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

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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 CaCl₂ at pH 7 and 11). Our results showed that increasing ionic strength (IS) inhibited GONMs' transport, and the impact of K⁺ was less than Ca²⁺. 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 Ca²⁺. 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 ($\Phi_{\min 2}$) 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 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.

Graphical Abstract

Keywords

Graphene oxide nanomaterials; Uncoated and iron oxide-coated sand; Transient solution chemistry; Retention; Release; Surface element integration

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. Feriencikova 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, Wang et al., 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, Bergendahl and Grasso, 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 (IS) (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 of 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 $\pm$ 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 S4. Physicochemical properties of the iron oxide coating have been characterized previously (Wang et al., 2012b). The iron oxide was hematite based on X-ray photoelectron spectroscopy (XPS) analysis. Careful examinations of Fe—S using SEM-EDX (scanning electron microscope energy dispersive X-ray) combined with chemical analyses indicate that $75 \pm 3\%$ of the sand surfaces were covered by hematite (Supplementary Material S3). To accurately assess the impact of hematite coating on the retention and release of GONMs, the hematite used for pH_{PZC} measurements was synthesized using the same procedure as used in the preparation of Fe—S (Supplementary Material S4) but without adding Un-S in the reaction solution. The pH_{PZC} of hematite was determined by measuring the ζ -potential of hematite suspension at varying pH conditions (pH: 4–11) and was found to be at pH 8.4 (Wang et al., 2012a).

The ζ -potentials of Un-S and hematite at employed solution chemistries were determined using the Particle Size and Zeta Potential Analyzer described above. Colloidal particles ($< 2 \mu\text{m}$) from pulverized Un-S were used as surrogates for ζ -potential measurements (Elimelech et al., 1995, Zhou et al., 2011). In comparison, a gentle low-powered sonication method was employed to obtain the colloidal fraction of hematite-quartz mixture that was used for ζ -potential measurements representing Fe—S. Briefly, the Fe—S was transferred into

employed electrolyte solution, and the as-prepared solution was then sonicated in a water bath at 20 W and 45 kHz twice (1 h each time). Colloidal hematite-quartz mixture was obtained from the supernatant of the solution and was used for ζ -potential measurements (three replicates were performed).

2.3. GONMs retention and release experiments

GONMs retention and release experiments were conducted using a glass chromatography column with 2.6-cm inner diameter and 20-cm long. The column was packed with either Un-S or Fe—S. Column packing procedures were reported in our previous studies (Wang et al., 2011b); and porosity of the packed column was determined gravimetrically to be ~ 0.40 .

Two sets of experiments, retention-excavation (first-set) and retention-release-excavation (second-set) experiments, were done to explore mechanisms controlling GONMs retention and remobilization. Each column was first conditioned by injecting 10 pore volumes (PVs) of pH 7.0 DI water, followed by 5 PVs of GONMs-free background electrolyte (pH 7.0 KCl or CaCl_2) to standardize pore-water solution chemistry. Several PVs of GONMs influent at employed solution chemistries (1, 10, 50, and 100 mM KCl; and 0.1, 0.5, 1.0, and 10 mM CaCl_2 at pH 7.0) were then injected into the column, followed by elution with GONMs-free background electrolyte. The experiments are referred to as GONMs retention experiments. The Darcy velocity used was $0.0188 \text{ cm min}^{-1}$, controlled with a peristaltic pump.

For the second-set experiments, a stepwise reduction in pore-water IS was performed to release retained GONMs by sequentially injecting lower IS background electrolyte, which is referred to as GONMs release experiments. For example, in Un-S, when the initial influent IS of GONMs was 100 mM KCl during retention experiment, 50 mM KCl, 10 mM KCl, 1 mM KCl, and DI water (pH 7.0) were sequentially injected to initiate GONMs release. The DI water was chosen as the final eluting solution in Un-S to eliminate the secondary minimum (Hahn and O'Melia, 2004, Redman et al., 2004, Shen et al., 2007). In Fe—S experiments, an additional phase (1 mM NaOH at pH 11) was injected in the column following the introduction of DI water to create highly unfavorable conditions (Bradford and Kim, 2012, Zhou et al., 2011), and release retained GONMs by hematite. The effluents of retention and release experiments were collected using a fraction collector. The effluent GONMs concentration was determined spectrophotometrically at the wavelength of 227 nm. To understand the retention and release mechanisms of GONMs, the D_H values of GONMs in selected effluents and retentates collected during retention and release experiments were determined using the procedure described above.

