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Heteroaggregation of graphene oxide nanoparticles and kaolinite colloids

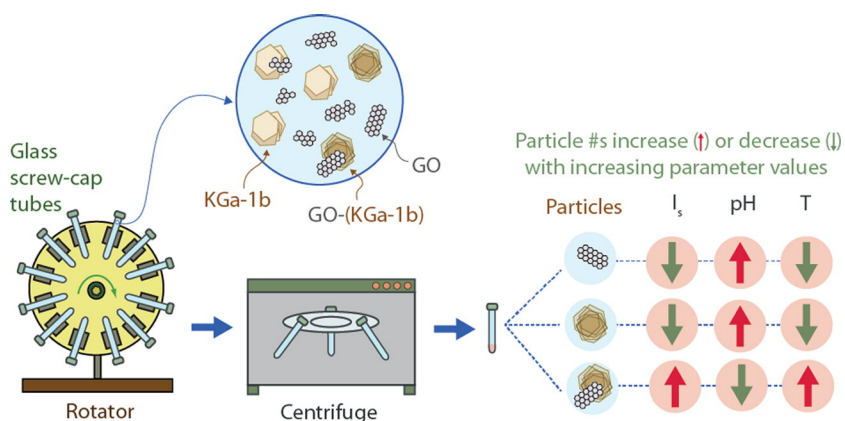
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HIGHLIGHTS

- Heteroaggregation between GO and KGa-1b is not favorable under normal conditions.
- High ionic strength and low pH values enhance the attachment of GO onto KGa-1b.
- The attachment of GO onto KGa-1b is exothermic and not spontaneous.
- GO–(KGa-1b) formation is attributed to surface charge changes of KGa-1b colloids.
- The CCC for the heteroaggregation between GO and KGa-1b is 152 mM NaCl.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) is a material with rapid production growth, and consequently GO nanoparticles are expected to eventually penetrate subsurface formations, where fine mineral particles are in abundance. This study examines the heteroaggregation of GO nanoparticles with kaolinite (KGa-1b) colloids under various conditions. Dynamic batch experiments were conducted in solutions with different pH values (pH = 4, 7, and 10), different ionic strengths ($I_s = 7, 12, \text{ and } 27 \text{ mM}$), and at three controlled temperatures (8, 14, and 25 °C). The experimental results showed that a relatively small amount of GO nanoparticles (5–20% of the initial concentration) attached immediately onto KGa-1b colloids, and reached equilibrium in <20 min. It was shown that neither temperature nor pH played a significant role in the attachment of GO nanoparticles onto KGa-1b colloids. In contrast, the attachment of GO nanoparticles onto KGa-1b colloids was shown to increase with increasing I_s . Additionally, time-resolved dynamic light scattering (DLS) was used to identify the influence of I_s on heteroaggregation between GO nanoparticles and KGa-1b colloids. The critical coagulation concentration (CCC) for the interaction between GO nanoparticles and KGa-1b colloids was 152 mM (NaCl). The interaction energies were calculated, for all experimental conditions, by using measured zeta potentials and applying the classical DLVO theory. The equilibrium experimental data were fitted with a Freundlich isotherm, and the attachment kinetics were described very well with a pseudo-second-order model. Furthermore, thermodynamic analysis revealed that the attachment process was nonspontaneous and exothermic.

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1. Introduction

The growing production of engineered nanomaterials and their use in a wide range of engineering applications and commercial products

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increased the probability of their emissions into environmental systems (Mueller and Nowack, 2008; Gottschalk et al., 2009, 2010; Keller et al., 2013; Keller and Lazareva, 2014). Because of the direct or indirect release of nanoparticles in the environment, numerous nanoparticles are detected in soil, water and air (Brar et al., 2010). Consequently, understanding thoroughly the fate and transport of nanoparticles in environmental systems and the related human health implications, is of paramount importance (Klaine et al., 2012; Sasidharana et al., 2014).

One very promising nanomaterial is graphene oxide (GO), which is a two-dimensional graphene-layered nanomaterial, composed of oxygen-bearing functional groups (Dreyer et al., 2010; Kim et al., 2012). Because of its excellent physiochemical properties, GO is used in a wide range of applications in various fields, including electrochemistry (Chen et al., 2012), biomedicine (Chung et al., 2013), energy storage (Lightcap and Kamat, 2013), and catalysis (Pyun, 2011). Numerous laboratory investigations have suggested that GO nanoparticles are toxic to a variety of mammalian organisms, as well as to bacterial cells (Akhavan and Ghaderi, 2010; Wang et al., 2011; Chang et al., 2011; Vallabani et al., 2011; Singh et al., 2011; Seabra et al., 2014; Hu et al., 2015). To assess these potential risks, the GO fate and transport in environmental systems and particularly in subsurface formations, where the migration behavior of nanoparticles is relatively complex, should be carefully investigated (Klaine et al., 2012; Lanphere et al., 2014; Zhou et al., 2016). Furthermore, the stability of GO nanoparticles plays significant role on their fate and transport in underground water environment. Many studies have explored the effect of solution chemistry (e.g. pH, ionic strength, cation valence, nanoparticle concentration, presence of organic matter) on GO nanoparticles aggregation (Chowdhury et al., 2013; Wu et al., 2013; Zhao et al., 2014; Hua et al., 2015; Huang et al., 2016).

