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Aggregation and resuspension of graphene oxide in simulated natural surface aquatic environments

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A B S T R A C T

A series of experiments were performed to simulate the environmental behavior and fate of graphene oxide nanoparticles (GONPs) involved in the surface environment relating to divalent cations, natural organic matter (NOM), and hydraulics. The electrokinetic properties and hydrodynamic diameters of GONPs was systematically determined to characterize GONPs stability and the results indicated Ca^{2+} (Mg^{2+}) significantly destabilized GONPs with high aggregate strength factors (SF) and fractal dimension (FD), whereas NOM decreased aggregate SF with lower FD and improved GONPs stability primarily because of increasing steric repulsion and electrostatic repulsion. Furthermore, the GONPs resuspension from the sand bed into overlying water with shear flow confirmed that the release would be restricted by Ca^{2+} (Mg^{2+}), however, enhanced by NOM. The interaction energy based on Derjaguin–Landau–Verwey–Overbeek theory verifies the aggregation and resuspension well. Overall, these experiments provide an innovative look and more details to study the behavior and fate of GONPs.

1. Introduction

The unique physicochemical properties of graphene oxide derived from its extraordinary thin two-dimensional structure show tremendous potential for applications in the electronic, medical, energy, and environmental sectors (Chen et al., 2012; Joshi et al., 2014; Ruan et al., 2011). Predictably, with their widespread use and growing demand, graphene oxide nanoparticles (GONPs) would inevitably be released into and exposed to the environment during their production, transport, application, and disposal processes (Hammes et al., 2013; Sanchez et al., 2011). Although the environmental concentration of GONPs may still be insignificant, some experiments were recently conducted to verify the toxicity of GONPs; their results showed that GONPs can be toxic to organisms, and their toxicology is closely related to their concentration and size (Ahmed and Rodrigues, 2013; Akhavan et al., 2012, 2013). Environmental risk caused by GONPs would occur once they are exposed the environment; the risk would particularly increase during their transportation and transformation (Batley et al., 2012; Lowry et al., 2012). Thus, the environmental behavior and fate of GONPs in the aquatic environment should be studied before predicting the particle size and environmental concentrations (Arvidsson et al., 2014; Hu and Zhou, 2013).

Several articles have recently been published to discuss the aggregation kinetics of GONPs related to the solution chemistries in the aquatic system based on traditional Derjaguin–Landau–Verwey–Overbeek (DLVO) theory; results indicated that high ionic strength could facilitate GONPs destabilization, and divalent cations such as Ca^{2+} and Mg^{2+} aggregate GONPs more significantly than monovalent cations such as Na^{+} and K^{+} according to the Schulze–Hardy rule (Chowdhury et al., 2013; Wu et al., 2013). In particular, Ca^{2+} ions can form a bridge with GONPS functional groups and destabilize the GONPs suspension (Chowdhury et al., 2013). Another study on GONPs aggregation kinetics reported that the pH-dependent deprotonation of carboxylic groups on the edge of GONPs can influence the aggregation of GONPs, as well as GONPs orientation during aggregation (Wu et al., 2013); the stability of GONPs notably improve in the presence of natural organic matter (NOM) because of steric repulsion, which may lead to extensive transportation and environmental risk (Lanphere et al., 2014; Ren et al., 2014). Apart from the aggregation kinetics, long-term stability studies showed that GONPs are highly stable in natural surface water (Chowdhury et al., 2013). In addition, column experiments that studied the deposition and

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transportation of GONPs in saturated porous media, which simulate subterrane sand layer, have also been summarized (Chowdhury et al., 2014a, b; Feriancikova and Xu, 2012); these experiments found that the transport of GONPs is highly mobile in the column and the retention of GONPs involves reversible physical (straining) and chemical (electrostatic) interactions. The aforementioned results indicated the potential long-term transport of GONPs in natural surface water.

Apart from the solution chemistries that influence the stability and transportation on GONPs, hydrodynamics may also cause effective differences in the natural aquatic environment; some articles have proposed that hydraulics would affect the environmental behavior and fate of other nanomaterials such as TiO_2 (Boncagni et al., 2009; Godinez and Darnault, 2011). When introduced to aquatic environments such as streams, the shear rate caused by water flow may influence the particle size of GONPs aggregates; although GONPs would be ultimately deposited into the sedimentary layer, changes in hydraulics could lead to resuspension of GONPs from the sedimentary layer. Regrettably, almost no research has been published on the GONPs aggregates and resuspension between stream beds and overlying water with the changes of hydraulics.

This study aims to improve the current understanding of the aggregation and transportation of GONPs in complex surface aquatic environments. Serial experiments to study the effects of cations and NOM on the stability and aggregate fractal dimension of GONPs at different pH levels consider the heterogeneity and complexity in aquatic environments, and the effect of shear rate on the GONPs aggregates breakage to calculate the aggregate strength factors was first quantitated. To determine the GONPs' mobility and fate in the surface aquatic environment, the resuspension of GONPs from the sand bed into overlying water with water flow rather than the breakthrough in saturated porous media was conducted in an annular flume.