After completion of GONMs retention and release experiments, the retention profiles of GONMs were determined using a protocol similar to that of Bradford et al. (2002). Briefly, the sand was carefully excavated from the column and segmented into 2-cm fractions. Each segment was immersed into 25 mL of DI water (pH 7.0) and gently mixed for 2 h to liberate GONMs that were retained due to pore structure restriction (e.g., straining) (Bradford et al., 2002, Xu et al., 2006). In Fe—S, 1 mM NaOH (pH 11) was chosen as the eluent instead of DI water to release the retained GONMs. The concentration of GONMs in the supernatant for each segment was determined spectrophotometrically.

2.4. XDLVO interaction energy calculation

The XDLVO theory was used to calculate the total interaction (U) between GONMs and Un-S and between GONMs and hematite as the sum of van der Waals attractive interaction (U^{VDW}), electrostatic double layer interaction (U^{EDL}), Born repulsive (U^{BR}), and hydration repulsive (U^{HR}) interaction (Pazmino et al., 2014). The surface element integration (SEI) method (Bhattacharjee and Elimelech, 1997, Bhattacharjee et al., 1998) was employed to compute the interaction energy (E) at employed solution chemistries. Given that GO is a carbon sheet with the identical length of carbon bond, a cuboid-plate configuration was used to calculate the interaction energy (Supplementary Material S5). For SEI calculation, the GONMs, Un-S, or hematite surfaces were discretized into small area elements. The total interaction energy was determined as the sum of differential interaction energy ($E^{VDW} + E^{EDL} + E^{BR} + E^{HR}$) between each area element on the NM surface and the corresponding area element (projected area of the element) on the sand/hematite surface. The governing equations for calculating E^{VDW} , E^{EDL} , E^{BR} , and E^{HR} are provided in Supplementary Material S5 and Table S1. The SEI technique can accurately determine the interaction energy between GO and Un-S (or hematite) with a plate shape (Bhattacharjee and Elimelech, 1997, Bhattacharjee et al., 1998).

2.5. Statistical analysis

The one-way analysis of variance (ANOVA) was conducted to identify statistically significant differences in measured parameters. Mean separations were performed using Tukey's honestly significant difference (HSD) test. All statistical analyses were conducted using SPSS 16.0 software and the differences were considered significant at $p < 0.05$.

3. Results and discussion

3.1. Physicochemical properties of GONMs influent and sand grain

Morphology and particle size of GONMs determined by TEM (Supplementary Material S6) show that the GONMs were sheet-shaped with lateral diameter of 1.2–4.5 μm , consistent with the data reported by the manufacturer. The ζ -potentials of GONMs, sand grains, and hematite at varying solution chemistries (pH 7.0) are presented in Fig. 1, which shows that the GONMs and sand grains were negatively charged and their ζ -potentials became progressively less negative with increasing IS (Fig. 1). In contrast, the hematite was positively charged and became less positive with increasing IS. Moreover, divalent Ca^{2+} had a more marked impact than monovalent K^+ in reducing GONMs ζ -potential, as indicated by the larger linear slope of ζ -potential vs. IS in Ca^{2+} than in K^+ (i.e., $0.86 > 0.12$; Supplementary Material S7). This is largely due to charge screening (for K^+ and Ca^{2+}) and charge neutralization (for Ca^{2+} only) effects (Elimelech et al., 1995). Similar results were reported for GONMs (Feriancikova and Xu, 2012, Lanphere et al., 2013, Wu et al., 2013), cleaned sand (He et al., 2015, Torkzaban et al., 2010, Zhou et al., 2011), and iron oxide-coated sand (Wang et al., 2012a, Wang et al., 2012b). While surface charge heterogeneity (hematite coating) was reported to have a minor impact on the ζ -potential of collector (Elimelech et al., 2000), our results show that the ζ -potential of Fe—S was less negative compared to that of Un-S at a given IS (e.g., -19.4 mV vs. -77.5 mV when IS was 1 mM KCl at pH 7.0; Fig. 1). Note Fe—S was negatively charged at employed solution

chemistries, likely because the negatively charged quartz sand dominated the overall ζ -potential of Fe—S. Elimelech et al. (2000) also found that the mixtures of clean sands and aminosilane (positively charged)-coated sands (75% aminosilane coating) were negatively charged when solution pH was above 6.5 using a streaming potential analyzer.

