Transformation of graphene oxide by chlorination and chloramination: Implications for environmental transport and fate

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ABSTRACT

The rapidly increasing and widespread use of graphene oxide (GO) calls for immediate attention on the environmental fate of this material. To date, very little is known about the environmental transformation of GO. This study explored the changes of physicochemical properties of GO from chlorination and chloramination, which simulated the reactions occurring in water and wastewater treatment systems. Significant changes of GO surface O-functionalities occurred and scrolling of graphene sheets (those of very large sizes) were observed upon the treatments. Chloroform, a byproduct from chlorination was also detected, indicating the ring-opening on the edge of GO nanosheets. The changes of GO surface O-functionalities were attributable to the oxidation of quinone groups of GO by chlorine or chloramine. The scrolling of large-sized GO sheets may be attributable to the destruction of benzene rings at the edge of the GO. The results of membrane filtration experiments and column transport experiments indicated that chlorination and chloramination enhanced the mobility and transport of GO, likely by increasing the colloidal stability and inhibiting the agglomeration of GO nanosheets. The findings of this study further underline the significant implications of GO transformation on the fate and transport of this new nanomaterial.

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1. Introduction

Graphene oxide (GO), which is a structural analog to graphene with additional functionalities such as epoxy, hydroxyl, carbonyl and carboxyl groups, has received unprecedented attention for its fundamental properties and broad applications, such as energy-related materials (Yin et al., 2011), sensors (Ren et al., 2015), bio-medicines (Chen et al., 2015), mechanic resonators (Robinson et al., 2008) and ultracapacitors (Stoller et al., 2008). The rapidly increasing production and use of GO will inevitably lead to its release into the environment, with potential negative impact on ecosystem and human health. Thus, it is of critical importance to understand the fate and effects of GO in the environment (Schmidt, 2009).

To date, most of the studies on the environmental implications of GO have focused on the toxicity and human health effects (Chang et al., 2011; Akhavan et al., 2012, 2013; Liu and Chen, 2015), and on colloidal stability and transport (Chowdhury et al., 2013; Lanphere et al., 2013; Qi et al., 2014), whereas the physicochemical transformation of GO in natural systems and the associated effects on transport and fate are not well understood. However, several recent studies have shown that GO is highly reactive under environmentally relevant conditions, in that it can be easily reduced by naturally occurring reducing agents such as sulfide (Stankovich et al., 2007; Wang et al., 2015a,b) and ferrous iron (Wang et al., 2015a,b) or under simulated sunlight exposure (1 kW xenon arc lamp) (Hou et al., 2015). Furthermore, reduced GO may exhibit markedly different colloid stability and capability to accumulate toxic contaminants (Wang et al., 2015a,b; Xia et al., 2015). Such transformation-induced changes of GO may significantly alter its environmental fate and toxicity (Hou et al., 2015; Xia et al., 2015).

A large fraction of nanomaterials released into the environment will likely end up in natural water systems or waste streams (Weinberg et al., 2011; Mueller and Nowack, 2008; Liu and Cohen, 2014). This fraction of nanomaterials may enter drinking water or wastewater treatment systems (Mueller and Nowack, 2008; Perez et al., 2009), and then undergo physical, chemical and biological transformation during the treatment processes (Amin et al., 2014; Adeleye et al., 2016). The transformed nanomaterials can reenter

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the environment through effluent discharge and disposal or application of biosolids (Gottschalk et al., 2009; Wang et al., 2012a,b). Nonetheless, the fate and transport of the transformed nanomaterials found in the effluent and sludge of treatment plants can be substantially different from those of the respective pristine materials, due to the changes of nanomaterial physicochemical properties induced by the treatment processes. One important process of water/wastewater treatment that may largely affect the physicochemical properties of GO is disinfection, which involves oxidants such as chlorine. To date, research on the oxidation of graphene oxide is very limited (Kotchey et al., 2011) and transformation of GO by common disinfectants involved in water and wastewater treatments has not been directly studied. Herein, we hypothesize that disinfectants can induce changes in the abundance and types of surface O-functional groups, and consequently, can alter the mobility and transport of GO in aqueous environments.

The main objectives of this study were to understand how commonly adopted disinfection processes may affect the physicochemical properties of GO, and to identify the underlying mechanisms. Chlorine and chloramine were selected as the disinfectants because they are two of the most commonly used disinfectants in water and wastewater treatments. Aqueous suspension of GO was treated with chlorine or chloramine using doses similar to those applied in disinfection processes. The physicochemical properties before and after the treatments were compared, to understand the reaction mechanisms. The effects of disinfection treatments on the fate and effects of GO were demonstrated with membrane filtration and column transport experiments.

