Frontier article

Chloramination of graphene oxide significantly affects its transport properties in saturated porous media

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ABSTRACT

Wastewater treatment effluents and sludge can be an important source for engineered nanomaterials entering aquatic systems. However, nanomaterials in the discharge may have markedly different properties compared with the pristine materials, as affected by the treatment processes. Herein, we show that graphene oxide (GO) can undergo further oxidation from chloramination, a commonly adopted disinfection process in wastewater treatment, resulting in substantial changes in the concentration and distribution of GO surface O-functional groups. The chloraminated GO and the untreated GO exhibited comparable transport properties in saturated quartz sand when the background cation was Na^+. However, the treated GO had significantly lower mobility than GO when the background cation was Ca^{2+}. The lower mobility was against the common paradigm that more oxidized carbon nanomaterials should be more mobile. We attribute the surprisingly lower mobility of chloraminated GO to the increase of surface carboxyl groups from chloramination, which induced more significant deposition of GO nanosheets in the presence of Ca^{2+}, through cation-bridging between GO and surface hydroxyl groups of quartz sand. An important implication is that mobility of GO-based materials is controlled primarily by the type and concentration of their surface functional groups, and less so by their degree of oxidation.

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1. Introduction

Graphene-based materials are an important class of engineered carbon nanomaterials with potential applications in many areas, such as energy, biomedicine, and environmental applications (Dreyer et al., 2010). The increasing production and use of graphene-based materials will eventually result in their environmental release (Zhao et al., 2014; Servin and White, 2016). To ensure the responsible development of graphene-based nanotechnology, improved understanding of environmental fate, transport, and transformation of these materials is warranted (Zhao et al., 2014; Wohlleben and Neubauer, 2016).

Wastewater treatment plants can be an important source for engineered nanomaterials entering aquatic systems (Gottschalk et al., 2009; Nowack and Bucheli, 2007; Upadhyay et al., 2014). It is necessary to note that nanomaterials entering wastewater treatment systems are subjective to physical, chemical and biological transformation, as affected by different treatment processes (Lowry et al., 2012; Mishra and Ramaprabhu, 2011; Zhao et al., 2014). Consequently, nanomaterials found in the effluents and sludge of wastewater treatment plants may

have significantly different physicochemical properties compared with the respective pristine materials. To date, most of the studies on the fate and transformation of nanomaterials in wastewater treatment systems have focused on Ag and metal oxides (Escher et al., 2014; Gottschalk et al., 2009; Kiser et al., 2009; Limbach et al., 2008), whereas very little is known about transformation of graphene-based nanomaterials in wastewater treatment processes, as well as the subsequent effects on transport, fate and risks of these materials.

Transport and fate of graphene-based nanomaterials are largely dependent on their physicochemical properties (e.g., size, shape, hydrophobicity and surface O-functionalities) (Chowdhury et al., 2015; Xia et al., 2015; Sun et al., 2015). The degree of surface oxidation can significantly affect the transport of graphene-based nanomaterials. It is generally believed that the more oxidized materials are more hydrophilic and negatively charged than the less oxidized ones and should therefore possess greater colloidal stability and mobility (Sánchez-Hidalgo et al., 2015; Paneri and Moghaddam, 2015). The types of surface O-functionality are also a critical factor determining the transport properties (Qi et al., 2014; Xia et al., 2015; Fan et al., 2015). For instance, in our previous study we showed that for graphene oxide (GO) materials rich in surface phenolic groups, cation-bridging can be the most predominant retention mechanism (Xia et al., 2015). Thus, depending on the extent

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of transformation, graphene-based materials released from wastewater treatment plants can differ substantially from the respective pristine materials in terms of transport properties.

The objective of this study was to understand the potential impact of disinfection, an important process in wastewater treatment, on the transport properties of GO in saturated porous media. Chloramination was selected as a model disinfection approach, and the treatment was carried out using a chloramine dose similar to those used in disinfection processes. The electrokinetic, aggregation and transport properties of the chloraminated GO were compared with those of the pristine GO, and the differences were linked to the changes in GO surface properties from chloramination. The environmental implications of the findings are discussed.

2. Materials and methods

2.1. Preparation and characterization of GO and chloraminated GO

Graphene oxide (GO) was synthesized using a modified Hummers method (Duch et al., 2011). The detailed procedures were reported in our previous study (Xia et al., 2015). Chloramination of GO was carried out using the following procedures. First, a GO stock suspension (300 mg/L) was added to a 500-mL glass bottle and diluted with deionized (DI) water to obtain a 10 mg/L GO suspension. Then, 10 mM phosphate buffer was added to the suspension to keep the pH at neutral. Next, a chloramine solution of 10 mg/L (as Cl_2) was added to the GO suspension. The mixture was kept in the dark for 5 d to mimic the disinfection process by chloramination (Li et al., 2010). Then, the GO suspension was ultra-filtrated using an ultrafiltration cell (Model 8200, Millipore Corporation, USA) equipped with ultrafiltration membranes of 3 kDa molecular weight cut-off to remove phosphate, free Cl_2 residuals and other ions (Rosenberger et al., 2006; Yang et al., 2006). The resulting GO suspension was kept at 4 °C for future use. The chloramine-treated GO is referred to as GO/NH_2Cl hereafter. The concentrations of GO in the stock suspensions were determined by measuring the total organic carbon (TOC) content of the stock suspension (Wang et al., 2012), with a high sensitivity total organic carbon analyzer (Shimadzu Scientific Instruments, Japan).