Fig. 1 also presents GONMs D_H in the influents under different solution chemistries. Consistent with previous findings at various electrolyte (e.g., K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) concentrations (Lanphere et al., 2013, Wu et al., 2013), increasing IS caused greater aggregation and larger D_H for the GONMs. The linear slope of D_H vs. IS was substantially higher in Ca^{2+} than in K^+ (i.e., $95 > 3.6$; Supplementary Material S7), confirming that Ca^{2+} significantly promoted aggregation of GONMs. This is due to cross-linking between GONMs sheets by Ca^{2+} via bridging of carboxylic functional groups (e.g., $-COOH^-$) at the edges, i.e., edge-to-edge aggregation (Chowdhury et al., 2015, Ren et al., 2014, Wu et al., 2013).

3.2. Retention of GONMs

Breakthrough curves (BTCs) and retention profiles (RPs) of GONMs under different KCl and $CaCl_2$ concentrations in Un-S and Fe—S for the first-set experiments are shown in Fig. 2. Virtually all of the injected GONMs were recovered in the column experiments, confirming a high reliability of our experimental procedures and protocols (Table 1). Retention of GONMs increased with increasing influent IS (Fig. 2). Similar results have been documented for GONMs (Feriancikova and Xu, 2012, Lanphere et al., 2013) and other types of colloids/NMs (e.g., hydroxyapatite) (Wang et al., 2011a, Wang et al., 2011b). The XDLVO interaction energies between GONMs and Un-S at employed solution chemistries are shown in Supplementary Material S8; and primary minimum (Φ_{pri}), maximum energy barrier (Φ_{max}), and secondary minimum (Φ_{min2}) are provided in Table S2. Our calculations show that: (i) the depth of secondary minimum increased and the distance became closer to the grain surface as IS increased, consistent with previous findings (Hahn and O'Melia, 2004, Redman et al., 2004, Shen et al., 2007); and (ii) the Φ_{max} was huge especially in KCl, which is substantially greater than the average kinetic energy of a colloid ($1.5 kT$; where k is the Boltzmann constant and T is the absolute temperature), meaning that the GONMs could not overcome the high energy barrier and be deposited in the primary minimum via random Brownian motion (Hahn and O'Melia, 2004). Hence, the GONMs are expected to be trapped mainly in the secondary minimum and the trapping is more significant at higher ISs due to the deeper and closer secondary minimum. Recent studies suggest that particles retained in the secondary minimum can be translated along the grain surfaces due to hydrodynamic forces until they are recaptured into low-velocity locations such as grain-grain contacts, eddy zones, and surface roughness locations (Torkzaban et al., 2010). Therefore, greater GONMs retained in the secondary minimum are likely to be translocated to these low-velocity locations at higher ISs, further enhancing the retention of GONMs. The impact of Ca^{2+} on GONMs retention is greater as indicated by the larger slope (absolute value) between M_{eff} and IS in $CaCl_2$ than in KCl (Supplementary Material S9). This is because larger aggregated particles are more easily retained in porous media due to greater gravitational effect based on the colloid filtration theory (CFT) (Yao et al., 1971).

The BTCs show that blocking (a decreasing rate of retention with time; Fig. 2) occurred in Un-S because the sites for GONMs retention were limited and were progressively occupied (Wang et al., 2012a). Interestingly, the RPs of GONMs evolved from linear (1 mM KCl; Fig. 2b) to exponential (10 mM KCl) and then to hyperexponential (50 and 100 mM KCl) with depth as influent IS increased in Un-S. Enhanced aggregation of GONMs (Fig. 1) and straining particularly close to the column inlet were responsible for the transformation of RPs vs. IS (Bradford et al., 2002, Wang et al., 2015). The D_H values of GONMs in the influent, effluent, and retentate in Un-S are given in Supplementary Material S10, which shows that D_H values varied in the order: effluent < influent < retentate. These observations reflect that larger GONMs were more efficiently retained in the column during transport, i.e., larger GONM aggregates were preferentially retained particularly near the column inlet, whereas smaller ones eluted out, developing the size-selective retention (Wang et al., 2015). This retention effect became more significant ($p < 0.05$) at higher ISs (S10), contributing to the hyperexponential RPs (Fig. 2).

