Role of solution chemistry in the retention and release of graphene oxide nanomaterials in uncoated and iron oxide-coated sand

Dengjun Wang [a,b], Chongyang Shen [c], Yan Jin [d], Chunming Su [e], Lingyang Chu [a], Dongmei Zhou [a,*]

[a] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Soil and Water Sciences, China Agricultural University, Beijing 100193, China
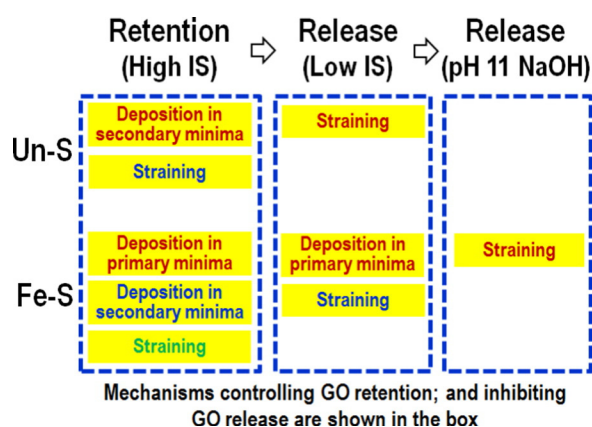[d] Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA
[e] Ground Water and Ecosystems Restoration Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Ada, OK 74820, USA

HIGHLIGHTS

- Retention and release of sheet-shaped GONMs were examined in uncoated and iron oxide-coated sand.
- Surface element integration technique was used to calculate the XDLVO interaction energy.
- Secondary minimum modulated both retention and release of GONMs.
- Aggregation and straining contributed to the hyperexponential retention profiles of GONMs.
- XDLVO theory well-interpreted GONMs' retention and release.

GRAPHICAL ABSTRACT

Mechanisms controlling GO retention; and inhibiting GO release are shown in the box

ARTICLE INFO

ABSTRACT

Understanding the fate and transport including remobilization of graphene oxide nanomaterials (GONMs) in the subsurface would enable us to expedite their benign use and evaluate their environmental impacts and health risks. In this study, the retention and release of GONMs were investigated in water-saturated columns packed with uncoated sand (Un-S) or iron oxide-coated sand (Fe—S) at environmentally relevant solution chemistries (1–100 mM KCl and 0.1–10 mM CaCl$_2$ at pH 7 and 11). Our results showed that increasing ionic strength (IS) inhibited GONMs' transport, and the impact of K$^+$ was less than Ca^{2+}. The positively charged iron oxide coating on sand surfaces immobilized the negatively charged GONMs (pH 7) in the primary minimum, yielding hyperexponential retention profiles particularly in Ca^{2+}. A stepwise decrease in pore-water IS caused detachment of previously retained GONMs. The mass of GONMs released during each detachment step correlated positively with the difference in secondary minimum depth ($\Delta\Phi_{min2}$) at each IS, indicating that the released GONMs were retained in the secondary minimum. While most retained GONMs were re-entrained upon lowering pore-water IS in Un-S, decreasing IS only released limited GONMs in Fe—S, which were captured in the primary minimum. Introducing 1 mM NaOH (pH 11) released most retained GONMs in Fe—S; and average hydrodynamic

* Corresponding author.
E-mail address: dmzhou@issas.ac.cn (D. Zhou).

diameters of the detached GONMs upon injecting NaOH were significantly smaller than those of GONMs in the influent and retentate, suggesting that NaOH induced GONMs disaggregation. Our findings advance current knowledge to better predict NMs' fate and transport under various solution chemistries such as during rainfall events or in the mixing zones between sea water and fresh water where transient IS changes drastically.

1. Introduction

Graphene oxide nanomaterials (GONMs) have sparked great interest due to their novel physicochemical properties, exhibiting potential medical, energy, and environmental applications (Dreyer et al., 2010). Increasing production and use of GONMs elevate the likelihood of their environmental release. Evidence suggests that GONMs have high bacterial toxicity (Akhavan and Ghaderi, 2010) and cytotoxicity (Chang et al., 2011), and can induce severe lung diseases in human (Wang et al., 2011c). Understanding the fate and transport of GONMs is thus critical to promote their benign use and evaluate their environmental impacts and health risks.

Transport of GONMs has been increasingly studied in porous media. Lanphere et al. (2013) showed that transport of GONMs at high ionic strengths (ISs) was limited due to straining. Feriancikova and Xu (2012) observed that increasing IS resulted in greater GONMs deposition. GONMs transport has also been shown to be modulated by other physicochemical factors such as pH (Lanphere et al., 2013), stabilizing agents (natural organic matter), and biofilm and extracellular polymeric substance (He et al., 2015). Surface charge heterogeneity occurs ubiquitously in the subsurface; and patches of iron (Fe) and aluminum (Al) oxides are common forms of surface charge heterogeneity (Johnson and Elimelech, 1995; Johnson et al., 1996; Ryan and Gschwend, 1992). Although surface charge heterogeneity is known to affect colloid (Johnson and Elimelech, 1995; Johnson et al., 1996; Ryan and Gschwend, 1992) and NM (Wang et al., 2012a, 2013) deposition, no investigation has been done deciphering the role of surface charge heterogeneity on GONMs release, which is an important environmental process governing GONMs fate in the subsurface.

