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Heteroaggregation and sedimentation of graphene oxide with hematite colloids: Influence of water constituents and impact on tetracycline adsorption

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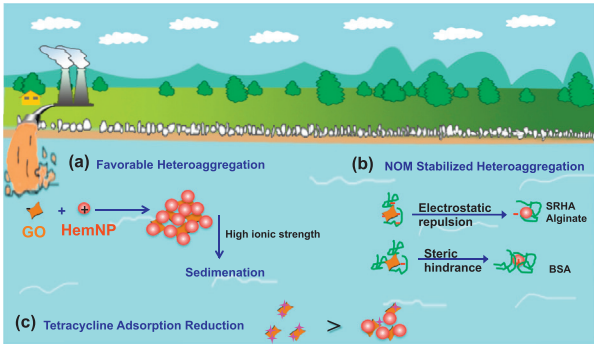
HIGHLIGHTS

- Favorable heteroaggregation and sedimentation occurred between oppositely charged GO and HemNP.
- NOMs suppressed the sedimentation of GO—HemNP heteroaggregates through various mechanisms.
- High ionic strength enhanced the heteroaggregation and sedimentation of GO—HemNP heteroaggregates.
- Elevated pH partially disaggregated the GO—HemNP heteroaggregates.
- Coexistence of HemNP greatly reduced the adsorption of tetracycline on GO.

GRAPHICAL ABSTRACT



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ABSTRACT

Because the transport of graphene oxide nanosheets (GO) from water to sediments is influenced by their heteroaggregation and sedimentation with natural colloids, knowledge on the interdependence of heteroaggregation and sedimentation for GO is needed to gain a better insight on the environmental fate of these nanosheets. However, this phenomenon is still not well understood. In this study, the heteroaggregation and sedimentation behaviors of GO with hematite nanoparticles (HemNPs) were investigated at various conditions. It has been found that negatively charged GO rapidly underwent heteroaggregation with positively charged HemNPs, leading to the sedimentation of GO. Significant sedimentation occurred when the net charge of the GO—HemNP mixture was close to zero. The presence of various natural organic matters suppressed the sedimentation of the heteroaggregates through various mechanisms. Specifically, adsorption of humic acid and alginate reversed HemNP surface charge from positive to negative, leading to a slow sedimentation of the GO—HemNP mixtures due to the increase in nanoparticle electrostatic repulsion. Adsorption of bovine serum albumin raised steric hindrance effect between GO and HemNP, which in turn inhibited their heteroaggregation and sedimentation. At high ionic strength conditions, the sedimentation of GO and HemNP was enhanced, possibly through the combination of homo- and hetero-aggregation. At elevated pH, the heteroaggregates were partially disaggregated, probably due to the weakening of GO—HemNP bonds as the surface charges of these nanomaterials became more negative. Moreover, heteroaggregation of GO with HemNP likely to occupy the adsorption sites on

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GO surfaces, thus greatly reduced the adsorption of tetracycline on GO. These findings highlighted the important roles of natural colloids on the fate and transport of GO, together with the importance of heteroaggregation on the adsorption of co-existing pollutants to GO in natural aquatic environments.

1. Introduction

Graphene oxide nanosheets (GO), which have a layered structure with oxygen-containing functional groups on the basal plane and the sheet edges, and can be used in the production of graphene or graphene-based composite materials (He et al., 1998; Kim et al., 2012; Zhu et al., 2010). As a result of worldwide commercial interests, GO and GO-based nanomaterials will be inevitably released into the environment during their production, transport, use, and disposal (Zhao et al., 2014). The potential environmental impacts of GO have raised significant concerns. Many investigations demonstrated that GO could induce toxic effects on bacteria and mammalian cells (Akhavan and Ghaderi, 2010; Bianco, 2013; Chang et al., 2011; Liao et al., 2011; Liu et al., 2011; Yang et al., 2013; Yang et al., 2010). Several studies have also found that the presence of GO amplified the toxicity of heavy metals to plant and algae (Hu et al., 2014; Tang et al., 2015).

Natural colloids, such as metal oxide particles, and natural organic matters (NOMs), are ubiquitously present in environmental systems. Their estimated concentrations in the environment are in the range of 1–20 mg/L, which are typically several orders of magnitude higher than that of engineered nanoparticles (e.g., GO and carbon nanotubes) (Batley et al., 2013). Therefore, once released into the natural aquatic environment, the fate and transport of GO are expected to be greatly influenced by their heteroaggregation with natural colloids. Recently, much attention has been given on the heteroaggregation between GO and montmorillonite, kaolinite, or goethite (Huang et al., 2016; Sotirelis and Chrysikopoulos, 2016; Zhao et al., 2015), layered double hydroxides or oxides (Wang et al., 2017; Zou et al., 2016a; Zou et al., 2016b), SiO_2 (Chowdhury et al., 2014a), hematite (Feng et al., 2017), and Al_2O_3 (Chowdhury et al., 2014b; Ren et al., 2014). The results obtained from these studies revealed that surface charge and functional groups of the natural particles, as well as solution chemistry, could affect the heteroaggregation behavior of GO.