Surface charge heterogeneity (hematite coating) had a marked impact on GONMs retention (Fig. 2e–h). At a given IS, the mobility of GONMs was lower in Fe—S than in Un-S (Table 1). The XDLVO interaction energies between GONMs and hematite at varying solution chemistries are given in Table S3, in which the surface charge heterogeneity (S_{hetero}) is assumed as square-in-shape with surface areas of 1×1 , 10×10 , 50×50 , 100×100 , 200×200 , and $500 \times 500 \text{ nm}^2$, respectively. The results show that when the S_{hetero} located within the nanoscale range ($< 200 \times 200 \text{ nm}^2$), increasing S_{hetero} had a minor influence on the change of Φ_{max} . However, when S_{hetero} reached sub-microscale range ($500 \times 500 \text{ nm}^2$), the Φ_{max} decreased rapidly to 0 and thus substantial amounts of GONMs can be retained in the primary minimum. GONMs can also be retained at the secondary minimum in Fe—S when the S_{hetero} was at the nanoscale or absent. Our data also show that the primary minimum was very deep (on the magnitude of -10^{-5} to $-10^{-6} kT$; Table S3) and became even deeper as the influent IS increased. These results suggest that most retained GONMs were captured in the primary minimum where sub-microscale heterogeneity dominated and greater GONMs are expected to be retained in the primary minimum at higher ISs. The secondary minimum became deeper with increasing ISs, acting as a larger reservoir in capturing GONMs at higher ISs.

The relationship of M_{eff} vs. IS in Fe—S is presented in Supplementary Material S9, which again confirms that Ca^{2+} reduced the mobility of GONMs to a greater extent than K^+ . The hyperexponential RPs of GONMs became significantly more pronounced in Fe—S than in Un-S (Fig. 2f and h). This is likely because surface charge heterogeneity caused more retention of GONMs and the retained GONMs narrowed down the pore throats that further induced GONMs retention via straining. Hence, surface charge heterogeneity aggravated straining. Indeed, the D_H of GONMs in the influent, effluent, and retentate in Fe—S depicted in S10 clearly indicate that size-selective retention occurred in Fe—S particularly at higher ISs. Interestingly, once the effect of size-selective retention was significant ($p < 0.05$; S10), the hyperexponential RPs occurred (Fig. 2). Thus, the size-selective retention due to straining likely contributed to the hyperexponential RPs of GONMs.

Relationship of secondary minimum ($\Phi_{\min 2}$) and retained mass of GONMs (M_{sand} ; Table 1) under different KCl and CaCl_2 concentrations in Un-S and Fe—S is shown in Fig. 3a. A strong linear correlation existed between $\Phi_{\min 2}$ and M_{sand} , confirming that the secondary minimum was the main pool in capturing GONMs. The linear slope of $\Phi_{\min 2}$ vs. M_{sand} was higher in Un-S than in Fe—S for a specific cation type, signifying a greater role of secondary minimum in Un-S than Fe—S. This is anticipated because in the presence of hematite, the GONMs are more likely to be trapped in the primary minimum than secondary minimum. Furthermore, the slope was larger in Ca^{2+} than in K^+ (Fig. 3a), implying that secondary minimum played a more pivotal role in CaCl_2 compared to KCl, which is within the framework of DLVO (XDLVO) theory.

3.3. Release of GONMs

Fig. 4, Fig. 5 present retention and release of GONMs under different KCl and CaCl_2 concentrations in Un-S and Fe—S, respectively, in the second-set experiments. A stepwise reduction in IS caused sequential detachment of retained GONMs (Figs. 4a, b and 5a, b). Greater GONMs were re-entrained in K^+ than in Ca^{2+} in Un-S (Fig. 4a, b and Table 1), suggesting that larger aggregated GONMs (Ca^{2+}) were less likely to be released upon lowering pore-water IS. Similar detachment behaviors of colloids upon decreasing pore-water ISs have been reported in saturated sands (Bradford and Kim, 2012, Torkzaban et al., 2010). Interestingly, for both Un-S and Fe—S, the release of retained GONMs during successive detachment processes exhibited some clear trends that have not been reported previously. The released GONMs in the effluent during each detachment step decreased progressively when successively lowering pore-water IS. Similarly, the maximum C_i/C_0 value of GONMs during each detachment step decreased gradually. During a specific detachment step, a larger portion of GONMs was released if greater GONMs were initially retained in the column; e.g., injecting DI water released 2.3%, 3.0%, 7.8%, and 8.5% of GONMs when the initial influent IS was 1, 10, 50, and 100 mM KCl, respectively (Fig. 4a and Table 1).

