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Effects of surfactants on graphene oxide nanoparticles transport in saturated porous media

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ABSTRACT

Transport behaviors of graphene oxide nanoparticles (GONPs) in saturated porous media were examined as a function of the presence and concentration of anionic surfactant (SDBS) and non-ionic surfactant (Triton X-100) under different ionic strength (IS). The results showed that the GONPs were retained obviously in the sand columns at both IS of 50 and 200 mmol/L, and they were more mobile at lower IS. The presence and concentration of surfactants could enhance the GONP transport, particularly as observed at higher IS. It was interesting to see that the GONP transport was surfactant type dependent, and SDBS was more effective to facilitate GONP transport than Triton X-100 in our experimental conditions. The advection–dispersion–retention numerical modeling followed this trend and depicted the difference quantitatively. Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction calculations also were performed to interpret these effects, indicating that secondary minimum deposition was critical in this study.

Introduction

Graphene oxide (GO) is an oxidized form of graphene-based nanomaterials, featuring fascinating nanostructure with hydroxyl and epoxy bridge functional groups on the basal plane and carbonyl and carboxyl groups on the edges (Dreyer et al., 2010). These abundant hydrophilic O-functional groups on the surfaces were useful in synthesizing GO hybrids and composites, and then maximize the benefit of the unique properties in different applications (e. g. electronic, medical and environmental sectors) (Srivastava et al., 2014; Zhang et al., 2014). However, recent studies found that GO would be the most toxic graphene-based nanomaterial due to its considerable water solubility and noticeable cell damage. Exposures to GO might induce severe cyto-toxicity and lung diseases (Wang et al., 2011; Ahmed and Rodrigues, 2013). Increased applications and production of GO will likely lead to its release in the environment (such a as landfill leachate and wastewater infiltration) (Novikov et al., 2006; Hennebert et al., 2013), therefore, research attention should be dedicated to investigate the fate and transport of such an emerging materials for the public health concerns.

The threat extent of graphene oxide nanoparticles (GONPs) to the environment and public health is correlated to their ability to remain dispersed in the environment or to form particle aggregations, and consequently their mobility (Petosa et al., 2010; Ju-Nam and Lead, 2008). Nanoparticles with high mobility probably penetrate the soil layers and enter ground

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water system, which posed potential risks for drinking water (Hennebert et al., 2013; Saito et al., 2013). Researchers suggested that the mobility and retention of GONPs in saturated porous media packed in columns were controlled by complexity of the porous media matrix (*e.g.*, grain surface, moisture content) (Liu et al., 2013a,b), the physicochemical parameters of solution chemistry (*e.g.*, ionic strength, pH and the presence of natural organic matter) (Feriancikova and Xu, 2012; Lanphere et al., 2013), and the fluid dynamics characteristic of the column system (Liu et al., 2013a; Qi et al., 2014). Although progress has been made towards a better understanding of the environmental fate and transport of GONPs, the current knowledge of the fate and transport of GONPs in porous media is far from complete. This is particularly true for the influence of other coexisting compounds in solution. To our knowledge, no research has been conducted to examine the effect of surfactants on the transport behavior of GONPs in saturated systems. Surfactants are widely present in water environments with the concentration even up to several thousand mg/L in municipal wastewaters (Adak et al., 2005), and it can likely coexist with the released GONPs during accidental infiltration or artificial groundwater recharge. Due to their surface-active properties, surfactants may adsorb to GONPs and affect their solubility and transport in porous media by modifying the particle surface chemistry and changing their interactions (Tkachenko et al., 2006; Lin et al., 2010).

The objective of this work was thus to examine the influence of surfactant on GONP transport through saturated porous media, and therefore obtain insight into the mechanism of mediated transport by coexisting compounds. The approach focused on a systematic identification of the mechanisms for enhanced transport of GONPs through sand columns with surfactants. The GONP transport experiment results were interpreted through surface property measurement of sand and GONPs, breakthrough curve (BTC) monitoring, numerical modeling and Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.

