be evaluated.

Organic matter. Ethylenediaminetetraacetic Acid (EDTA, 99% purity, Acros Organics, Geel, Belgium) acted as model organic ligand. EDTA is a 4-protonic acid with a molar weight of 292.25 g mol⁻¹ and the formula C₁₀H₁₆N₂O₈. The employed EDTA injection level was 0.4 mM, which falls within the range occurring in wide environments. An HPLC UV-vis spectrophotometer (VWD) (Agilent 1100 Series, Waldbronn, Germany), set at 230 nm, was installed to continuously measure online the concentrations of EDTA and the iron oxide potentially mobilized from sand surface. Preliminary experiments injecting nanoparticles, EDTA, and iron oxide into the flow cell of VWD suggest that the three tracers were all detectable, their optical signals being additive.

Experiment setup. A WellChrom HPLC pump with 10 ml analytical head (K-120, KNAUER, Berlin, Germany) provided a stable flow of 1 ml min⁻¹ during all column experiments. Three columns and one bypass line were connected in parallel to two five-port high pressure distribution valves (Omnifit, UK). This permitted the column experiment to be conducted in triplicate under the same conditions. A third valve used to connect the three feeding reservoirs to the pump allowed switching between nanoparticle suspensions, EDTA solutions and flush water. An HPLC fluorescence detector (FLD, Agilent 1200 Series, Waldbronn, Germany) and an HPLC UV-vis spectrophotometer (VWD) (Agilent 1100 Series, Waldbronn, Germany) were installed in parallel to continuously measure online the...
concentrations of latex nanoparticles, EDTA, and mobilized iron oxide in column effluent. A pH electrode (SenTix 41, WTW, Weilheim, Germany) monitored the column effluent pH for all experiments to ensure no significant differences developed with pH levels in source reservoirs. The sustained constant signals for nanoparticle and EDTA generated during their injection via the by-pass line permitted to determine the source concentration responses (C0) in tracer reservoirs. These were identical to levels generated following direct injection into the FLD and VWD flow cells, showing that the experimental apparatus did not attenuate the tracers.

**Experiment protocol.** Three 8 cm long, 10 mm diameter length adjustable borosilicate glass columns (Omnifit, Cambridge, UK) were wet-packed with 3 cm thick iron-oxide-coated quartz sand as the porous matrix. Wall effect was negligible, considering a column-to-grain-diameter ratio of above 20. All solutions were degassed under vacuum for 15 minutes before experiments while nanoparticle suspensions were simultaneously dispersed in an ultrasonic bath (Retsch UR1, Haan, Germany). Prior to each experiment, the column was equilibrated with approximately 75 pore volumes of flushing solution to ensure the absence of air bubbles. Following hydraulic and chemical stabilisation, triple pulse experiments (TPEs) were conducted to quantify the impact of EDTA on nanoparticle deposition. The TPE consisted of a prolonged pulse of 13 pore volumes (PV) of latex nanoparticles, a 13 PV pulse of EDTA, and a second 13 PV of the nanoparticles. Each injection pulse was followed by a tracer free flushing for 9 PVs. Moreover, a separate series of TPEs injecting three successive pulses of nanoparticles through uncoated sand provided a qualitative indication of the relative abilities of coated and uncoated porous media to remove the nanoparticle from suspension. Repetition of all experiments in triplicate allowed experimental variability to be determined.

### 2.2. Numerical modelling and quantification

Numerical modelling of nanoparticle breakthrough curves was carried out to quantify the number of nanoparticle that must be deposited in order to generate equivalent nanoparticle breakthrough curves (BTCs) to those generated in the TPEs following EDTA injection. A one-dimensional transport model describing advection, dispersion, and random sequential adsorption (RSA) simulated experimental breakthrough curves. The model validity for the experimental system employed in this study had been verified in our previous studies conducted under comparable conditions (Fig. S37).

