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Concurrent aggregation and transport of graphene oxide in saturated porous media: Roles of temperature, cation type, and electrolyte concentration☆

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Simultaneous aggregation and retention of nanoparticles can occur during their transport in porous media. In this work, the concurrent aggregation and transport of GO in saturated porous media were investigated under the conditions of different combinations of temperature, cation type (valence), and electrolyte concentration. Increasing temperature (6–24 °C) at a relatively high electrolyte concentration (i.e., 50 mM for Na^+, 1 mM for Ca^{2+}, 1.75 mM for Mg^{2+}, and 0.03 and 0.05 mM for Al^{3+}) resulted in enhanced GO retention in the porous media. For instance, when the temperature increased from 6 to 24 °C, GO recovery rate decreased from 31.08% to 6.53% for 0.03 mM Al^{3+} and from 27.11% to 0 for 0.05 mM Al^{3+}. At the same temperature, increasing cation valence and electrolyte concentration also promoted GO retention. Although GO aggregation occurred in the electrolytes during the transport, the deposition mechanisms of GO retention in the media depended on cation type (valence). For 50 mM Na^+, surface deposition via secondary minima was the dominant GO retention mechanism. For multivalent cation electrolytes, GO aggregation was rapid and thus other mechanisms such as physical straining and sedimentation also played important roles in controlling GO retention in the media. After passing through the columns, the GO particles in the effluents showed better stability with lower initial aggregation rates. This was probably because less stable GO particles with lower surface charge densities in the porewater were filtered by the porous media, resulting in more stable GO particle with higher surface charge densities in the effluents. An advection–dispersion-reaction model was applied to simulate GO breakthrough curves and the simulations matched all the experimental data well.

1. Introduction

Graphene has sparked much research interest since this first single atomic layer of carbon was produced in isolated form in the year 2004 (Pei and Cheng, 2012). Despite its short history, this two-dimensional (2D) crystalline material, as well as its derivatives, has been widely applied in various industrial fields due to their remarkable mechanical, electrical, thermal, and optical properties. Mass production and consumption of graphene-based materials inevitably results in their release into soils and natural water bodies, which has aroused wide concerns over their adverse environmental impacts. Several investigations have already shown that graphene-based materials have toxic effects on ecosystems and public health (Akhavan et al., 2012, 2013; Chen et al., 2012b).

Graphene oxide (GO) consists of individual sheets of graphene decorated with oxygen-containing groups (e.g., hydroxyl, carboxyl, and epoxy groups) on both the basal planes and edges. It is an important intermediary in producing graphene sheets by various chemical reduction approaches (Pei and Cheng, 2012). The oxygen functionalities of GO not only enhance it dispersibility in water but also provide a variety of sorption sites for various contaminants (Ding et al., 2014; Ramesha et al., 2011). After released into soils, GO thus can impose a serious threat on groundwater safety considering that well-dispersed nanoparticles including GO have shown

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relatively good mobility in the subsurface systems (Fang et al., 2009). Therefore, knowledge of fate and transport of GO in porous media is crucial for understanding and reducing its potential environmental impacts.

The fate and transport of nanoparticles in soils are governed by various environmental factors, including physical and chemical properties of both porous media (e.g., moisture content, grain size, and grain surface properties) and flow (e.g., pH, ionic strength, natural organic matter concentration, and flow rate) (Wang et al., 2016). Those factors can influence not only nanoparticle aggregations in porewater but also their interactions with the media to control their retention and transport in porous media (Solovitch et al., 2010). In the subsurface, nanoparticles and their primary aggregates initially can be stable and very small in size, but the aggregates may grow dramatically and subsequently dominate fate and transport processes under certain conditions. For instance, the physicochemical conditions of subsurface environment may change during a rain, irrigation, fertilization, or artificial ground water recharge, causing the perturbations of metal cations such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminum (Al^{3+}) in porewater to affect the aggregation, retention, and transport of nanoparticles in soils (Larssen and Carmichael, 2000; Solovitch et al., 2010).

Aggregation is an important and ubiquitous process occurring among nanoparticles in aqueous solutions. Some researchers have observed spatial and temporal variations in particle size during the transport of nanoparticles in porous media (Sun et al., 2015). Investigations on the effects of aggregation on nanoparticle retention in saturated porous media have been conducted recently (Areepitak and Ren, 2011; Chatterjee and Gupta, 2009; Solovitch et al., 2010; Sun et al., 2015; Taghavy et al., 2015). Solovitch et al. (2010) reported that the aggregation of TiO_2 nanoparticles during their transport favored their deposition in porous media. Areepitak and Ren (2011) observed a similar phenomenon that aggregation promoted colloid deposition in porous media if the primary particle size or the aggregate size was over 480 nm. However, they also found that the aggregates were mobile when their size was smaller than 480 nm (Areepitak and Ren, 2011). Furthermore, dramatic increase of particle size may form large aggregates to even cause sedimentation (Areepitak and Ren, 2011). Concurrent aggregation and deposition of nanoparticles thus can complicate their transport process in porous media. To the best of the authors' knowledge, however, little attention has been paid to study the concurrent aggregation and deposition of GO in saturated porous media. The effect of aggregation on GO transport in porous media has been overlooked by previous studies because GO nanoparticles are generally regarded as stable in dispersion because of their hydrophilic surface functional groups. However, some studies have reported that GO particles can easily be destabilized by adding electrolytes, especially electrolytes with multivalent metal cations (Chowdhury et al., 2013; Wang and Hu, 2013; Wu et al., 2013). Because cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+} are ubiquitous in soil and groundwater systems, concurrent aggregation and deposition of GO in saturated porous media are highly probable and thus require further investigations.

