



Adsorption and co-adsorption of graphene oxide and Ni(II) on iron oxides: A spectroscopic and microscopic investigation[☆]



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ABSTRACT

Graphene oxide (GO) may strongly interact with toxic metal ions and mineral particles upon release into the soil environment. We evaluated the mutual effects between GO and Ni (Ni(II)) with regard to their adsorption and co-adsorption on two minerals (goethite and hematite) in aqueous phase. Results indicated that GO and Ni could mutually facilitate the adsorption of each other on both goethite and hematite over a wide pH range. Addition of Ni promoted GO co-adsorption mainly due to the increased positive charge of minerals and cation- π interactions, while the presence of GO enhanced Ni co-adsorption predominantly due to neutralization of positive charge and strong interaction with oxygen-containing functional groups on adsorbed GO. Increasing adsorption of GO and Ni on minerals as they coexist may thus reduce their mobility in soil. Extended X-ray absorption fine structure (EXAFS) spectroscopy data revealed that GO altered the microstructure of Ni on minerals, i.e., Ni formed edge-sharing surface species (at $R_{\text{Ni-Fe}} \sim 3.2$ Å) without GO, while a GO-bridging ternary surface complexes (at $R_{\text{Ni-C}} \sim 2.49$ Å and $R_{\text{Ni-Fe}} \sim 4.23$ Å) was formed with GO. These findings improved the understanding of potential fate and toxicity of GO as well as the partitioning processes of Ni ions in aquatic and soil environments.

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1. Introduction

Graphene oxide (GO) is a unique layered material with a graphene nanosheets functionalized with oxygen-bearing functional groups (Sotirelis and Chrysikopoulos, 2015; Pei et al., 2013; Zhao et al., 2011c, 2015). Graphene oxide materials are mainly synthesized via a chemical exfoliation process of oxidized graphite under the assistance of sonication, and after oxidation, carboxylic groups mainly locate on the edges of GO, whereas hydroxyl and epoxide groups dominate on its basal plane (Chen et al., 2012; Dreyer et al., 2010; Sotirelis and Chrysikopoulos, 2015). GO, which is similar to

graphene (G), has been increasing attention and changed many fields of science, engineering, and industry, due to its remarkable physicochemical properties including high surface area, excellent mechanical strength and structural transformability, good functionalizability and dispersibility (Dreyer et al., 2010; Machida et al., 2006; Sotirelis and Chrysikopoulos, 2015; Wang et al., 2014a, b).

Thus, GO has increasingly received potential applications in various fields. Consequently, the production growth of GO is rapid, and hence a large number of GO are expected to be eventually released into natural environmental systems, including surface waters and groundwater (Sotirelis and Chrysikopoulos, 2015). It should be noted that the solubility of GO in water is very high, and the presence of soluble GO in surface waters and groundwater may significantly affect the fate and transport of dissolved species and suspended particles (Sotirelis and Chrysikopoulos, 2015). For instance, it was widely reported that GO could have strong

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interaction with a large number of organic and inorganic contaminants, natural colloids like goethite, Al_2O_3 , layered double hydroxides (Chen and Chen, 2015; Machida et al., 2006; Wang et al., 2014a, b; Wang and Chen, 2015; Zhao et al., 2014a). Therefore, it is very necessary to understand the fate of GO in water and soil environmental systems.

Iron oxides such as goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$), a class of typical suspended particles, are commonly present in many natural media in contact with water. Owing to their large specific surface area and abundant surface functional groups, iron oxides should exhibit high scavenging affinity for dissolved species such as heavy metal ions in the natural surface waters and groundwater systems (Arai, 2008; Gimenez et al., 2007; Gräfe et al., 2008; Gräfe and Sparks, 2005; Huang et al., 2016; Mustafa et al., 2010; Reiller et al., 2005). For example, Arai (2008) found that the surface species of Ni(II) on iron (hydr)oxides are sensitive to its crystallinity. Huang et al. (2016) observed a facet-dependent of chromate (Cr(VI)) adsorption on hematite, i.e., Cr(VI) was adsorbed on (001) and (110) facets in inner-sphere monodentate mononuclear and bidentate binuclear configurations, respectively. Besides, Zhao et al. (2015) reported that GO was able to irreversibly interact with goethite through electrostatic attraction, leading to the deposition of GO on goethite. Yang et al. (2013) attempted to use GO as a suitable flocculant to remove suspended particles, and found that GO were able to interact with positively-charged hematite. Compared with the separate studies on the interaction of heavy metals (Arai, 2008; Gimenez et al., 2007; Gräfe et al., 2008; Gräfe and Sparks, 2005; Huang et al., 2016; Mustafa et al., 2010; Reiller et al., 2005) or GO nanosheets (Yang et al., 2013; Zhao et al., 2015) with iron oxides, there is little information on the effect of heavy metals on GO interaction and vice versa, particularly at a molecular level (Hu et al., 2017). However, it should be realized that, upon release into the water and soil environmental systems, GO may occur together with metal ions and minerals and thus strongly interact with each other. Therefore, it is important to investigate the interaction mechanism of heavy metals with iron oxides in the presence of GO and vice versa. Besides, extended X-ray absorption fine structure (EXAFS) is a very useful approach to investigate the interaction mechanism and microstructure of metal ions on surfaces (Hu et al., 2016; Sheng et al., 2014, 2016a, b, c, d), which has nearly not been used to study the interaction mechanism of metal ions in the GO/mineral interfacial systems.