Particle transport and attenuation in a 1D column under steady flow conditions may be described by eqn (1):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{f}{\pi a_p^2} \frac{\partial \theta}{\partial t}$$

where $C$ is the number concentration of nanoparticles in aqueous suspension, $D$ is the hydrodynamic dispersion coefficient, $v$ is the interstitial particle velocity, $a_p$ and $a_c$ are the radius of particle and sand grain, respectively, $f$ is the collector surface area per unit volume of packed bed, and $\theta$ is the fraction of collector surface covered by deposited particles. For particle deposition by a monolayer process, the covered fractional area ($\theta$) increases as more particles deposit.

Eqn (2) describes the evolution rate of $\theta$:

$$\frac{\partial \theta}{\partial t} = \alpha K \pi a_p^2 B(\theta)$$

where $\alpha$ is the particle collection efficiency, $K$ is the particle transfer coefficient, and $B(\theta)$ is the RSA dynamic blocking function.

The particle transfer coefficient ($K$) is obtained from the fluid approach velocity ($U$) and the single collector efficiency ($\eta$) using eqn (3):

$$K = \eta U / 4$$

The dynamic blocking function ($B(\theta)$) simulates the decline in particle deposition rate with increasing fractional coverage, up to a maximum of $\theta_{max}$. Eqn (4) describes the correlation between fractional surface coverage ($\theta$) and the blocking function ($B(\theta)$):

$$B(\theta) = 1 - 40 \theta (\frac{1}{\theta_{max}}) \theta$$

$$+ 3.308 (\frac{1}{\theta_{max}}) \theta^2 + 1.4069 (\frac{1}{\theta_{max}}) \theta^3$$

where $\theta_{max}$ is the maximum surface coverage for non-interacting deposited particles (hard sphere) and corresponds to approximately 0.546. Maximum surface coverage for soft sphere ($\theta_{max}$) may vary depending on the repulsive forces operating between deposited and suspended particles and is usually less than $\theta_{max}$.

Model formulae were solved recursively using a Crank–Nicolson finite difference numerical scheme. Model calibration of TPE nanoparticle responses was completed by fitting $\eta$ to the rising limb of the first nanoparticle BTC. The subsequent more gradual rise in the nanoparticle concentration, observed in this pulse as injection continued, was fitted by adjusting $\theta_{max}$.

Quantification was carried out based on the method established in Yang et al. Briefly, this involves model simulation, employing the calibration parameters estimated from the first nanoparticle BTC, to predict the second nanoparticle BTC (third pulse). As the second nanoparticle BTC, developed following the EDTA pulse, reflects the impact of EDTA on nanoparticle transport, a correspondence between it and the model generated curve indicates the equivalent influence was generated by EDTA and the deposited nanoparticles (or the deactivated/eluted nanoparticle sites) predicted by the model. In order to intercept with the model curve, the second nanoparticle BTC needs to shift laterally along the $x$-axis to variable lengths, depending on the degree of EDTA influence. Integration of the model generated curve for the resulting time interval between the first and the relocated second nanoparticle BTCs provides an estimate of the number of nanoparticles that must be deposited (or the number of nanoparticle sites that must be deactivated/eluted) in order to generate equivalent responses as EDTA. Combining this information with the total injected EDTA mass, the influence of EDTA on the nanoparticle deposition could be quantified.
3. Experimental results and discussions

3.1. Analysis of nanoparticle breakthrough curves

Fig. 1 summarises the nanoparticle breakthrough curves (BTCs) of triple pulse column experiments (TPEs) using uncoated sand and in the absence of EDTA. The BTCs were derived by normalizing the continuously monitored FLD signal of nanoparticles in the column effluent against that in the source reservoir (relative concentration, \( C/C_0 \)). The relative concentrations of all the three nanoparticle BTCs rose to an inflection of about 100% within an injection period of two column Pore Volumes (PVs), and remained stabilized at that altitude until the start of the flushing effect, which led to abrupt decline of the concentrations to zero.

