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Nanoparticle transport in saturated porous medium using magnetic resonance imaging

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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 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 groundwater 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 contaminated 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 metal 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 ~5 × 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]:

$$|C| = \frac{1}{R} \left( \frac{1}{T_{2,i}} - \frac{1}{T_{2,0}} \right)$$

(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

![Flow diagram](image)

**Fig. 1.** Photograph of the experimented porous column.
micro-imaging gradient insert (model BG-6) and 200-A gradient amplifiers were used to provide strong linear magnetic field gradient pulses of up to 1000 mT/m, thus allowing the system to perform micro-imaging experiments. Further technical details of MR imaging can be found in Phoenix et al. [22].

NP transport imaging was performed using a Rapid Acquisition Relaxation Enhanced (RARE) Sequence. The experiments were performed with the following imaging parameters: echo time (\(T_E\)) 22 ms, repetition time (\(T_R\)) 5000 ms with a RARE factor of 8, field of view was 8.1 cm \(\times\) 4.5 cm, imaging matrix was 108 \(\times\) 60 pixels, giving an in-plane resolution of 750 \(\mu\)m with a slice thickness of 3 mm. The imaging time was approximately 3 min. To obtain comparable \(T_2\)-weighted images these imaging parameters were kept identical during the entire experiment.

During the NP transport experiment, MR imaging was used to acquire spatially and temporally resolved \(T_2\)-weighted images of the column. \(T_2\) is the spin–spin relaxation time of \(^1\)H nuclei of the water phase. \(T_2\)-weighted images acquired before and after introducing NP can be used to quantify the NP concentration.

2.3. Quantitative measurement of NP concentration

The signal decay at a particular concentration \(C\) is obtained using a Rapid acquisition Relaxation Enhancement pulse sequence (RARE) and it is represented by [23]:

\[
\frac{S}{S_0} = \exp\left(-\frac{t_e}{T_2}\right)
\]

where \(S\) is the MRI signal, \(S_0\) is the signal at zero echo time and \(T_2\) is the spin–spin relaxation time. The effective echo time \(t_e\) was chosen to maximize the signal contrast as described in von der Schulenburg et al. [24] and was determined to be 22 ms.

Combining Eqs. (1) and (2) gives the following equation:

\[
C = \left[\ln\left(\frac{S}{S_0}\right) - \frac{1}{T_2}\right] \frac{1}{R}
\]  \hspace{1cm} (3)

A RARE image of the sample containing only water was appropriately scaled, to get a maximum signal intensity map of \(S_0\). Hence, NP concentrations can be calculated from Eq. (3), using \(T_2\)-weighted images acquired before and after introduction of NP.

2.4. Transport parameters estimation

Transport parameters are estimated by using the CXTFIT model and the analytic solutions of the linear convection–dispersion equation (CDE) with a first-order loss term in the model is [25]:

![Fig. 3. Calibrated concentration images of Carboxyl NP transport inside the sandstone core at 10 min time interval. (a)–(e) NP transport and (f)–(g) movement of NP transport (red in colour region represents the rock core and brighter region represents NP transport). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
and it is possible to gain further insights into the mechanism using colloidal filtration theory. The edge of the characteristics of the gravel it is possible to gain further insights into the mechanism using colloidal filtration theory.

Concentration profiles of NP interaction to the grain surface, especially estimating particle attraction number from 95% to 99%. The fitted transport parameters with 95% confidence interval are shown in Table 1. The averaged disper-

\[
\eta = 2.4A^1.3 N_R^0.081 N_{pe}^{-0.715} N_{vder}^0.052 + 0.55A^1.675 N_R^0.125
\]

where \(A\) a constant specific to the porous medium and it is defined as:

\[
A_s = \frac{2(1 - \gamma^5)}{(2 - 3\gamma^5 + 3\gamma^5 - 2\gamma^6)}
\]

where \(\gamma = 1 - d_s/d_p\), where \(d_s\) and \(d_p\) denote the diameter of the particles and grains, the Peclet number \(N_P\), the van der Walls number \(N_{vder}\), \(N_C\) is the gravity number and the attraction number \(N_s\) is the ratio of \((N_{vder}/N_{pe} - N_s)\).

3. Results and discussion

3.1. Determination of the relaxivity constant

In order to measure the relaxivity constant, five different NP concentrations were prepared and each one was injected through a saturated sandstone core, similar to the one used for the transport experiment. \(T_2\) measurement for each sample was recorded with MR Imaging and using the calibration expression (Eq. (1)), relaxation rate \((1/T_2)\) has a linear relationship with the concentration and this is shown in Fig. 2.

From the slope of Fig. 2, the relaxivity constant \(R\) for the Carboxyl NP was determined by the least square fit method to be 123 mM⁻¹ s⁻¹.