The magnitude of colloids released from primary and secondary minima upon changing IS correlates with the decrease of $\Phi_{\max} - \Phi_{\text{pri}}$ (detachment energy barrier from primary minimum) and $\Phi_{\min 2}$ (detachment energy barrier from secondary minimum), respectively (Ryan and Elimelech, 1996). A linear correlation occurred between the difference in secondary minimum depth ($\Phi_{\min 2}$; the decrease of secondary minimum depth due to decreasing IS) and the overall released mass of GONMs in both Un-S and Fe—S (Fig. 3b). Consistent with the results of $\Phi_{\min 2}$ vs. M_{sand} (Fig. 3a), the slope was larger in Ca^{2+} and in Un-S (Fig. 3b). A higher slope in Ca^{2+} than in K^+ indicates that retained GONMs were easier to be released when injecting a low IS of CaCl_2 than KCl, again due to greater aggregation of GONMs in Ca^{2+} than in K^+ .

Substantial amounts of retained GONMs were re-entrained upon introducing 1 mM NaOH; and again larger portions of GONMs were re-entrained when the initial influent ISs were higher. The NaOH released 22.9–44.4% and 33.6–40.7% of the injected GONMs in Fe—S under different KCl and CaCl_2 concentrations, respectively (Fig. 5 and Table 1). In comparison, 8.3–45.6% and 35.1–61.8%, respectively, of the injected GONMs were still

retained in the column at varying KCl and CaCl₂ concentrations due to the presence of hematite coating (described in Section 3.2). These data show that pH 11 NaOH solution cannot release all the retained GONMs due to the hematite coating especially in Ca²⁺, likely because some of the GONMs are attached in the primary minimum and straining is also involved in GONMs retention.

The RPs of GONMs shown in Fig. 2, Fig. 4, Fig. 5 provide important information for a more complete understanding of GONMs retention and release. When the influent IS was low, decreasing solution IS gradually released GONMs that were previously retained in the secondary minimum in Un-S, developing the linear RPs (1–10 mM KCl and 0.1–1.0 mM CaCl₂; Fig. 4b, d). Although hyperexponential RPs still occurred after the completion of detachment experiments in Un-S when the influent IS was high, the extent of the hyperexponential RPs was weakened significantly (50–100 mM KCl and 10 mM CaCl₂; Figs. 2b, d and 4b, d). The D_H values of GONMs in the influents (Fig. 1) and retentates (S10) were substantially larger at higher ISs; and thus straining was more pronounced at higher ISs. It is expected that the GONMs captured by straining were less likely to be re-entrained back to the pore-water compared to those retained in the secondary minimum (Jaisi and Elimelech, 2009). Therefore, the hyperexponential RPs became less pronounced when lowering pore-water IS in Un-S but could not transform into the linear RPs when the initial influent IS was high, due to the appreciable contribution of straining. By comparison, in Fe—S, the hyperexponential RPs frequently occurred even after injecting 1 mM NaOH (Fig. 5b, d). Consistent with the results obtained in the first-set experiments (Fig. 2b, d, f, and h), the retention of GONMs throughout the column profile was again greater in Fe—S than in Un-S (Figs. 4b, d) due, likely, to greater straining in Fe—S than in Un-S.

The D_H values of GONMs in the influents, effluents collected from detachment experiments (designated as effluent_IS and effluent_NaOH, respectively, when the detachment is initiated by lowering transient IS or injecting NaOH), and retentates under different KCl and CaCl₂ concentrations in Un-S and Fe—S are shown in Fig. 6. In Un-S, the D_H value of GONMs varied in the following order: influent < effluent_IS < retentate; and this size fractionation effect became more significant ($p < 0.05$) at higher ISs (Fig. 6a, b). The observations suggest that lowering IS alleviated the extent of GONMs aggregation among retentate populations. Similarly, in Fe—S, the D_H value followed the same order: influent < effluent_IS < retentate (Fig. 6c, d). Interestingly, the D_H value of detached GONMs caused by injection of 1 mM NaOH (effluent_NaOH) was much smaller than that of GONMs in the influent particularly at high ISs (Fig. 6c d). Upon injecting the NaOH solution, the EDLs of negatively charged GONMs and hematite were expanded and the ζ^{EDL} between GONMs and between GONMs and hematite was elevated accordingly, thereby promoting GONMs disaggregation. These disaggregated thus smaller GONMs have high mobility and are easily released and detected in the effluents.