Release is the reverse process of deposition that enhances colloid transport in porous media (Ryan and Elimelech, 1996). A perturbation must occur in the system to initiate colloid detachment (Bergendahl and Grasso, 1999, 2000). This perturbation can be a change in chemical factors (thermodynamics) such as pH and IS; or hydrodynamics (flow rate) of the system (Ryan and Elimelech, 1996). For instance, a reduction in pore-water IS induces colloid detachment by altering the electrostatic double layer (EDL) thicknesses and electrostatic interactions between colloids and collectors (Elimelech et al., 1995). The mass of retained colloids that are expected to detach correlates positively with reduction in pore-water IS (ΔIS) (Ryan and Elimelech, 1996). However, the role of changing IS on NMs detachment in porous media is largely obscure.

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) has commonly been applied to interpret colloid transport in porous media. It assumes a perfectly spherical shape for colloids in calculating the interaction energy between colloids and collectors. It is anticipated that, however, the DLVO theory without any modification cannot adequately explain the transport of sheet-shaped GONMs. Shape is also likely to affect retention, release, and retention hysteresis of GONMs without/with surface charge heterogeneity on sand grains (Supplementary Material S1). It is thus critical to understand how particle shape alters retention, release, and retention hysteresis of sheet-like GONMs in porous media without/with surface charge heterogeneity.

The objectives of this study were to: (1) investigate retention of GONMs in saturated sand columns without/with surface charge heterogeneity using uncoated and iron oxide-coated sand; (2) examine release of retained GONMs upon stepwise lowering pore-water IS or injecting 1 mM NaOH; and (3) verify whether the DLVO theory well-interprets retention and release of GONMs and probe whether particle shape influences GONMs' retention and release in saturated porous media without/with surface charge heterogeneity.

2. Materials and methods

2.1. GONMs influent suspensions

GONMs stock suspension (2 g L^{-1}) was purchased from XFNANO Materials Technology Co., Ltd., Nanjing, China. The manufacturer reported that the GONMs were primarily (>99%) single-layered with lateral diameter of 1–5 μm and layer thickness of 0.8–1.2 nm according to transmission electron microscope (TEM) and atomic force microscope (AFM) measurements (Supplementary Material S2). The TEM sizes of GONMs were verified using JEM-2100 TEM (JEOL, Japan). The characteristic absorption wavelength of GONMs was determined at 227 nm using the UV–vis spectrophotometer (Model UV-3000D, Mapada Instruments Co., Ltd., Shanghai, China). Before preparing GONMs influent suspension, GONMs stock suspension was sonicated in a water bath at 100 W and 45 kHz (Model KQ-3000 VDE, Kunshan Sonicator Co., Ltd., Shanghai, China) for 30 min to disperse the GONMs. An aliquot of the dispersed GONMs stock suspension was then transferred to electrolyte solutions with environmentally relevant ISs (1, 10, 50, and 100 mM KCl; and 0.1, 0.5, 1.0, and 10 mM $CaCl_2$) (Stumm and Morgan, 1995). The resulting concentration of GONMs in the influent suspension was 10 mg L^{-1}. The pH of GONMs influent suspensions was adjusted to 7.0 ± 0.2 using 1 mM HCl or NaOH.

Physicochemical properties including electrophoretic mobility (EM) and average hydrodynamic diameter (D_H) of GONMs in the influent were characterized. The EMs of GONMs in the influents were measured using a NanoBrook 90Plus PALS Particle Size and Zeta Potential Analyzer (Brookhaven Instruments Corporation, Holtsville, NY). The D_H GONMs in the influents were determined using the same Particle Size and Zeta Potential Analyzer. Three replicates were performed for the EM and D_H measurements and mean values ± standard deviations were reported. In this study, the hydrodynamic diameter of GONMs (not TEM size) was used to determine the interaction energy between GONMs and uncoated sand and between GONMs and iron oxide using the extended DLVO (XDLVO) theory (described below) because hydrodynamic diameter is more relevant to colloid Brownian motion (Elimelech et al., 1995).

2.2. Porous media

Quartz sand was used as a model granular porous medium. Quartz sand (purity > 99%) with size of 0.60–0.70 mm (average diameter = 0.65 mm) was obtained from Sinopharm Chemical Co., Ltd., Beijing, China. Prior to use, the sand was thoroughly cleaned using a sequential acid-base procedure (1 M HCl and 1 M NaOH) (Wang et al., 2012a; Zhou et al., 2011). The cleaned sand (designated as uncoated sand; Un-S) was observed to exhibit various degrees of surface roughness (Supplementary Material S3) (Wang et al., 2011b).

To examine the role of surface charge heterogeneity, iron oxide coating (Cornell and Schwertmann, 2003; Johnson et al., 1996) in the retention and release of GONMs, a portion of the cleaned sand (Un-S) was coated with iron oxide (designated as iron oxide-coated sand; Fe—S); and detailed coating procedures were given in Supplementary Material