3.2. MRI measurements of NP transport through sandstone core

A series of \(T_2\)-weighted images were recorded for the transport of Carboxyl NP into the sandstone with a time interval of 5 min. These images were calibrated to produce quantitative concentration maps by using Eq. (4). NP transport at 10 min time interval are shown in Fig. 3(a)–(e). After 50 min of NP transport, deionised water was then pumped through for approximately 60 min to capture the NP transport movement. These images are shown are shown in Fig. 3(f)–(j) at 10 min time interval. During the experiment, the transport of NP shortens the \(T_2\) values and this is shown by the increase in measured MRI signal.

All the data was obtained from a 2-D slice through the centre of the column using rapid acquisition sequence. This is desirable for the interpretation of the data analysis and estimating the transport properties. The averaged Carboxyl NP concentrations along the column width at 10 min time interval are shown in Fig. 4 and it reaches the sandstone column outlet at 130 min.

3.3. NP transport modelling

The experimental results from the sandstone column are modelled with CXTFIT software. The transport parameters can be estimated at any point along the length of column. The experimental data set from 60 to 80 min gives full transport profiles and concentration profiles at 60, 65, 70 and 75 min are chosen for the analysis. Concentration profiles at 60, 65, 70 and 75 min are chosen for the analysis. The concentration profiles and the corresponding CXTFIT model data are shown in Fig. 5.

From the graphs we can see that model profiles are largely coinciding with the experimental data, giving goodness-of-fit values (\(R^2\)) from 95% to 99%. The fitted transport parameters \(D, v_p\) and \(k\) are obtained through the CXTFIT model. Fast deposition rate constant \(k^{fast}\), the non-permanent attachment rate is calculated from Eq. (6) and the Sticking efficiency factor \(\eta\) is calculated through Eq. (5). The fitted and derived transport parameters with 95% confidence interval are summarized in Table 1. The averaged disper-
sion coefficient $D_{ave}$ is $1.92 \times 10^{-7}$ m$^2$/s. Khrapitchev and Callaghan [31] reported the relationship between the dispersion coefficient and the porous media characteristics for various literature studies. Their relationship gives a $D_{ave}$ value of $1.52 \times 10^{-7}$ m$^2$/s which is same order of magnitude. This supporting the robustness of the MRI approach, in quantifying NP transport. During the progress of NP plume, almost constant dispersion coefficient achieved for the first three profiles which is in between 2.55 and $2.12 \times 10^{-7}$ m$^2$/s and then starting to have a drop by factor of 0.60 for the subsequent data sets.

The other derived parameters also showed some variation; $\nu_p$ increased by a factor of $\sim 0.5$ over the time and distance. This could be due to the heterogeneity in NP characteristics, finer grain systems and column length.

Fast deposition rate constant $k^{fast}$ is in the range of $4.32 - 8.79 \times 10^{-2}$ (1/s). The rate constant $k$ is known as permanent attachment rate and it is in the range of $6.70 - 9.13 \times 10^{-4}$ (1/s). The calculated sticking efficiency factor $\alpha$ was found to be less variation till 70 min and then it varies from 0.013 to 0.09. Earlier literature suggests [32] that some deposition could occur in secondary energy minima between the same surface charge NP and the porous medium. As we have seen in the analysis, certain amount of deposition is observed as a measure of deposition rate constants ($k$ and $k^{fast}$). NP–grain surface interactions and the interaction energy profiles including secondary energy minima usually described by DLVO theory and derivatives. The following section explores this deposition behaviour using this classical DLVO theory.

### 3.4. DLVO interaction energy profiles

Particle deposition behaviour is classified as favourable and unfavourable interactions [32]. When the particle and collector have similar surface charge, the interactions are classified as unfavourable and the deposition can occur in secondary energy minima.

### Table 1
Transport parameters for Rock core experiment using CXTFIT.

<table>
<thead>
<tr>
<th>Time intervals</th>
<th>$D$ (m$^2$/s)</th>
<th>$\nu_p$ (m/s)</th>
<th>$k$ (1/s)</th>
<th>$k^{fast}$ (1/s)</th>
<th>$\alpha$</th>
</tr>
</thead>
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<tr>
<td>60</td>
<td>2.55E-07</td>
<td>2.23E-04</td>
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<td>0.013</td>
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<tr>
<td>65</td>
<td>2.19E-07</td>
<td>2.90E-04</td>
<td>7.32E-04</td>
<td>5.63E-02</td>
<td>0.011</td>
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<tr>
<td>70</td>
<td>2.12E-07</td>
<td>3.82E-04</td>
<td>9.36E-04</td>
<td>7.40E-02</td>
<td>0.0108</td>
</tr>
<tr>
<td>75</td>
<td>1.53E-07</td>
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<td>9.30E-04</td>
<td>8.38E-02</td>
<td>0.095</td>
</tr>
<tr>
<td>80</td>
<td>1.21E-07</td>
<td>4.53E-04</td>
<td>9.13E-04</td>
<td>8.79E-02</td>
<td>0.089</td>
</tr>
</tbody>
</table>

![Fig. 5. Carboxyl NP concentration profiles at (a) 60 min (b) 65 min (c) 70 min, (d) 75 min (e) 80 min. Closed symbol represents experimental data, and open symbols represent model data.](image-url)


