



# Deposition and remobilization of graphene oxide within saturated sand packs

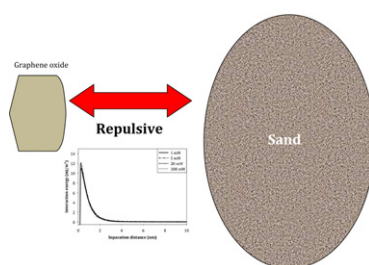
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## HIGHLIGHTS

- ▶ Graphene oxide displays high mobility within saturated sand packs.
- ▶ The immobilization of graphene oxide by quartz sands is reversible.
- ▶ The transport behavior of graphene oxide within saturated sand packs can be described by a Langmuir-type mathematical model.
- ▶ The extended DLVO theory can explain the observed trends in the mobility of graphene oxide within saturated quartz sands.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this research, we examined the deposition kinetics of graphene oxide (GO) particles within saturated sand packs as a function of ionic strength as well as the remobilization of previously retained GO particles due to chemical perturbation. The retention of GO particles within saturated quartz sand was found to be strongly dependent on ionic strength. At low ionic strength (e.g., 1 mM of NaCl), little retention of GO particles occurred. When the ionic strength was increased to 100 mM of NaCl, the retention of GO particles increased significantly but would be limited by its retention capacity. The reduction of ionic strength from 100 mM (NaCl) to 1 mM (NaCl) released ~100% of previously retained GO particles. The transport behavior of GO particles within saturated sand packs could be described by the Langmuir-type of transport model. The extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory, which considers Lifshitz–van der Waals (LW) interaction, the electrostatic double layer (EDL) interaction as well as the Lewis acid–base (AB) (i.e., hydrophobic) interaction between GO plates and the surface of quartz sand, could explain the observed trend of GO retention under various ionic strength conditions.

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## 1. Introduction

Graphene oxide (GO) is a layered carbon-based nano-material that contains graphene sheets and oxygen-bearing functional groups [1]. For the past decade, there has been exploding interests in the industrial use (e.g., drug delivery, biosensing, nano- and micro-electronics) of this group of materials due to their unique electronic, thermal and mechanical properties [e.g., 2,3–12]. As the production and use of this group of nano-materials are predicted to grow rapidly in the future, it is expected that substantial quantities

of GO particles could potentially be released into the natural environment throughout its industrial life cycle [13].

Thanks to the hydrophilic oxygen-bearing functional groups, GO has high solubility in water [11]. Several recent studies examined the biocompatibility and potential toxicity of GO particles suspended in aqueous solutions. The results suggested that GO particles can be toxic to human, animal (e.g., mice) and bacterial cells [2,14–17]. Akhavan and Ghaderi [14], for instance, reported that the GO particles could significantly reduce the viability of *Escherichia coli* and *Staphylococcus aureus* because the sharp edges of GO particles could damage cell membranes. Wang et al. [15] documented that the ingestion of small quantities (~0.4 mg) of graphene oxide by mice could cause death and lung granuloma formation. Vallabani et al. [16] observed that GO particles

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could significantly increase the apoptosis of normal human lung cells.

The findings from the toxicity studies raised serious concerns about the potential environmental and health impacts of GO particles that could be released into the natural system. As an integral part of the water cycle, the soil-groundwater system represents an important pathway for the potential spread of GO particles within the natural environment. For this subsurface system, which supplies ~40% of drinking water in the United States [18], the fate and environmental impacts of GO particles will strongly depend on its mobility within the soil and aquifer materials. To our knowledge, no study has examined the transport behavior of GO particles within the subsurface environment. The primary goal of this research is to investigate the deposition kinetics of GO within saturated quartz sands under different ionic strength conditions. Additionally, we examined the remobilization of previously retained GO particles as a result of chemical perturbation (e.g., when the ionic strength is lowered). Finally, the transport behavior of GO within the sand packs was related to the energy interaction profiles between GO particles and quartz sands, which were calculated using extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory.

