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Magnetic resonance imaging reveals detailed spatial and temporal distribution of iron-based nanoparticles transported through water-saturated porous media

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ABSTRACT

The application of engineered nanoparticles (ENP) such as iron-based ENP in environmental systems or in the human body inevitably raises the question of their mobility. This also includes aspects of product optimization and assessment of their environmental fate. Therefore, the key aim was to investigate the mobility of iron-based ENP in water-saturated porous media. Laboratory-scale transport experiments were conducted using columns packed with quartz sand as model solid phase. Different superparamagnetic iron oxide nanoparticles (SPION) were selected to study the influence of primary particle size (d_P = 20 nm and 80 nm) and surface functionalization (plain, –COOH and –NH_2 groups) on particle mobility. In particular, the influence of natural organic matter (NOM) on the transport and retention behaviour of SPION was investigated. In our approach, a combination of conventional breakthrough curve (BTC) analysis and magnetic resonance imaging (MRI) to non-invasively and non-destructively visualize the SPION inside the column was applied. Particle surface properties (surface functionalization and resulting zeta potential) had a major influence while their primary particle size turned out to be less relevant. In particular, the mobility of SPION was significantly increased in the presence of NOM due to the sorption of NOM onto the particle surface resulting in a more negative zeta potential. MRI provided detailed spatially resolved information complementary to the quantitative BTC results. The approach can be transferred to other porous systems and contributes to a better understanding of particle transport in environmental porous media and porous media in technical applications.

1. Introduction

Engineered nanoparticles (ENP) are increasingly used in technical, industrial and medical applications, in consumer products as well as in environmental remediation (Delay and Frimmel, 2012). This inevitably leads to a release of ENP into environmental systems (Gottschalk et al., 2013; Gottschalk and Nowack, 2011; Mueller and Nowack, 2008), but also stimulates further optimization of ENP regarding their beneficial use. Recently, there is an increasing interest in magnetic ENP such as superparamagnetic iron oxide nanoparticles (SPION) due to their utility in numerous biomedical applications: They are used in vivo as contrast agents in MRI (Babes et al., 1999; Vuong et al., 2012), to target and image cancer cells (Vigor et al., 2010), as a new drug delivery system (Neuberger et al., 2005) or for magnetic cell separation (Gao et al., 2009; Gupta and Gupta, 2005). Iron nanoparticles, mainly nano-zerovalent iron (nZVI),

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have also shown their potential for environmental remediation such as treatment of groundwater and hazardous waste (Braunschweig et al., 2013; Rakshit et al., 2013; Yan et al., 2013; Zhang, 2003).

Regarding SPION, their widespread application in biomedicine might result in their release into the environment (Lecoanet et al., 2004; Thomas and Sayre, 2005), where their fate will notably depend on their stability and on their transport behaviour in soil and aquatic systems. The successful application of iron-based ENP for groundwater remediation also significantly depends on their mobility after the injection. However, the knowledge regarding mobility and transport behaviour of iron-based ENP in soils and aquatic systems is still incomplete (Cornelis et al., 2013), especially with respect to their interaction with natural water contents such as natural organic matter (NOM). The examination of their mobility in aquatic systems such as water-saturated porous media is therefore of high relevance and will open the door to assess their environmental fate and to further improve their beneficial application.

