



Effect of co-existing kaolinite and goethite on the aggregation of graphene oxide in the aquatic environment



Guanxing Huang^{a,b}, Huiyuan Guo^b, Jian Zhao^{c,**}, Yonghong Liu^{b,d}, Baoshan Xing^{b,*}

^a Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, 050061, China

^b Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA, 01003, USA

^c Institute of Coastal Environmental Pollution Control, and Ministry of Education Key Laboratory of Marine Environment and Ecology, Ocean University of China, Qingdao, 266100, China

^d Department of Chemistry, College of Science, Huazhong Agricultural University, Wuhan, 430070, China

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ABSTRACT

Broad applications of graphene oxide (GO) will result in the release of GO into aquatic environments, where clay minerals and metal (hydr)oxides are commonly present. Thereby the interactions between GO and a binary system containing clay minerals and metal (hydr)oxides can occur. We investigated the aggregation of GO with kaolinite and kaolinite-goethite associations (KGAs) in aquatic systems under different pHs, ionic strengths, and GO concentrations. GO suspension was unstable at low pHs, and the aggregation of GO occurred in the presence of KGA-4% and KGA-10% until pH 5 and 6, respectively. Kaolinite decreased the critical coagulation concentration (CCC) of GO at pH 5.5 from around 50 to 20 mM NaCl due to the reduced energy barrier. Heteroaggregation of GO with KGAs was extremely sensitive to ionic strength at pH 5.5, and the CCC of GO in the presence of KGA-10% increased from less than 1 mM NaCl to 5 mM NaCl with the increase of pH from 5.5 to 9. The heteroaggregation extent of GO with KGAs was enhanced firstly, then reduced with the increase of GO concentrations at pH 5.0, which is likely because KGA plates were more efficiently wrapped by large-size GO sheets with increasing GO concentrations. These findings are useful for understanding and predicting the fate of GO in the relatively complicated aquatic and soil environments where binary minerals co-exist.

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1. Introduction

Graphene oxide (GO) is a unique two-dimensional carbon nanomaterial with many carboxyl groups on the edge and hydroxyl and epoxy groups on the basal plane. It is usually produced by oxidation of graphite (Chen et al., 2012; Dreyer et al., 2010). Owing to the polar oxygen functional groups, GO is strongly hydrophilic and can be easily dispersed in water (Chowdhury et al., 2013). Nowadays, GO holds great promises in many applications, such as nanomedicine and water purification (Chen and Chen, 2015; Sun et al., 2008; Wang et al., 2013), because its functional groups serve as sites for chemical modification or functionalization (Dreyer et al., 2014). The increasing application and production of GO makes its release into the aquatic environment inevitable during

production, transport, usage, and disposal processes (McWilliams, 2012; Zhao et al., 2014).

Although the toxicity of GO to organisms is unclear, some recent studies showed that GO caused cytotoxicity in some bacteria and cells (Combarros et al., 2016; Nguyen et al., 2015), while another recent study reported that purified GO did not have in-vitro cytotoxicity (Ali-Boucetta et al., 2013). Moreover, the environmental impact of GO on some organisms and the fate of inorganic substances can be significant (Mukherjee et al., 2016; Zhao et al., 2014). The environmental impact of GO was highly related to its dispersibility because GO with higher dispersion has more opportunities to directly contact bacterial cells (Das et al., 2013). Therefore, in order to assess the environmental impact of GO, it is essential to investigate the aggregation and fate of GO in the environment.

To date, previous studies have focused on the stability and aggregation kinetics of GO in the aquatic environment over a broad range of solution chemistry conditions (Chowdhury et al., 2013; Wu et al., 2013). The results indicated that GO stability was highly dependent on cation valence, ionic strength (IS) and pH, and less

* Corresponding author.

** Corresponding author.

E-mail addresses: jzhao@ouc.edu.cn (J. Zhao), bx@umass.edu (B. Xing).

affected by the anion valence. Furthermore, the aggregation and deposition of GO in the aquatic environment in the presence of metal oxides have been reported (Ren et al., 2014), indicating that the extent of GO aggregation and deposition in the aquatic environment increased in the presence of metal oxides (Al_2O_3). In addition, higher interactions of GO with natural organic matter (NOM) coated surfaces than with silica was observed by Chowdhury et al. (2014a). These results facilitate our understanding on the behavior of GO in simple aqueous-solid systems. However, in real environments, natural solid particles are usually associated with each other. How these associations affect the fate of GO in waters is still unknown. Therefore, further investigations are needed to unravel the behavior and fate of GO in the relatively complicated systems.

In our previous study, it is found that goethite could reduce GO dispersion through heteroaggregation while other minerals such as kaolinite cannot influence GO dispersion (Zhao et al., 2015). However, in natural environments, goethite and kaolinite more often associate with each other rather than in discrete, separate form, and the physicochemical properties such as specific surface area and cation exchange capacity of this association are different from that of their individual minerals (Wei et al., 2012, 2014). Therefore, goethite and kaolinite were chosen as the representative hydrous oxides and clay minerals respectively, and the kaolinite–goethite association (KGA) was prepared and used in this study. By using batch experiments, the aggregation of GO with kaolinite alone and KGAs was investigated across a wide range of solution chemistry conditions (pH and IS). The findings will provide new insight into the fate of GO in relatively complicated aqueous and porous systems such as aquatic–terrestrial transition zones and aquifers, where hydrous oxides and clay minerals usually co-exist.

