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Nanoparticle transport in saturated porous medium using magnetic resonance imaging

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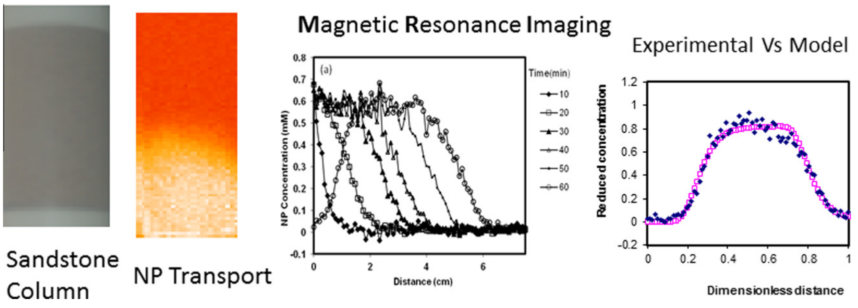
HIGHLIGHTS

- Carboxyl-functionalized nanoparticle through sandstone rock core was studied.
- MR imaging technique was used to image the NP transport.
- Transport parameters were estimated using CXTFIT computer package.
- Nanoparticle–surface interactions were investigated using DLVO.

GRAPHICAL ABSTRACT



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ABSTRACT

Transport study of nanoparticle (NP) through matrix flow dominated aquifer sand and soils have significant influence in natural systems. To quantify the transport behaviour, magnetic resonance imaging (MRI) was used to image the iron oxide based nanoparticle, *Molday ION* (carboxyl terminated) through saturated sandstone rock core. T_2-weighted images were acquired and the changes in image intensity were calibrated to get a quantitative concentration profiles at various time intervals. These profiles were evaluated through CXTFIT transport model to estimate the transport parameters. These parameters are estimated at various points along the length of the column while classical breakthrough curve analysis cannot provide these details. NP–surface interactions were investigated using DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. The dispersion coefficients ($2.55–1.21 \times 10^{-7}$ m^2/s) were found to be decrease with distance, deposition rate constant k ($6.70–9.13 \times 10^{-4}$ (1/s)) and fast deposition rate constant k^{fast} ($4.32–8.79 \times 10^{-2}$ (1/s)) were found to be increase with distance. These parameter variations over length will have a scaling up impact in developing transport models for environmental remediation and risk assessment schemes.

1. Introduction

Nanotechnology and nanoparticles (NPs) which are defined as less than 100 nm in length in at least one dimension, is a relatively recent research field that is expanding and diversifying rapidly. NPs have already been utilized in a in a diverse range of applications including textiles, agro-chemicals, electronics, cosmetics, new materials and environmental remediation [1] and the list is expanding. NPs released into environment that moves to ground water and surface water through soil layers can be hazardous to humans and the environment [2]. There is very limited knowledge about the movement and fate of the fast growing engineered nanoparticles, especially when they are released into the ecosystems of environment.

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In contrast to the unintentional release of manufactured NPs, nanoparticles are also being designed for in situ remediation of groundwater pollutants, such as polyaromatic hydrocarbons, polychlorinated biphenyls, pesticides, heavy metals [3]. In these cases bespoke nanoparticles, such as zerovalent iron, are injected direct into the groundwater. However, this technology is still in its infancy and their transport behaviour and thus their ability to be delivered to the site of pollution, is still poorly understood [3]. These studies underline the risks associated with nanoparticles to environment and living organisms including humans. Hence accurate data on transport behaviours of NPs in such systems are important in order to design effective remediation strategies.

A number of studies have been carried out to investigate the transport of NPs through water-saturated porous media. Often packed column studies are used to represent the aquifer system. In these conventional methods, the concentration of NPs is calculated from the breakthrough-curve measurement at the column outflow and the data generated is one-dimensional. Even though these experiments provide valuable data on NP transport using colloid filtration theory (CFT), they often fail to predict the transport measurements [4]. In addition, these column tests do not allow the direct observation of local processes [5]. Some of them used this approach to evaluate the deposition by destructively opening packed columns after fixed time intervals [6–8] and often it could disrupt the local flow field or alter the column chemistry [9]. Natural systems (e.g. aquifers and soils) are highly complex and it is important to determine the spatial variability inside packed columns. Changes in particle deposition can occur along the length of the column [10] and these methods could not provide these details. In order to overcome this, non-invasive techniques are required to view the transport processes.