3.4. Retention hysteresis of GONMs

Retention hysteresis occurs in column studies under transient solution chemistry for spherical colloids; and hysteresis becomes more significant at higher ISs (Bergendahl and Grasso, 1999, Bergendahl and Grasso, 2000, Bradford and Kim, 2012, Torkzaban et al.,

2010). It is therefore worthy of investigation whether retention hysteresis occurs for the sheet GONMs. The GONMs mass recoveries in the effluents (M_{eff}) during retention and detachment experiments in Un-S and Fe—S are provided in Supplementary Material Table S4. The M_{eff} refers to the M_{eff} difference between direct retention of GONMs at relatively low influent ISs (e.g., 1 mM KCl) and initially deposited at high ISs (e.g., 10 mM KCl) and then detached at the same low IS (i.e., 1 mM KCl); and $M_{\text{eff}} > 0$ indicates that the retention hysteresis occurs. Our measurements show that the hysteresis of GONMs occurred in both Un-S and Fe—S. The correlation of M_{eff} vs. IS in Un-S and Fe—S is presented in Supplementary Material S11. A positive correlation existed between M_{eff} and IS; and the linear slope was higher in Ca^{2+} than in K^{+} . These observations suggest that greater GONMs among retentate populations became undetachable as influent IS increased particularly in CaCl_2 due to the greater contribution of primary minimum, straining, and (or) low-velocity region in GONMs retention. However, the hysteresis was less significant in Fe—S than in Un-S, as reflected by the low slope in the presence of hematite coating. These results are consistent with the results of M_{eff} vs. IS (Supplementary Material S9) because irreversible retention dominated the retention of GONMs due to the presence of surface charge heterogeneity. Our findings confirm that retention hysteresis also occurred for sheet-like GONMs, and the extent of hysteresis depended on solution chemistry and collector type.

Straining has been demonstrated to account for the hyperexponential RPs (Bradford et al., 2002). For spherical colloids, Bradford et al. (2002) first reported that when the diameter ratio (d_c/d_g) of colloid (d_c) to collector grain (d_g) was 0.002, straining was considered to be insignificant. Please note that the sand collector used in Bradford et al. (2002) was not cleaned thoroughly, so the value of d_c/d_g was underestimated because the impurities (e.g., Fe/Al oxides) sorbed on the collector surfaces immobilized certain amount colloids. By using the cleaned sand grain, Xu et al. (2006) reported that straining started to play a critical role when the d_c/d_g value was 0.008 for spherical colloids. For tubular carbon nanotube (CNT), Thus far, however, no d_c/d_g data has been proposed to account for the retention particularly the hyperexponential RPs of sheet GONMs in porous media. In this study, the hyperexponential RPs occurred when the influent ISs were 50 and 100 mM KCl and 10 mM CaCl_2 in Un-S (Figs. 2b, d and 4b, d). The values of d_c/d_g were calculated to be 0.0013, 0.0016, and 0.0028, respectively (Supplementary Material Table S5), when the influent ISs were 50 and 100 mM KCl, and 10 mM CaCl_2 , using the D_H value of GONMs in the influents (Fig. 1) as d_c . We propose that the threshold value of d_c/d_g is 0.0013 for sheet-like GONMs, above which the hyperexponential RP is likely to occur.

Particle shape plays a critical role in the retention and release of colloids in porous media (Liu et al., 2010, Seymour et al., 2013). Liu et al. (2010) found that retention of spherical- and rod-colloids occurred in secondary minimum and in both primary and secondary minima, respectively; and straining was less for rod colloids compared with spherical ones. Seymour et al. (2013) reported that deposition of spherical colloids was much greater than rod colloids under favorable conditions because rod ones can counterbalance the attractive energies due to higher hydrodynamic forces and torques (Shen et al., 2012). In this study, while we did not investigate the retention and release of spherical colloids in our column system, some general conclusions can still be reached including: (1) the GONMs were highly mobile in Un-S at low influent ISs (Fig. 2) due to the high hydrodynamic forces/

torques acting on the sheet GONMs (S1); (2) the contribution of straining in GONMs retention was relatively small in Un-S at low influent ISs (Liu et al., 2010), despite straining was pronounced in the copresence of Fe coating and high concentrations of Ca^{2+} (Fig. 2); (3) retained GONMs were likely to be released from both primary and secondary minima upon lowering pore-water ISs (Liu et al., 2010); and (4) retention, release, and retention hysteresis of GONMs were expected to be less sensitive to surface charge heterogeneity (Fe coating) than those of spherical colloids, likely due to the effects of hydrodynamic interaction and XDLVO-type interaction described above (Shen et al., 2013).