Fig. 2A summarises the nanoparticle BTCs, derived from the FLD signals, for TPEs using iron-oxide-coated sand and in the presence of EDTA. Fluorescence signals were significant in the first and third pulses (nanoparticle pulse) but absent in the intermediate (EDTA) pulse. The first nanoparticle BTC rose rapidly till an inflection point of 5.7%, followed by a rise at moderate rates to 7.0%. By comparison, the second nanoparticle BTC (3rd pulse), rising from an inflection height of 8.3% to 9.0%, has a higher inflection point and a lower slope. Tailing was absent in both nanoparticle BTCs.

Developing a plateau at about 100% on nanoparticle BTCs (Fig. 1) indicates almost complete recovery of injected nanoparticles from the uncoated sand, implying the absence of favorable deposition sites on the uncoated sand surface. By contrast, the low inflection point (Fig. 2A) suggests that a high fraction of the injected nanoparticles were attenuated by the iron-oxide-coated sand. This confirms that the iron oxide coating acted as favorable deposition sites for the nanoparticles. The phase of gradual rise developed following the inflection point, as shown on the first nanoparticle BTC, suggests declining deposition rates (or increasing recovery rates). Zeta potential measurement data suggests that the nanoparticles exhibit high surface charge densities. Dynamic light scattering measurement showing absence of nanoparticle aggregation confirms that the electrostatic repulsion between nanoparticles effectively prevented their aggregation at the experimental time scale. Thus, the observed nanoparticle behavior during column experiments may be attributed to the gradually increasing repulsion from the deposited nanoparticles on the depositing ones (a phenomenon called blocking\(^{6,23}\)). Absence of fluorescence signals during the EDTA (2\(^{nd}\) injection pulse) suggests that EDTA did not mobilize already deposited nanoparticles significantly. Previous studies performing multiple pulse microsphere injection experiments noted the inflection point of a subsequent pulse was in comparable level with the peak of the previous pulse and attributed this phenomenon to that comparable number of deposition sites occurred at the end and the beginning of the two successive injection pulses.\(^{18,39}\) By analogy, the higher inflection point developed on the second nanoparticle BTC implies lower number of deposition sites than the first nanoparticle pulse. This suggests that EDTA might have reduced available nanoparticle sites, i.e. iron-oxide coatings. Further evidence will be presented in Section 3.2. The lower slope occurring in the second nanoparticle BTC, in comparison to the first, indicates decreasing blocking rates,\(^{40,41}\) which contrasted with the enhanced blocking effect imposed by humic acid (HA) adsorption shown in our previous work.\(^{19}\) Chen et al.\(^{42}\) noted that collector surface heterogeneity played a key role controlling colloidal deposition. Other authors also noted that surface heterogeneity may enhance\(^{43}\) or reduce\(^{44}\) blocking, depending on the relative dimension of the heterogeneity to that of depositing colloids. Given that comparable solution chemistry and sand surfaces were employed in both the EDTA and HA experiments, we hypothesized the observed contrast, following organic matter adsorption, might be related to the distinct roles...
the natural and the synthetic organic matter compounds played modifying the collector surface, i.e., HA adsorbing to iron oxide sites imposed more electrosteric heterogeneity on the collector surface, while EDTA, by eluting the randomly distributed micron to submicron-size oxide sites, might have made the collector surface more homogeneous. Further work investigating blocking on a range of tailored surface heterogeneity features could enhance our understanding of this transient process in organic matter present environment. The novel technique developed by Chen et al. for creating the microscopic chemical/charge heterogeneity on collector surface provides a realistic means for conducting those experiments. Absence of tailing in the first and second nanoparticle BTCs suggests that the deposition was an irreversible process and that EDTA adsorption did not weaken particle attachment on porous medium significantly.