1. Materials and methods

1.1. Porous media

Quartz sand was used as the porous medium with a size range of 0.36–0.50 mm and average diameter (d_{50}) of 0.42 mm. The sand was treated sequentially by 10% nitric acid (*V*/*V*) to remove metal oxides, and then 10% peroxide to eliminate organic materials. Subsequently, the sand was repeatedly rinsed with deionized (DI) water until a neutral pH (7.1 ± 0.1 finally) was achieved and water conductivity reduced to zero. The sand was dried in an oven at 110°C for 48 hr.

1.2. Graphene oxide

GO was purchased from Institute of Coal Chemistry, Chinese Academy of Sciences, which was synthesized by a pressurized oxidation method described by Bao et al. (2012). According to the manufacture, the GONPs had an average height of 0.7 ± 1.2 nm, and an average perimeter of 781.1 ± 502.2 nm. The GONP stock solution used in this study was prepared at 20 mg/L, and all solutions were previously sonicated (40 min) each time. To prepare the GONP dilution at specific ionic strength (IS), sodium chloride (NaCl, p.a. quality) was used as the background electrolyte (dissolved in DI water). All column experiments below were performed at two IS: 50 and 200 mmol/L.

1.3. Transport experiments

Transport experiments were conducted by pumping a suspension of GONPs through an acrylic column packed with clean quartz sand (Fig. 1). The acrylic column was 3 cm in diameter and 15 cm in height. Standard gravimetric methods were used to determine the sand density (1.61 g/cm^3) and a column packing porosity of 0.36 ± 0.01. The column was vertically oriented and operated in an upflow mode using a peristaltic pump at a constant Darcy's velocity of 7.5×10^{-3} cm/sec. Prior to each experiment, 20 pore volumes (PVs) of the background electrolyte solution of interest were first passed through the column to ensure that the column was fully equilibrated with this solution. Then suspension of GONPs within the same background electrolyte composition was injected into the packed column for 4 PVs (phase 1), followed by elution with GO-free solution again (phase 2). The outflow from the columns was connected by an auto fraction sampler (Huxi, CBS-A 100, Shanghai, China), and the effluent GONP concentration was monitored using UV–Vis spectrophotometer (Shimadzu, UV-2450, Kyoto, Japan) at a wavelength of 230 nm. Prior to the GONP transport experiments, the tracer (Br^-) breakthrough tests were performed to estimate the hydraulic dispersion coefficient.

In order to elucidate the influence of surfactants on GONPs transport, typical anionic (sodium dodecylbenzene sulfonate, SDBS) and non-ionic surfactants (Triton X-100) were added into the background electrolyte composition. Dispersions were prepared to have five systems per IS: no surfactant, 50% and 100% critical micelle concentration (CMC) SDBS, 50% and 100% CMC Triton X-100. The CMC for Triton X-100 and SDBS were reported to be 0.24 mmol/L (Du et al., 2013) and 963 mg/L (Godinez et al., 2013), respectively. These systems became the feeding solutions for the different experiments conducted in this study.

1.4. Mathematical modeling

The DLVO theory was used to calculate the interaction forces between GONPs and sand grains under the tested conditions. The DLVO forces consider van der Waals (VDW) attraction and electric double layer (EDL) repulsion. The total interaction energy is the sum of energies of these two interactions. In this study, the Hamaker approximate expression for a sphere-plane case (Gregory, 1981) was used for calculating the retarded VDW attractive interaction; with the assumption of constant potential at the surface, the EDL interaction was calculated by the method derived by Hogg et al. (1966). The average hydrodynamic radius and zeta potential involved into these calculations were determined by dynamic light scattering (DLS) and electrokinetic characterization measurements using ZetaSizer Nano (Malvern).

The transport process of GONPs within the saturated sand column was described by an advection–dispersion–