Sedimentation is also a crucial process affecting GO transport in aquatic to terrestrial environments (Quik et al., 2014). However, the sedimentation of GO has not been thoroughly investigated. Although heteroaggregation has been considered to be a vital process for the sedimentation of nanoparticles, the interdependence between heteroaggregation and sedimentation has not been well understood. Our previous study demonstrated that GO interacted favorably with the oppositely charged hematite colloids, leading to the sedimentation of hematite colloids (Feng et al., 2017). Nevertheless, natural aquatic environment is complex, and other factors, including NOMs, pH, and ionic strength, might influence the heteroaggregation and sedimentation behaviors of GO (Huynh et al., 2014; Quik et al., 2014; Wang et al., 2015a; Wang et al., 2015b; Zhao et al., 2015; Zhou et al., 2012). Therefore, in this study, the effects of these factors on interdependence of the heteroaggregation and sedimentation of GO with hematite nanoparticles (HemNP) were examined. Suwannee River humic acid (SRHA), alginate, and bovine serum albumin were respectively used here as representations of the humic substance, polysaccharide, and protein fractions of NOM to study the influences of these fractions on the heteroaggregation and sedimentation behaviors of GO. From experimental observations, the role of heteroaggregate sizes and zeta potentials on GO—HemNPs heteroaggregate sedimentation rates were elucidated.

In the natural aquatic environment, GO will be co-existed with environmental pollutants (Zhao et al., 2014). For example, that tetracycline is a popular antibiotic and could be present in the environment at concentrations up to 110 μg/L (Zhang et al., 2015). Due to the high adsorption capacities of GO, adsorption of co-existing pollutants on GO is likely to occur and thus influences the fate and toxicity of these contaminants (Hu et al., 2014; Kyzas et al., 2014; Li et al., 2013; Zhao et al., 2011). (Jiang et al., 2018; Sun et al., 2017)As the heteroaggregation of GO with natural colloids can possibly change the structures and properties of GO, this process is expected to affect GO adsorption ability for co-existing pollutants. Former studies found that heteroaggregation between GO and natural minerals (e.g., montmorillonite, kaolin, and goethite) or metal oxide particles (e.g., SiO_2 and Al_2O_3) greatly inhibited the adsorption of 17β-estradiol and bisphenol A on GO (Jiang et al., 2018; Sun et al., 2017). Therefore, the influence of heteroaggregation on the adsorption ability of GO toward tetracycline was also investigated in this study.

2. Experimental section

2.1. Preparation and characterization of GO and HemNPs

Well-dispersed water suspension of graphene oxide (>99% purity) was purchased from XFNANO Materials Tech Co. (Jiangsu, China). Based on the information provided by the supplier, the GO were produced by the modified Hummers method (Hummers and Offeman, 1958) with the flake size of 50–200 nm and the thickness of 0.8–1.2 nm. The properties of GO were extensively characterized using various techniques. In the GO stock suspension, total organic carbon content (TOC) and GO hydrodynamic diameters were determined through high temperature (1200 °C) catalytic oxidation (Vario TOC, Elementar, Germany) and dynamic light scattering (DLS) (Malvern Zetasizer Nano series Nano-ZS, MA, USA), respectively. Surface elemental compositions of GO were determined by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer PHI 550 ESCA/SAM, USA). GO UV–vis spectra analysis was performed on a Varian Cary 50 spectrophotometer (Varian, USA). Transmission electron microscopy (TEM) images of GO were collected on a JEM-200 CX (JEOL, Japan). In addition, Fourier transform infrared (FTIR, Vector-22 spectrometer, Bruker, Germany) and Raman spectra (Raman Senterra microscope, Bruker, Germany) of GO were also obtained.

Hematite nanoparticles (HemNPs, <50 nm) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). The stock suspensions of HemNPs were prepared by dispersing the nanoparticle powder into deionized (DI) water (18.2 mΩ·cm, Milli-Q, Millipore, USA). The concentrations of the HemNPs in stock suspensions were determined through gravimetric analysis. Detailed characterization results of GO and HemNPs can be found in Fig. S1 and Table S1 of the Supplementary Materials (SM).

2.2. Preparation of stock solutions

A NaCl stock solution was prepared with DI water and filtered through a 0.22-μm syringe filter (Millipore, MA). Suwannee River humic acid (SRHA) was obtained from International Humic Substances Society. Bovine serum albumin (BSA), sodium alginate, and tetracycline hydrochloride ($C_{22}H_{24}N_2O_8 \cdot HCl$, 99% purity) were purchased from Sigma-Aldrich (Shanghai, China). SRHA, BSA and alginate stock solutions were prepared by dissolving 5.0 mg macromolecules in 20 mL DI water. In the case of SRHA, the solution pH was adjusted to ca. 10 using NaOH to ensure that SRHA had completely dissolved. After