4. Conclusions

Column experiments were used to unravel GONMs retention and release in Un-S and Fe—S at environment-relevant solution chemistries. XDLVO theory calculations indicate that sub-microscale heterogeneity dominated GONMs retention in Fe—S. A strong positive correlation occurred between the secondary minimum ($\Phi_{\text{min}2}$) and retained mass (M_{sand}) of GONMs in both Un-S and Fe—S, indicative of the reservoir role of secondary minimum in capturing GONMs. Furthermore, the linear slope of $\Phi_{\text{min}2}$ vs. M_{sand} was larger in Un-S than in Fe—S, because the primary minimum determined the retention of GONMs in the presence of hematite coating. These findings demonstrate that XDLVO theory can adequately describe the retention and release behaviors of GONMs at varying solution chemistries when calculations are based on the actual shape of the GONMs.

A similar positive correlation existed between the difference in secondary minimum depth ($\Phi_{\text{min}2}$) and released mass of GONMs (M_{eff}) during successive detachment experiments, substantiating that secondary minimum also mediated the release of GONMs in Un-S. However, substantial amounts of GONMs were not re-entrained upon injecting DI water in Fe—S due to irreversible retention of GONMs in the primary minimum and strong straining. Most GONMs were detached upon injecting 1 mM NaOH due mainly to the enhanced repulsive interaction energy between GONMs and sand grains under highly unfavorable conditions (pH 11). The threshold value of the diameter ratio of colloid and collector was determined to be 0.0013 for sheet-like GONMs, above which the hyperexponential RP started to occur.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

ζ -potential (left y-axis) of GONMs, uncoated sand (Un-S), iron oxide-coated sand (Fe-S), and hematite; and average hydrodynamic diameter (D_H ; right y-axis) of GONMs under different KCl (1, 10, 50, and 100 mM; a) and CaCl_2 concentrations (0.1, 0.5, 1.0, and 10 mM; b) at pH 7.0. Error bars represent standard deviations in triplicate experiments. Note x-axis is shown in log-scale.

Fig. 2.

Retention-excitation experiments (the first-set experiments): breakthrough curves (BTCs; a, c, e, and g) and retention profiles (RPs; b, d, f, and h) of GONMs (10 mg L⁻¹ at pH 7.0) under different KCl (1, 10, 50, and 100 mM; a, b, e, and f) and CaCl₂ concentrations (0.1, 0.5, 1.0, and 10 mM; c, d, g, and h) from Un-S (a–d) and Fe–S (e–h), respectively. In this figure (a, c, e, and g), the normalized concentration (C_i/C_0) of GONMs is plotted as a function of eluted pore volume (PV). In this figure (b, d, f, and h), the normalized solid-phase concentration (S/C_0) of retained GONMs is plotted as a function of distance from the column inlet.

Fig. 3.

Relationship between secondary minimum ($\Phi_{\min 2}$) and retained mass of GONMs (M_{sand} ; see Table 1) during retention in the first-set experiments (a); and relationship between difference in secondary minimum depth ($\Delta \Phi_{\min 2}$) and released mass of GONMs (M_{eff} ; see Table 1) during successive release of the second-set experiments (b) under different KCl (1, 10, 50, and 100 mM) and CaCl₂ concentrations (0.1, 0.5, 1.0, and 10 mM) at pH 7.0 in Un-S and Fe—S. Pearson's r is shown in this figure. The values of secondary minimum during retention and successive release experiments are summarized in Tables S2–S3.

Fig. 4.

Retention-release-excitation experiments in Un-S (the second-set experiments): normalized effluent concentration of GONMs versus eluted PV (a, c) and retained mass of GONMs after the successive release versus distance (b, d) for transient IS experiments in saturated columns packed with Un-S. During retention experiment, 3 PVs of GONMs influent suspensions (10 mg L^{-1} at pH 7.0) were injected in the column followed by elution with GONMs-free background electrolyte solution. During successive detachment experiment, a stepwise reduction in IS was performed to release previously retained GONMs, as shown in (a, c). For example, when the initial influent IS was 100 mM KCl; 50 mM KCl, 10 mM KCl, 1 mM KCl, and DI water (all at pH 7.0) were sequentially injected during detachment experiment to initiate GONMs release (a).