In addition, fine mineral particles are important components of sediments and soils, and inevitably they are widely present in groundwater (Han et al., 2008). In groundwater, the heteroaggregation of nanoparticles with clay minerals is a critical process for the stability of nanoparticles (Wang et al., 2015a, 2015b), and the deposition of nanoparticles onto immobile surfaces can play a dominant role. Various investigators have examined the interaction between engineered nanoparticles (e.g. Ag, TiO₂ and Al₂O₃) with clay minerals (e.g. montmorillonite, kaolinite and goethite) (Zhou et al., 2012; Labille et al., 2015; Wang et al., 2015a, 2015b; Bayat et al., 2015). These studies suggest that the surface charge and the shape of the clay particles affect the stability of engineered nanoparticles due to heteroaggregation. Consequently, the interaction between GO nanoparticles and clay minerals may be critical for the transport and retention of GO nanoparticles in porous media.

Kaolinite is one of the most common clay minerals in the subsurface, so it is possible to interact with GO nanoparticles. Zhao et al. (2015) have investigated the destabilization of GO nanoparticles via heteroaggregation with kaolinite at only one controlled condition ($T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 6.5$) in presence of Na⁺ and Ca⁺, and observed that heteroaggregation was unfavorable. Huang et al. (2016) have examined the influence of pH, I_s and initial nanoparticle concentration on heteroaggregation of GO nanoparticles with kaolinite and kaolinite-goethite complex, and reported that heteroaggregation was favorable for low pH, high I_s and low GO concentrations.

The aim of this work was to investigate the effect of water chemistry and temperature on the heteroaggregation between GO nanoparticles and kaolinite colloids. Dynamic batch experiments were conducted at three controlled temperatures, using GO nanoparticles and kaolinite colloids in suspension at different pH values and ionic strengths (I_s). It is worthy to note that the selected temperature range (8–25 °C), and pH range (4–10) considered in this study, are representative of the conditions observed in various ground and surface waters (Collins, 1925). To the best of our knowledge, no previous study has investigated the effect of temperature on the heteroaggregation between GO nanoparticles and KGa-1b colloids in conjunction with the associated thermodynamics.

2. Methodology

2.1. Materials

GO suspensions were prepared by mixing the appropriate amount of GO sheets (Sigma Aldrich, St. Louis, USA) with a phosphate buffered solution (PBS) with relatively low ionic strength (I_s = 7 mM). Afterwards, the suspensions were sonicated (37 kHz) (Elmasonic S 30/(H), Elma Schmidbauer GmbH, Singen, Germany) for 2 h to ensure that the dispersion is thoroughly uniform, as suggested by Sotiirelis and Chrysikopoulos (2015). All aggregation experiments were conducted with a concentration of GO nanoparticles of C_{GO} = 5 mg/L, whereas for the isotherm experiments the range of GO nanoparticles concentrations was 1–25 mg/L. However, it should be noted that concentrations of GO in environmental systems could be smaller than the 5 mg/L used in this study.

The kaolinite (KGa-1b, well-crystallized kaolin, from Washington County, Georgia) (Pruett and Webb, 1993) used in this study was purchased from the Clay Minerals Society (Columbia, Missouri, USA). KGa-1b has specific surface area (SSA) of 10.1 m²/g, as evaluated by the Brunauer–Emmet–Teller (BET) method, and cation exchange capacity (CEC) of 2.0 meq./100 g (van Olphen and Fripiat, 1979). The <2 μm colloidal fraction, used in all of the experiments conducted in this study, was separated by sedimentation following the procedures outlined by Rong et al. (2008). Briefly, 12 g of KGa-1b were mixed with 25 mL of distilled deionized water (ddH₂O) in a 2 L beaker. Hydrogen peroxide (30% solution) was added to the suspension to oxidize organic matter, while the pH was adjusted to 10 with 0.1 M NaOH. The suspension was diluted to 2 L and the <2 μm colloid fraction was separated from larger particles by sedimentation for a time period of 1 h. The size of the colloids was confirmed using a Zeta-Sizer analyzer. Adding a 0.5 M CaCl₂ solution flocculated the separated colloid suspension. The colloid particles were washed with ddH₂O, ethanol and again ddH₂O, and finally dried at 60 °C. The KGa-1b suspensions were prepared by adding an appropriate amount of KGa-1b to PBS solution and sonicating for 10 min in order to obtain the desired colloidal suspension. The concentration of KGa-1b colloids used in all of the heteroaggregation experiments was C_{KGa-1b} = 50 mg/L.

All the solutions were prepared using ultrapure water (Easypure II, Barstead, USA) with specific resistivity of ~18.2 MΩ·cm. The various nanoparticle and colloid suspensions with different ionic strengths were adjusted with NaCl (C_{NaCl} = 0, 5, 20 mM for the batch experiments with I_s = 7, 12, 27 mM, respectively); whereas, the suspensions with different pH values were adjusted with either H₃PO₄ or NaOH. All chemicals employed in this study were of analytical reagent grade, employed without any additional purification.

The optical density of the GO nanoparticles was analyzed at the optimal wavelength of 231 nm following the procedure outlined by Liu et al. (2013). Calibration curves were prepared for each set of solution chemistry (pH and I_s) examined in this study, in order to establish the relationship between absorbance, Abs [–], and GO, in the range 0–30 mg/L. A series of diluted samples were prepared from an aqueous solution with known GO concentration, and the absorbance of each diluted sample was measured with a UV–visible spectrophotometer (Cary 400 BIO, Varian, Palo Alto, California). Furthermore, the hydrodynamic diameter and the zeta potentials of the GO nanoparticles and KGa-1b colloids under the various experimental conditions considered in this study at 25 °C were measured with a zetasizer (Nano ZS90, Malvern Instruments, Southborough, MA) (see Table 1). All zeta potential and hydrodynamic diameter measurements were obtained in triplicates.

2.2. Batch experiments

Dynamic batch experiments were conducted under various solution chemistry conditions at 8, 14, and 25 °C, in order to examine the effect of pH, I_s, and temperature on GO and KGa-1b heteroaggregation. All batch

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