3.2. Analysis of VWD optical signals recorded during the EDTA injection pulse

Fig. 2B presents the optical signals measured by VWD during the EDTA pulse. The UV-vis signals climbed rapidly to a peak of 371 AU, followed by a gradual recession to 316 AU. These values are substantially higher than the 266 AU signal recorded for the input level of EDTA. Upon the beginning of the flushing effect, significant tailing developed in the optical signal curves.

An optical signal intensity of column effluent higher than that of the input EDTA suggests that other optical sensitive substances, in addition to the EDTA, occurred in the effluent. Control experiments confirmed that the VWD could detect nanoparticles and iron-oxides mobilized from sand surface. Combining this with the absence of nanoparticles during the EDTA pulse, as discussed in Section 3.1, it may be inferred that the mobilized substance might be the iron oxide coatings from the sand surface. Additional experiments injecting EDTA directly into uncoated quartz sand matrix shows the optical signal, measured by the VWD, reached a level comparable to that of the EDTA sources (=266 AU) (Fig. S2†), thus confirming the additional optical signal was related to the release of iron oxide coatings. EDTA, as a powerful complexing agent, has been widely recognized for its competency in mobilizing metal oxides from mineral surfaces. Liang et al. noted that injection of a comparable chelating agent through an iron oxide coated sand column resulted in abrupt release of iron oxide from sand surface and the obtained iron oxide BTC displayed the characteristic configuration of rapid rise followed by gradual recession, as manifested on the VWD-recorded signal curve observed in our study. They explained the phenomenon of abrupt iron oxide release as the effect of repulsive electrostatic interaction between the organic chelate and the sand which substantially weakened the attachment of iron oxide on the sand. The prolonged tail shown in the optical signal curve had also been noted by Liang et al., who explained this as slow mobilization of iron oxide due to chemical reaction, i.e., ligand exchange, between the chelate and the iron oxide. The identified iron-oxide elution by EDTA further supports the analysis of Section 3.1, stating that EDTA enhanced the nanoparticle mobility by removal of favorable deposition sites (iron-oxide coatings). In Section 4 the EDTA influence was quantified.

4. Mathematical modelling and quantification

Transport through columns packed with water-saturated homogeneous sand could be modelled as a one dimensional process (along the column axis). Yang et al. developed a 1D approach for quantifying the site coverage influence of humic acid on enhancing microsphere mobility in porous medium. In this study, the approach was tested for quantifying the mobility-enhancing effect of EDTA by site elution. Fig. 3 summarises the simulation results.

An existing RSA model was calibrated against the first nanoparticle BTC to determine the modelling parameters. Maximum surface coverage, a critical parameter quantifying the strength of blocking, was determined by fitting the model output to the section of gradual rise shown on the nanoparticle BTC. The estimated value (=0.17) was significantly lower than the maximum surface coverage for non-interacting deposited nanoparticles (hard sphere) (=0.546), indicating that on average every charged nanoparticle (soft sphere) blocked a collector surface area about three times that it physically occupied. Single collector efficiency, a parameter reflecting the clean bed deposition rate, was estimated to be 0.021, based on the experimental BTC using the approach of Yao et al. Additionally, the collector efficiency for completely favorable deposition conditions was also calculated (=0.033), using the filtration theory of Tufenkji and Elimelech. The ratio of the experimental single collector efficiency to the theoretical value gives a collision efficiency of 0.64, indicating an unfavorable collector system (details on calculation presented in Table S1†). SEM image of sand surface (Fig. S1†) showing discrete distribution of pointwise oxide clusters on the sand surface at random confirms that not all the collector surface were coated by favorable sites.