Surface elemental compositions of GO and GO/NH_2Cl were determined by X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe, Japan). Fourier transform infrared (FTIR) transmission spectra were obtained using a 110 Bruker TENSOR 27 apparatus (Bruker Optics Inc., Germany). Raman spectra were recorded with a Renishaw inVia Raman spectrometer (RM2000, UK).

2.2. Characterization of electrokinetic and aggregation properties of GO suspensions

Working suspensions of GO/NH_2Cl and GO (i.e., the influents of column experiments) were prepared by diluting a GO/NH_2Cl or GO stock suspension in electrolyte solution and stirring for 2 h. The pH of the suspensions was adjusted using 0.1 M HCl and 0.1 M NaOH. All the working suspensions were filtered through 0.45-μm membrane filters to remove large aggregates, if any, before being characterized for electrokinetic and aggregation properties or used in column experiments. The electrophoretic mobility (EPM) and average hydrodynamic diameters (Z_{ave}) of the GO/NH_2Cl and GO suspensions were measured using a ZetaSizer Nano ZS (Malvern Instruments, UK).

2.3. Column transport experiments

The protocols of the column experiments are given in Supplementary information (SI) Table S1. Quartz sand was dry-packed into Omnifit borosilicate glass columns (10 cm × 0.66 cm, Bio-Chem Valve Inc., USA) with 10-μm stainless-steel screens (Valco Instruments Inc., USA) on both ends. Each column contained approximately 3.6 g sand (dry

weight) with an average length of 6.8 ± 0.1 cm and average bulk density of 1.52 ± 0.03 g/cm³. The columns were operated in an upward direction using syringe pumps (KD Scientific, USA). The sand packed columns were equilibrated by flushing with 100 mL DI water at a flow rate of 3 mL/h followed by 180 mL of background electrolyte solution. Two background electrolyte solutions, including 35 mM NaCl and 0.3 mM CaCl₂, were selected on the basis of our previous study (Xia et al., 2015), to ensure that the differences in transport properties can be easily seen for GOs of varied degrees of surface oxidation. Both the columns and syringe were wrapped with aluminum foils during the transport experiments.

In a typical column experiment, the influent (containing approximately 10 mg/L of GO/NH_2Cl or GO) was pumped into the column from a 100-mL glass syringe (SGE Analytical Science, Australia). (All the influents were prepared immediately before the column experiments, and no apparent changes in aggregation state were observed for any influents in the duration of the respective column experiments.) Column effluent samples were collected in 4-mL glass vials every 2–3 pore volumes (PV) to determine the concentrations of GO/NH_2Cl or GO. The concentrations of GO/NH_2Cl or GO in the influent (C_0) and effluent (C) were determined by measuring the UV absorbance (UV-2401, Shimadzu Scientific Instruments, USA) at 230 nm (SI Fig. S1) based on a pre-established calibration curve of GO/NH_2Cl or GO (SI Fig. S2).

The Derjaguin–Landau–Verwey–Overbeek (DLVO) particle–collector interaction energy profiles were calculated for selected water chemistry conditions (the equations and parameters are given in SI). Supplementary experiments were carried out to examine the binding of Ca^{2+} and GO to quartz sand, and the detailed procedures are given in SI.

3. Results and discussion

3.1. Changes of GO surface chemistry from chloramination

Chloramination resulted in marked changes of GO surface chemistry. The XPS results (Fig. 1a and b; Table 1) show that even though chloramination only resulted in slight further oxidation of GO (as indicated by the decrease of C/O ratio, from 2.02 for the untreated GO to 1.98 for the chloraminated one), the treatment resulted in substantial changes in the distribution of surface O-functional groups. In particular, a comparison of the C 1s XPS spectra between GO and GO/NH_2Cl shows that chloramination resulted in the increase of C–OH/C–O–C and –O–C=O, but the decrease of C=O (Fig. 1 and Table 1). The FTIR results (Fig. 1c) are generally consistent with the XPS data, indicating the increase of –COOH (at 1624 cm⁻¹) (Acik et al., 2011) and C–OH (at 1383 cm⁻¹) (Si and Samulski, 2008; Szabó et al., 2006), as well as the decrease of C=O (at 1735 cm⁻¹) (Li et al., 2012; Szabó et al., 2006). The Raman spectra show that the I_D/I_G intensity ratio changed little upon chloramination (SI Fig. S3 and Table 1), indicating that chloramination treatment had negligible effect on the in-plane sp² domains (Ferrari and Robertson, 2000). Overall, the combined microscopic evidence shows that chloramination had little effect on the graphitic structure of GO, and its primary effects were on the type and distribution of surface O functional groups.

Since it appears that chloramine, a relatively mild oxidant, only affected the edge O-functional groups of GO, the reaction mechanisms were likely similar to those reported for the chloramination of natural organic matter (NOM) (Bauer and Snoeyink, 1973; Rook, 1977). It has been reported that with chloramination the quinone groups of NOM can be oxidized to epoxy or hydroxyl groups (Vyas et al., 2003). Furthermore, oxidation of NOM by chlorine or chloramine can result in the opening of aromatic rings to form C–OH, which can be further oxidized to carboxyl groups (Chuang et al., 2013; Chuang and Tung, 2015; Rook, 1977; Xue et al., 2009). Similar reactions likely have happened during the chloramination of GO, resulting in the decrease of quinone group and increase of carboxyl and hydroxyl groups.