A range of non-invasive methods have been developed such as fluorescent imaging, gamma radiation and X-ray microtomograph. However, there are certain limitations to each of the above mentioned methods. Fluorescent imaging protocols have difficulty in imaging the tracking of fluorescent particles through a translucent packed sand bed [11]. This is due to the dependence of the number of photon penetration and hence the opaqueness of the gravels cannot be investigated. This issue can be overcome by using a scanning optical fibre fluorescence profiler to measure the 2D transport profile. The presence of buried sensors and fibres inside the columns could disturb the transport pathways [12]. Gamma radiation and X-ray micro tomography are widely used for porous media characterization [13], fluid distribution [14] and solute–fluid transport [15] experiments. A major shortcoming of this method is at a single location it requires relatively large counting times and total counting times could be varied between several hours up to one day to produce an image.

Another promising non-invasive technique is magnetic resonance imaging (MRI). Although MRI is mainly used in medical sciences, this technique has already been used in contaminant hydrology research to evaluate colloid transport mechanisms [16], sediment deposition [17], tracer transport through the sediment bed [18] and for investigating transport processes of heavy metals ions such as Gd^{3+}, Cr^{3+} and Cu^{2+} in a sandy aquifer matrix [19]. This method also has a strong potential to quantitatively image the transport of paramagnetic tagged molecules and particles. The transport of paramagnetic colloids through a matrix of silica gel was studied using this method and the spatially resolved data were analysed using the CXTFIT software and colloid filtration theory to predict the behaviour of colloids [20]. Recently the concentration of nanoparticles in a coarse grain system is quantified using this imaging technique [21] and the transport profiles were fitted simultaneously to produce a single set of transport parameters.

Here, we report the transport of NPs in a finer grained system and the transport parameters were estimated individually at various time intervals along the column. In this contribution, we aimed to study the transport of commercially available iron oxide based MRI compatible NP, negatively charged *Molday ION* (*carboxyl terminated*) was used. This is commercially available superparamagnetic iron oxide based NP and 35 nm in diameter and composed of an iron-oxide core surrounded by an organic polymer coating (0.1 mM Fe is equivalent to $\sim 5 \times 10^{15}$ particles/l). Bentheimer sandstone rock core is used to mimic the column test with sandy aquifer. Concentration profiles were analysed with CXTFIT software to estimate transport parameters. Particle–surface interactions were investigated using DLVO theory.

2. Materials and methods

2.1. Porous column and transport experiments

The experiments were performed on Bentheimer sandstone rock core (containing finer quartz grains). The rock core diameter is 37 mm and 75 mm long. Quartz grains are negatively charged at experimental pH conditions [30]. This core was encased in a silicone rubber tube to provide a confining system. This rubber tube has an internal diameter of 35 mm and the wall thickness is 3 mm (Fig. 1). Inlet end caps were used around the ends to make a water tight seal. The column was saturated with water prior to the experiment. The porosity of 0.23 was determined from the weight of the column before and after saturation with water.

The saturated sandstone column was placed horizontally inside a 72 mm diameter bird-cage RF coil at the centre of the MRI bore. All the tubing connected to and from the column was made of PVC. The flow was established by a flow rate of 0.2 ml/min using a HPLC pump (Agilent 1100 Series) using deionised water. An inlet solution of 0.7 mM of *Carboxyl* NP was first pumped into the sandstone column for approximately 50 min. In order to record the NP transport, MR imaging was performed every 5 min. Deionised water was then pumped through for approximately 60 min and the movement of NP transport was imaged.

The presence of NP causes a concentration dependent in T_2. This NP concentration is determined by the following expression [22]:

$$[C] = \frac{1}{R}\left[\frac{1}{T_{2,i}} - \frac{1}{T_{2,0}}\right] \tag{1}$$

where $T_{2,0}$ is the relaxation time in the absence of NP, $T_{2,i}$ is the relaxation time in the presence of NP, $[C]$ is the concentration of the NP, and R is the relaxivity constant of the NP.

2.2. MR imaging

The MR imaging experiments were performed on a *Bruker Avance BioSpec* system, using a 30 cm horizontal bore, 7T superconducting magnet (*Bruker BioSpin*, *Karlsruhe*, *Germany*). A *Bruker*

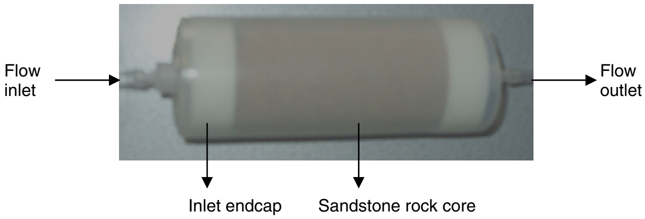

Fig. 1. Photograph of the experimented porous column.