2. Materials and methods

2.1. Materials preparation

GO was prepared by exfoliation of graphite flakes using an improved Hummers' method (Supporting Information (SI), Section 2.1) (Marcano et al., 2010). The dried GO was dispersed and exfoliated in deionized water (DW) under ultrasonication for 3 h (20 kHz, S-4000, Misonix) to prepare a GO stock suspension (200 mg/L). The pH and electrical conductivity (EC) of the GO stock suspension were 3.59 and 81.7 $\mu\text{S}/\text{cm}$, respectively. Kaolinite was prepared according to the procedure described by Kunze and Dixon with minor modification (SI, Section 2.1) (Kunze and Dixon, 1986). Two KGAs were prepared in this study, which were characterized by about 10% (KGA-10%) and 4% (KGA-4%) of goethite in the KGAs (equal to 6.3% and 2.5% Fe in KGAs), and represented the Fe-rich soils and Fe-poor soils, respectively. KGAs were prepared according to the method described by Wei et al. (2014). Briefly, 200/100 mL oxygen-free DW was added to 48.5/20.5 g kaolinite in a 1 L polyethylene flask, followed by vigorous stirring and ultrasonic dispersion. Then 95/12 mL 1 M FeCl_3 solution was poured into the kaolinite suspension under vigorous magnetic stirring, meanwhile the suspension was adjusted to pH 6. Thereafter pure N_2 was flowed through the suspension. After 30 min, 5.7/0.72 mL 1 M FeCl_2 solution was injected into the suspension, while the suspension was adjusted to pH 6 again, and the total volume was adjusted to 1 L. After a reaction time of 30 min, both the stirring and N_2 supply were stopped, and the polyethylene flask was tightly sealed and the suspension was aged in a water bath of 55 °C for 5 d, followed by a rest period of 30 d at 25 °C. The final product was centrifuged and washed with oxygen-free DW until the conductivity of the supernatant was <10 $\mu\text{S}/\text{cm}$. Then the product was freeze-dried in vacuum 72 h, and ground to pass a 100-mesh sieve (SI, Section 2.1).

2.2. Batch experiments

The aggregation experiments were performed in 20-mL vials with Teflon-lined screw caps at 25 °C. In the absence of minerals (unary system), the aggregation of GO as affected by solution chemistry was performed as a function of pH (2.0–9.2) and IS (NaCl, 0–500 mM) with 20 mg/L of initial GO. For the binary system, 20 mg of minerals (kaolinite, KGA-4%, or KGA-10%) were added into vials before the addition of solution and GO stock suspension. Correspondingly, the aggregation experiments were performed as a function of the IS (NaCl, 0–50 mM) at a fixed equilibrium pH (5.5 ± 0.2 for all minerals, 7.2 ± 0.2 for KGA-10%, 9.0 ± 0.2 for KGA-10%) with 20 mg/L of initial GO; as a function of GO concentrations (1–60 mg/L) at a fixed equilibrium pH 5.0 ± 0.2 without electrolyte (only in the presence of KGAs); and as a function of pH (2.0–9.0) at 20 mg/L of initial GO without electrolyte. The fixed equilibrium pH values of the solution in vials were adjusted by adding negligible volumes of 0.01–0.50 M HCl or NaOH. Vials were shaken at a speed of 150 rpm for 24 h at 25 °C to reach equilibrium (Fig. S1), and then left undisturbed in dark on a flat surface for 24 h to settle down minerals and GO aggregations (Fig. S2). After that, 5 mL supernatants were removed into 8-mL DW-washed plastic bottles, and the bottles were centrifuged at 3000 rpm for 30 min to separate suspended particles from the supernatants, while the GO in supernatants remained stable after centrifugation (Figs. S3 and S4). The GO concentrations in the supernatants (C_c , mg/L) were determined by UV–vis spectrophotometer (Agilent 8453, USA) at a wavelength of 226 nm (Fig. S5), and the standard curve of GO had a r^2 value of 0.999 (Fig. S6).

The release of Fe-related ions in solution from KGA-10% as a function of pH was examined. Briefly, 10 mL of DW was added into vials which already contained 20 mg of KGA-10%, and the solution pH was adjusted to a range of 3.5–9.0. After shaking for 24 h, the suspensions were settled for 24 h, and then 5 mL supernatants were centrifuged (3000 rpm, 30 min) and filtered through a Teflon membrane (0.45 μm). Concentrations of Fe-related ions in filtrates were determined using UV–vis spectrophotometer (Agilent 8453, USA) at a wavelength of 512 nm with o-Phenanthroline method (Analytical Methods Committee, 1978). The aggregation experiments at a fixed equilibrium pH were run in duplicate, while other experiments were run in triplicate. All the experimental data were the averages of duplicate or triplicate determinations.

2.3. Characterization of GO and minerals

The electrophoretic mobility (EPM) and hydrodynamic diameter were determined when GO suspension (20 mg/L) was under a range of pH (3.0–9.2) and IS (NaCl, 1–500 mM) at 25 °C. The zeta potentials of GO and minerals were measured as a function of pH and IS at 25 °C. EPM, hydrodynamic diameter, and zeta potential were measured with a particle size analyzer (90Plus, Brookhaven Instruments Co.). To further investigate the morphology and heteroaggregation of GO–KGAs complexes, the GO–KGA-10% suspensions were dropped onto the surface of silicon wafer disks, and then viewed under scanning electron microscopy (SEM, FEI Magellan 400 XHR) after drying. For comparison, individual KGA-10% samples were also prepared and observed using SEM integrated with an energy dispersive X-ray spectrometer (EDS, Oxford 80 mm² X-Max).

2.4. Derjaguin–landau–verwey–overbeek (DLVO) interaction energy

The energy barrier between GO sheets and minerals at different ISs was calculated according to DLVO theory. The total interaction

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