The objective of this work was to improve our understanding of the mutual effects of metal ions and GO interaction at the minerals-water interface. We chose goethite and hematite, as well as Ni as common representatives of iron minerals and heavy metal cations, respectively, and then examine the interaction between GO and Ni on their co-adsorption on goethite and hematite. The effect of pH on the co-adsorption of GO and Ni onto minerals is investigated by batch experiments. We further provide an insight into the relevant mechanisms using an advanced extended X-ray absorption fine structure (EXAFS) approach. To the best of our knowledge, no previous study has investigated colloidal mineral, GO, and metal ion interaction via a combined macroscopic and microscopic approaches, which are critical to better understand the fate and transport of GO and to predict the natural attenuation of heavy metal ions in the subsurface environment.

2. Materials and methods

2.1. Materials and chemicals

All chemicals including $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH, $\text{NH}_3 \cdot \text{H}_2\text{O}$, H_2SO_4 and KMnO_4 used in this experiment were analytical grade. All solutions were prepared using 18 M Ω de-

ionized water (Milli-Q Gradient, Millipore, and USA). The graphite (particle diameter of ~20 μm with ~99.95% purity) was purchased from Qingdao Graphite Company (China). The graphene oxide (GO) was synthesized according to the modified Hummers method from graphite using concentrated H_2SO_4 and KMnO_4 to oxidize graphite layer (Barkauskas et al., 2011; Huang et al., 2015; Wang et al., 2015; Zou et al., 2016). Goethite was synthesized according to a modified method described in previous studies (He et al., 2002, 2005; Hu et al., 2010). Hematite was synthesized according to a modified method described in previous studies (Zhao et al., 2011a). The solid materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transformed infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), X-ray diffraction (XRD), zeta potentials, extended X-ray absorption fine structure (EXAFS) spectroscopy. Detailed processes were described in the [supporting information \(SI\)](#).

2.2. Batch experiments

All the batch sorption experiments were conducted in a series of 25-mL vials equipped with Teflon-lined screw caps at $T = 298 \pm 1$ K under N $_2$ conditions. The stock suspensions of minerals (goethite and hematite) and background electrolyte solution were added into the vials and shaken for 1 h. Then Ni or GO stock solution was added, and the desired pH of the suspensions was adjusted in the range of 3.0–10.0 by adding negligible volumes of 0.05 mol/L HCl or NaOH. The vials containing these mixtures were placed on a horizontal shaker and shaken at a constant speed of ~150 rpm for 1 day. Subsequently, the vials were removed from the shaker and left undisturbed on a flat surface for 1 day to allow for the complete settlement of minerals and the large GO aggregates. Finally, the residual GO concentrations in supernatant were determined by UV–vis spectrophotometer (UV-2550, PerkinElmer) at a wavelength of ~210.0 nm (Fig. S1 in the SI). The concentration of Ni was measured by an inductively coupled plasma-atomic absorption spectrometer (ICP-AES, PerkinElmer). The adsorption of GO or Ni was calculated from the difference between initial (C_0) and equilibrium concentration (C_e). Removal (%) was calculated according to, $\text{removal} = (1 - C_e/C_0) \times 100\%$, adsorption capacity was calculated as, $q_e = (C_0 - C_e)/m \times V$, where V is suspension volume (L), and m is adsorbent mass (g) (Ren et al., 2014; Zou et al., 2016). All data were averages of duplicate determinations, and the relative errors were ~5%.

3. Results and discussion

3.1. Characterization of GO and mineral

The characterization of physicochemical properties for GO nanosheets and the minerals are shown in Fig. 1. From the SEM (Fig. 1A) and TEM (Fig. 1B) images of the as-synthesized GO, we can see that GO has lateral dimensions of several micrometers. Some tiny hole that is caused by the overexposure to sonication during the synthesis process can be observed. The SEM and TEM show that the GO nanosheets, which are partially transparent, are high quality with few layers although the exact layer number cannot be estimated from these images (Wang et al., 2015; Zhao et al., 2011b). The surface functional groups on GO can be identified by FT-IR analysis (Fig. 1C). The peak at ~ 1241 cm^{-1} can be attributed to C–O group, the peak at ~ 1625 cm^{-1} is characteristic of C=C group, whereas, the peak at ~ 1722 cm^{-1} is due to C=O group. These results indicated that a large amount of oxygen-bearing functional groups formed on GO due to the oxidation (Zhao et al., 2011b). The different surface functional groups on GO can be further evident of the C1s XPS

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