As far as the transport behaviour of (nano)particles is concerned, their retention in porous media is strongly determined by their collisions with the solid phase (collector, e.g. sand grain). It can typically be described by three mechanisms: interception, gravitational sedimentation and Brownian diffusion (Christian et al., 2008; Tufenkji and Elimelech, 2003). The latter is the dominant factor for the retention of ENP, as their high diffusivity leads to more contacts with the collector surface (Jeong and Kim, 2009). In addition, recent studies indicate that, depending on the flow velocity of the liquid phase, the influence of gravitational settling might also be an important retention mechanism (Chrysikopoulos and Syngouna, 2014; Ma et al., 2011). A common and widely spread approach to investigate in detail the transport behaviour of particles such as nanoparticles or colloids in porous media comprises column breakthrough experiments and the subsequent detection of the particle breakthrough curves (BTCs) at the column outlet or at points along the column length (Hosseini and Tosco, 2013; Lecoanet et al., 2004; Tian et al., 2010; Wang et al., 2008). The basic principle of these investigations is the coupling of a column (containing a porous medium) with analytical instruments for particle detection (e.g. inductively coupled plasma mass spectrometry, ICP-MS; light scattering detectors; UV/VIS detector) (Delay et al., 2010; Metreveli et al., 2010). There are numerous publications regarding the transport behaviour of nanoparticles and colloids in porous media (Frimmel et al., 2007; Pelley and Tufenkji, 2008). This research was basically stimulated realizing the role of particles for the co-transport of contaminants (particle-facilitated transport) (McCarthy and Zachara, 1989). Recently, these approaches were transferred to investigate the mobility of ENP such as magnetic ENP to assess their possible environmental impact and their performance for remediation (Esfahani et al., 2014).

In this context, BTC analysis provides sound information on the overall mobility of particles, but only little information on their spatial and temporal distribution in porous media. To meet this problem, MRI has shown its potential to characterize porous media and hydraulic conditions, and to elucidate transport mechanisms of (micro)particles (Baumann and Werth, 2005; Ramanan et al., 2011; Werth et al., 2010). MRI as a non-invasive and non-destructive analytical technique allows a spatially resolved in-situ and time-resolved characterization with respect to structure and morphology as well as fluid dynamics (Callaghan, 1993, 2011). In particular, MRI has been used in hydrology research to determine water flow in heterogeneous porous media (Yoon et al., 2008), to measure velocities of colloids (Creber et al., 2009), or to characterize porous media properties such as pore size, grain size and porosity (Song, 2000). To our knowledge, there are only few investigations regarding the applicability of MRI to follow the mobility of ENP in porous media (Fridjonsson et al., 2011; Lakshmanan et al., 2015; Ramanan et al., 2011). So far, the application of MRI has been limited to coarse-grained media ($d > 600$ μm) (Baumann and Werth, 2005; Ramanan et al., 2011) or to the imaging of particles in the μm-scale (1.28 μm) (Baumann and Werth, 2005). One could argue to use micro-computed tomography (μCT) which reveals a superior spatial resolution. However, MRI provides the flexibility to optimize the image contrast between the involved phases, being solid sand, nanoparticles, gas and liquid in the form of water.

The main objectives of our investigations are to:

(i) visualize and to follow in situ the spatial and temporal distribution of SPION in water-saturated porous media applying MRI,
(ii) compare the results of the complementary methods BTC and MRI, especially considering the influence of nanoparticle properties (surface functionalization and particle size) and NOM on their transport behaviour,
(iii) derive key parameters affecting the transport of nanoparticles in water-saturated porous media, and
(iv) demonstrate the general suitability and limitations of our experimental approach to investigate the environmental fate of nanoparticles and to generate data to validate mathematical simulations.

2. Materials and methods

2.1. Preparation of SPION suspensions

Dextran-iron oxide composite SPION (iron oxide core, dextran shell) with different surface functionalization provided as suspensions (micromod Partikeltechnologie GmbH, Rostock, Germany), were used and labelled as indicated in Table 1.

The stock suspensions were diluted to the desired concentration in ultrapure water (Milli-Q, Merck Millipore, Billerica, Massachusetts, USA) or in a solution of humic acid (HA; 2 mg/L dissolved organic carbon (DOC)). HA originated from the Lake Hohloh, a natural bog lake in the Black Forest (Germany) and was used as representative NOM (HO14 series from the International Humic Substances Society) (Frimmel et al., 2008). The suspensions were freshly prepared on each measurement day, except for the particle suspensions in HA, where an equilibration time of 24 h was allowed. The samples were prepared by adding the stock suspensions to a graduated glass flask containing the liquid phase and by carefully shaking the flask overhead. To prepare the suspensions in HA, a suspension in Milli-Q was mixed 1:1 (volumetric ration) with HA solution ($\rho(\mathrm{DOC}) = 4$ mg/L).

For the BTC analysis (see Section 2.3.3), SPION stock suspensions were diluted in Milli-Q or a solution of HA to obtain