Using the determined model parameters, model simulation was executed to predict the second nanoparticle BTC (Fig. 3). Meanwhile, in order to meet the model-generated curve, the second BTC has to move leftward along the x-axis for 27 column pore volumes (PVs), resulting in a time interval of 5.3 PVs between the first and the shifted second nanoparticle BTCs. A
close correspondence between the model-generated curve and the second nanoparticle BTC suggests EDTA generated equivalent influence on nanoparticle transport as the model predicted nanoparticles (injected during the 5.3 PVs). In other words, this means that 5.3 PVs of nanoparticles need to be injected following the first nanoparticle pulse, in order to occupy the same number of sites as those eluted by the injected EDTA. Integration of the model curve for the interval between the first and the relocated second BTCs gave the recovered fraction of total nanoparticles injected into the column. Combining this with the total nanoparticles injected, calculated by multiplying the injection concentration, duration, and flow rate, the deposited nanoparticle masses could be determined, by subtracting the fraction of nanoparticles recovered from the total injected. Calculation results show that $1.52 \times 10^{19}$ nanoparticles (92.3% of the injected nanoparticles) were predicted by the model to deposit during the 5.3 PV time interval. Combining this information with the total EDTA mass ($1.79 \times 10^3$ mg) injected into the column, it suggests that at the experimental time scale, 1 μg EDTA deactivates (by site elution) 8.50 ± 0.50 × $10^8$ nanoparticles sites. In other words, elution of one site needs injection of 2.4 × $10^{11}$ EDTA molecules. Yang et al.19 investigated the site blocking (coverage) effect of Suwannee River Humic Acid (SRHA) and found that under the same experimental conditions, 1 μg SRHA deactivated (by site blocking) 6.79 ± 0.30 × $10^9$ nanoparticles sites. By comparison, EDTA shows significantly lower capacity promoting nanoparticle mobility since an EDTA mass of 8.0 × $10^8$ times of SRHA has to be injected to achieve comparable mobility-enhancing effect. Yang et al.19 also show that a slight change in the chemistry of particle bearing solutions may substantially alter the effect of SRHA on microsphere mobility. Further study investigating the EDTA impact under a range of solution chemical conditions, i.e., ionic strength, may permit more systematic evaluation of the role of EDTA on nanoparticle transport in porous medium.

Prolongation of the simulation till the model-generated nanoparticle BTC reaches unity, which suggests a saturation of column sites by the deposited particles, allows to quantification of the total number of available nanoparticle sites on the column sand surface (Fig. 4). Mass balance calculation based on the simulated BTC suggests that $6.35 \times 10^{11}$ particles need to deposit in order to saturate the sites. Combining this information with the site elution capacity per unit EDTA mass, this indicates that 75 gram EDTA needs to be injected in order to clear all the sites from the column matrix at the experimental time scale.

5. Conclusions and implications

This research has demonstrated the utility of triple pulse experiments, integrated with numerical modelling, for quantifying the influence of a widely used anthropogenic organic ligand on the transport and deposition of polymer nanoparticles in iron-oxide coated porous medium. Experimental results demonstrated that EDTA is capable of eluting iron-oxide coatings from sand surfaces, resulting in enhanced mobility of the nanoparticle. However, quantification results indicate that the mobility enhancing-effect of EDTA (by site elution) was much lower than that of SRHA (by site blocking), as reported by Yang et al.19 Study findings have implications to improving understanding of nanoparticle movement and distribution in iron oxide-coated sand aquifers receiving wastewaters, i.e. those connected directly to river waters containing EDTA and those sites intentionally washed with EDTA.

On the other hand, despite the conditions imposed in the experiments aimed to correspond closely to those encountered in neutral groundwater environment, a more systematic study investigating the effect of a range of solution chemistry on the role of EDTA controlling nanoparticle movement is needed to gain more complete information. Moreover, further research work combining comparable field transport tests and 3D numerical modelling needs to be implemented in order to test the transferability of this technique to more heterogeneous natural systems.

Acknowledgements

We appreciate the useful comments from the anonymous reviewers and the editor who handled this publication. Our research was supported by the Natural Science Foundation of China (grant no. 41101475) and the Key Laboratory of Soil Environment and Pollution Remediation of CAS, Nanjing.

References