Temperature also plays a crucial role in nanoparticle aggregation and transport in aqueous systems. Some studies have shown that high temperatures may favor the aggregations of several types of nanoparticles (Chen et al., 2012c; Majedi et al., 2014). Increasing temperature can lead to increased random Brownian motion and collision, thus promoting nanoparticles aggregation. Only few studies have investigated the effect of temperature on the retention and transport of nanoparticles in saturated porous media (Sasidharan et al., 2017; Wang et al., 2017b). While most of the published work on nanoparticle transport in porous media were at room temperature (22–25 °C) despite the fact that the temperature of shallow subsurface environment can change over a wide range daily or seasonally (El All et al., 2015). Although it is still unclear, it is anticipated that temperature variation can alter both particle-particle interactions and particle-sand grain interactions, and thus affect the fate and transport of GO in saturated porous media.

The overarching objective of this work was to determine the role of nanoparticle aggregation in GO retention and transport in saturated porous media under various environmental conditions. These included different combinations of ambient temperature, electrolyte concentration, and cation types (i.e., Na^+, Ca^{2+}, Mg^{2+} and Al^{3+}). The specific objectives were as follows: (1) determine the effects of temperature, electrolyte concentration, and cation types on concurrent aggregation and transport of GO in saturated porous media; (2) compare the size variation of GO in influent and effluent; (3) understand the governing GO retention mechanisms when aggregation and deposition occurred concurrently; and (4) model the concurrent aggregation and transport of GO in saturated porous media.

2. Materials and methods

2.1. GO

GO nanosheets (ACS Material, Medford, MA) with 1–5 μm lateral diameter and 0.8–1.2 nm thickness were used as received from the manufacturer in all experiments. The average cross-sectional area of the GO sheet was 338,724 nm^2, measured by AFM in a previous study (Wu et al., 2013). To prepare the GO stock solution, 100 mg GO nanosheets were suspended in 1000 mL deionized (DI) water and subsequently ultrasonic-treated by Misonix S3000 ultrasonicator (QSonica, Newtown, CT) for 2 h. Analytical-grade NaCl, $CaCl_2$, $MgCl_2$, and $AlCl_3$ stock solutions were prepared as experimental electrolytes. Both the GO and electrolyte stock solutions were stored at 6 °C.

The GO stock suspension was diluted to a desired concentration of GO working suspension (20 mg L^{-1}) with NaCl stock solution and DI water to achieve a fixed ionic strength of 5 mM. The resultant GO working suspension was placed in glass reservoir (labeled as A in Fig. 1) for each experiment. In another glass reservoir (labeled as B in Fig. 1), different electrolyte stock solution was diluted to the desired concentration. The pH of all the working solutions was adjusted to 5.4 ± 0.2 with HCl and NaOH solutions.

The hydrodynamic radii of GO nanoparticles were determined using a ZetaSizer Nano ZS (Malvern Instruments, Worcester-shire, U.K.) with a 633-nm laser and a 173° detection optics. The zeta potential of GO particles under various physicochemical conditions was measured by a ZetaPlus (Brookhaven Instrument Co.,

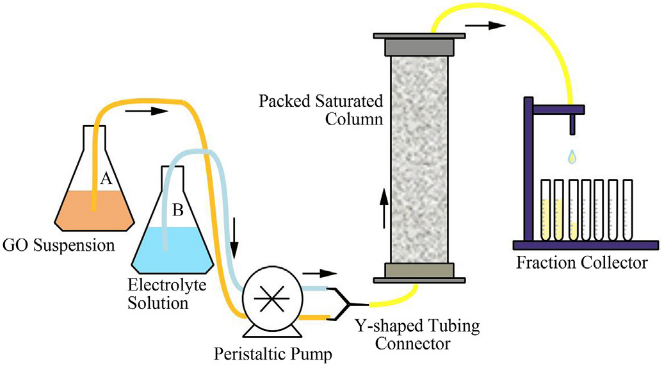

Fig. 1. Schematic of the experimental apparatus and set-up.