2. Materials and methods

2.1. Preparation of GONPs suspension

The graphene oxide used in this study was prepared from natural graphite by using a modified Hummers method (Kovtyukhova et al., 1999). The GONPs were previously horn sonicated in deionized (DI) water at the given concentration of 100 mg/L for 2 h for thoroughly disperse stock suspensions. Prior to each experiment, the stock solution was diluted to the desired GONPs concentration with DI water, and prepared analytical-grade electrolyte stock solutions (10 mM $CaCl_2$ or $MgCl_2$) and NOM solution (1000 mg/L). Suwannee River Humic Acid standard II (SRHA) (International Humic Substances Society, MN) was used as standard NOM, and the SRHA stock solution was prepared with accepted procedures (Chen and Elimelech, 2008). Stock NaOH (1 M) and HCl (1 M) solutions were used for all pH adjustments.

2.2. GONPs characterization

The average electrophoretic mobility (EPM) and zeta potential of GONPs over a wide range of solution chemistries were performed by using a Zeta PALS analyzer (Zetasizer Nano ZS90 zeta, Malvern) and determined by taking the average of three runs for three separate trials. Hydrodynamic diameter (HD) was determined by using static light scattering (SLS; Hydro2000Mu, Malvern) , with an array of photosensitive detectors positioned at different angles between 0 and 135° , capable of analysing particles from 0.02 to 2000 μm. The average diameter was determined from the average of three runs taken at 2 min/run for three trials. A UV–Vis spectrophotometer (DR 5000, Hach) was used to determine the optical absorption spectra as a function of the GONPs concentration (Supplementary material, Fig. S1) at wavelengths of 230 nm for graphene oxide. Ultrasound Doppler velocimetry was applied to measure the flow velocity of the overlying water in the flume.

2.3. Aggregation and breakage of GONPs

The experimental setup (SLS) has been mentioned in other articles (Chekli et al., 2015; Keyvani and Strom, 2014); to avoid possible changes of physical conditions that affect the samples (e.g. external forces that apply to the samples when introduced them inside the measurement cell and the increasing mixing speed inside the test jar to induce the breakage of the aggregates), we conducted the aggregation and breakage experiment in SLS to directly observe and measure the effects of such changes on aggregate size. For the aggregation experiment, the final concentration of GONPs was maintained at 40 mg/L (at which GONPs can provide a strong SLS signal for detection) with different solution chemistry, and the slow mixing speed of 600 rpm for 30 min was used for completely aggregating and obtained the HD_0. Subsequently, a high stepwise mixing speed (100 or 200 rpm) was used as the mechanical shear force after completely aggregation to induce aggregates breakage and obtain the HD_i.

Aggregate strength factors (SF) were used to evaluate the stability and propensity for the formation of the aggregates and determined based on previous methods as follows (Jarvis et al., 2005b; Zhao et al., 2012):

$$SF = 1 - k \cdot \Delta G^{-1} \tag{1}$$

where the k is the gradient obtained by fitting the diameter rate (HD_i/HD_0) with inverse shear rate G^{-1}, and the ΔG^{-1} is the variation of shear rate. More details on the breakage and SF can be found in Supplementary material.

In addition, the mass fractal dimension (FD) characterising disordered structure of colloidal aggregates used for the particle-size distribution was based on previous methods as follows (Ghanbarian and Daigle, 2015):

$$\frac{M(<R_i)}{M_t} = \left(\frac{R_i}{R_{max}}\right)^{E-FD}, \quad R_{min} \le R_i \le R_{max} \tag{2}$$

where E is the Euclidean dimension (E = 3 in three dimensions), M_t is the total mass of fragments, M(<Ri) is the cumulative mass of particles below an upper limit, R_i, practically the upper sieve size, and R_{min} and R_{max} are the lower and upper size limit (cutoff) for fractal scaling.

2.4. Resuspension of GONPs

The following experiments were conducted in a recirculating flume, which simulated the stream course, to study the resuspension of the GONPs via the streambed-overlying water interface. The flume's size and structure were custom designed and inspected (Supplementary material, Fig. S2). A rotational-speed screw propeller was employed to form water circular flow. To avoid violent turbulence that caused streambed deformation, an entanglement was fixed below the screw propeller for energy dissipation. The silica sand used as the model streambed was sieved at 250–300 μm fractions to obtain an average diameter (d_{50}) of 275 μm and then cleaned to remove any metal or organic impurities following previous protocols for sand preparation (Hong et al., 2009). After drying for 12 h, certain amounts of GONPs stock suspension and DI water, NOM and electrolyte stock solutions were evenly poured