Fig. 5. Retention-release-excavation experiments in Fe—S (the second-set experiments): normalized effluent concentration of GONMs versus PV (a, c) and retained mass of GONMs versus distance (b, d) for transient IS experiments in saturated column packed with Fe—S. During retention experiment, 4 PVs of GONMs influent suspensions (10 mg L^{-1} at pH 7.0) were injected in the column followed by elution with GONMs-free background electrolyte. During successive release experiment, a stepwise reduction in IS was performed to re-entrain previously retained GONMs, as shown in (a, c). For example, 50 mM KCl, 10 mM KCl, 1 mM KCl, DI water (all at pH 7.0), and 1 mM NaOH (pH 11) were sequentially injected during release experiment to initiate GONMs release when the initial influent IS was 100 mM KCl.

Fig. 6.

Average hydrodynamic diameter (D_H) of GONMs in the influents, effluents (via decreasing pore-water IS or injecting 1 mM NaOH; designated as effluent_IS or effluent_NaOH, respectively), and retentates during retention and release experiments under different KCl (1, 10, 50, and 100 mM; a, c) and CaCl_2 concentrations (0.1, 0.5, 1.0, and 10 mM; b, d) at pH 7.0 in Un-S (a, b) and Fe—S (c, d), respectively. Error bars represent standard deviations in triplicate experiments. The ANOVA was conducted to identify statistically significant difference and difference was considered significant at $p < 0.05$.

Table 1.

Experimental conditions and mass balances of graphene oxide nanomaterials (GONMs) retention, and retention and successive detachment under different KCl and CaCl₂ concentrations in uncoated sand (Un-S) and iron oxide-coated sand (Fe__S).

Collector	IS (mM)	M _{eff} in KCl tests (%)					M _{sand} (%)	M _{total} (%)	M _{eff} in CaCl ₂ tests (%)					M _{sand} (%)	M _{total} (%)
		100	50	10	1	DI			10	1	0.5	0.1	DI		
Un-S	KCl Retention	1			98.1		2.9	101							
		10		93.8			7.2	101							
		50	51.6				48.4	100							
		100	36.9				63.1	100							
	KCl Release	1			98.1	2.3	0.74	101							
		10		93.8	3.4	3.0	1.0	101							
		50	51.6	12.0	9.2	7.8	18.5	99.1							
		100	36.9	13.6	10.2	8.5	19.2	101							
	CaCl ₂ Retention	0.1										97.8		3.1	101
		0.5								88.7	94.6			6.4	101
		1.0												12.3	101
		10							50.3					49.6	100
	CaCl ₂ Release	0.1										97.8	2.3	0.57	101
		0.5									94.6	3.0	2.8	0.87	101
		1.0								88.7	4.8	3.8	3.2	1.1	102
		10							50.3	11.7	8.7	6.9	6.1	16.4	100
Fe__S	KCl Retention	1			55.4		44.6	100							
		10		48.2			51.8	100							
		50	43.3				56.7	100							
		100	13.7				86.3	100							
	KCl Release	1			55.4	2.4	15.4	96.1							
		10		48.2	3.2	2.8	18.5	98.4							
		50	43.3	3.5	3.4	2.8	20.2	99.8							

Collector	IS (mM)	M _{eff} in KCl tests (%)							M _{sand} (%)	M _{total} (%)	M _{eff} in CaCl ₂ tests (%)							M _{sand} (%)	M _{total} (%)	
		M _{eff} in KCl tests (%)									M _{eff} in CaCl ₂ tests (%)									
		100	50	10	1	DI	NaOH				10	1	0.5	0.1	DI	NaOH				
		100	13.7	4.5	3.9	3.6	3.4	44.4	27.4	101										
	CaCl ₂ Retention	0.1													48.1	54.6			45.4	100
		0.5												26.9				51.9	100	
		1.0																73.2	100	
		10									15.2							84.8	100	
	CaCl ₂ Release	0.1													48.1	54.6	2.4	33.6	12.3	103
		0.5													26.9	3.2	2.9	34.9	14.0	103
		1.0												15.2	9.5	4.4	3.3	38.4	20.6	103
		10													11.2	10.3	4.0	40.7	21.6	108

M_{eff} , M_{sand} , and M_{total} are mass percentages of GONMs recovered from the effluent, sand, and total, respectively.