2. Material and methods

2.1. Materials

Graphene oxide (GO) were purchased from Nano Materials Tech Co. (China). Based on the information provided by the supplier, the product was synthesized from graphite using a modified Hummers method. The GO product had an average lateral size of 149.8 ± 38.6 nm and an average thickness of 0.87 ± 0.11 nm (Supplementary data Fig. S1). A fresh stock of free chlorine solution was prepared from sodium hypochlorite (NaOCl) (5% available free chlorine), diluted to 2000 mg/L as Cl_2, and stored in an aluminum foil-covered flask. Monochloramine (NH_2Cl) solutions were prepared by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions, at a weight ratio of 4 mg/L Cl_2 to 1 mg/L N-NH_4^+.

2.2. Preparation of GO suspension

The stock suspension of GO was prepared using the following procedures. First, approximately 60 mg GO powder was added to 300 mL deionized (DI) water. Next, the mixture was ultra-sonicated at 100 W (Sonics & Material, USA) for 4 h. The obtained GO suspension had an average hydrodynamic parameter of 129.5 ± 23.2 nm (Supplementary data Fig. S2), and was stable over the period of the experiments. The stock suspension was stored in the dark at 4 °C for future use.

2.3. Chlorination and chloramination of GO

The concentrations of free chlorine and chloramine solutions were determined with the Water and Wastewater Standard Method 4500-Cl B (Iodometric Method) and 4500-Cl F (DPD Ferrous Titrimetric Method), respectively. To obtain the chlorine-treated GO sample, the GO stock suspension was added to a 500-mL glass bottle and diluted to 10 mg/L GO with DI water. The pH of the suspension was adjusted to approximately neutral using 10 mM phosphate buffer. Next, NaOCl of 10 mg/L as Cl_2 was added to simulate the doses in disinfection, and the mixture was equilibrated for 5 d in the dark (Li et al., 2010). Afterward, the suspension was ultrafiltrated with a stirred ultrafiltration cell (Millipore corporation, USA) to remove phosphate, free Cl_2 residuals and other inorganic salts (the detailed ultrafiltration procedures are given in Supplementary data). To obtain the chloramine-treated GO, a chloramine solution of 10 mg/L as Cl_2 was used as a disinfectant, using the same procedures as mentioned above. The chlorine-treated GO sample is referred to as GO-NaOCl hereafter, and the chloramine-treated sample as GO-NH_2Cl.

A separate experiment was conducted to understand the relationship between chlorine consumption and the formation of $CHCl_3$. Two liters of 10 mg/L GO was chlorinated with 10 mg/L chlorine for 5 d. The free chlorine in the solution was measured every 12 h. Additionally, 30 mL of the sample was extracted with methyl *tert*-butyl ether (MtBE) to determine the $CHCl_3$ formed. Chloroform was analyzed with USEPA Method 551.1 with minor modifications, using a gas chromatograph (Agilent 6890N, USA) equipped with an electron capture detector (GC-ECD) (Agilent Technologies, USA) and an HP-5 fused silica capillary column (30 m × 0.25 mm I.D. with 0.25-µm film thickness, J&W Scientific, USA).

2.4. Material characterization

The pristine GO, chlorine-treated GO and chloramine-treated GO were characterized by scanning electron microscopy (SEM) (FEI Nanosem 430, Netherlands), transmission electron microscopy (TEM) (FEI Tecnai G2100 F-20, Netherlands), X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe, Japan), Raman spectroscopy (Renishew InVia Raman spectrometer, England), and Fourier transform infrared (FTIR) transmission spectroscopy (110 Bruker TENSOR 27 apparatus, Germany). Dynamic light scattering (DLS) (ZetaPALS, Brookhaven Instruments, USA) was used to characterize the effects of chlorine and chloramine treatment on colloidal and agglomeration properties of GO (Chowdhury et al., 2013; Lanphere et al., 2013), including ζ potential and average hydrodynamic diameter (Z_{ave}). UV–Visible absorbance (Shimadzu Scientific Instruments, USA) and total organic carbon (multi N/C 3100, Germany) of the GO suspensions before and after treatment were also examined.

2.5. Column transport experiments

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. The columns were operated in an upward direction using syringe pumps (KD Scientific, USA). Initially, the sand-packed column was blown using carbon dioxide for 1 h to exhaust air, then the column was equilibrated by sequentially flushing with 100 mL DI water at a flow rate of 3 mL/h and 100 mL DI water at a flow rate of 6.6 mL/h, followed by 180 mL background electrolyte solution. To prepare the influents, aliquots of a GO or treated GO suspension or chlorine (chloramine) treated GO suspension were diluted with electrolytes to obtain the influent concentrations of approximately 10.0 mg/L and then stirred for 2 h. To initiate a column experiment, the influent pumped through the column using a syringe pump (SGE Analytical Science, Australia), and the effluent was collected at every 4–5 pore volume. Then the column was flashed using a GO-free background electrolyte solution until the effluent concentration was below the detection limit. The concentrations of GO and