## 2. Materials and methods

### 2.1. Graphene oxide

GO particles manufactured using the Hummers method was purchased from Cheaptubes Inc. (Brambleboro, VT). Atomic force microscopy (AFM) measurements performed by the manufacturer showed that the GO particles were generally single-layered and their horizontal sizes were between 300 to 800 nm. The GO particles received from the manufacturer were sonically (Branson Ultrasonic Bath) dispersed in electrolyte solutions that contained 1, 5, 20 and 100 mM NaCl, respectively [1,19]. All the electrolyte solutions were prepared using Nanopure water (Barnstead) that had a specific resistivity of ~18.2 MΩ cm. The pH of the GO suspensions was ~6.0. Scans of absorbance as a function of wavelength using a Shimadzu UV-1700 spectrophotometer for each of the sonicated suspensions showed that the optimal wavelength for GO concentration measurement was 220 nm. Calibration curves were then prepared to establish the relationship between absorbance and GO concentrations (up to 70 mg/L) ( $R^2 > 0.99$ ). Dynamic light scattering (DLS) measurement performed using a Brookhaven ZetaPALS showed that the average hydrodynamic radius of the GO particles was  $329 \pm 79$  nm, which was consistent to the AFM measurements, and did not vary with NaCl concentration.

### 2.2. Preparation of sand columns

The transport experiments were performed in duplicate using a pair of glass chromatography columns measuring 2.5 cm in diameter and 15 cm in length (Kontes, Vineland, NJ). The silica sands received from the manufacturer (US Silica, Ottawa, IL) were sieved for the 0.211–0.297 mm fraction. The sieved sands were then alternately cleaned using concentrated nitric acid to remove metal hydroxides and diluted NaOH solution to remove natural clay particles [20], rinsed with deionized water and dried at 80 °C. The porosity ( $n$ ) of the sand was determined using the bulk density method and equaled 0.37 [21]. The vertically oriented columns were wet-packed with the clean silica sands and care was taken to eliminate the possibility of trapped air bubbles. The packed saturated sand columns were equilibrated by pumping >30 pore volumes (PV) of appropriate background electrolyte (i.e., 1, 5, 20 or 100 mM NaCl) using peristaltic pumps (MasterFlex, Vernon Hills, IL). The Darcy velocity was maintained using peristaltic pumps

at 0.31 cm/min. Following the equilibration step, the packed sand columns were ready for the tracer or GO transport experiments.

### 2.3. Tracer tests

The primary goal of the tracer tests was to estimate the hydraulic dispersion coefficient [22]. Briefly, a tracer solution (9.75 mM NaCl and 0.25 mM KNO<sub>3</sub> with NO<sub>3</sub><sup>-</sup> being the tracer) was injected to the top of the pre-equilibrated columns and the concentrations of nitrate in the effluent was determined through measuring the absorbance at a wavelength of 220 nm using a Shimadzu UV-1700 spectrophotometer [23]. After 60 min of injection of the tracer solution (~3.5 PV), the columns were flushed with the background NaCl solution that did not contain KNO<sub>3</sub> until the absorbance of effluent returned to the background values. The transport of the conservative tracer within the saturated sand packs can be described by the advection–dispersion equation:

$$\frac{\partial C_T}{\partial t} = -v \frac{\partial C_T}{\partial x} + D \frac{\partial^2 C_T}{\partial x^2} \quad (1)$$

where  $C_T$  is the concentration of the tracer (NO<sub>3</sub><sup>-</sup>) in the pore water;  $t$  is time;  $v$  is the average linear pore water velocity, which equaled Darcy velocity divided by porosity;  $x$  is the coordinate parallel to flow; and  $D$  is the hydrodynamic dispersion coefficient.

Eq. (1) was approximated by a second-order, finite-difference scheme with a first-type boundary condition at the column inlet, and the resulting system of linear equations was solved iteratively to obtain effluent tracer concentrations as a function of time. The solutions of Eq. (1) were fitted to the tracer breakthrough data using the Levenberg–Marquardt least-squares algorithm to obtain the best-fit values of the hydrodynamic dispersion coefficient,  $D$  [22,24].

### 2.4. Transport of GO particles within the saturated sand packs

Similar to the tracer tests, the GO transport experiments were initiated by injecting GO suspensions (5 mg/L of GO, NaCl concentration: 1, 5, 20 and 100 mM) into the columns from the top. The outflow from the columns were connected to quartz flow-through cuvettes (NSG Precision, Farmingdale, NY) and the concentrations of the GO particles in the effluent were monitored using a Shimadzu UV-1700 spectrophotometer at 30-s intervals at a wavelength of 220 nm. The injection of the GO suspension lasted for 60 min (~3.5 PV). The columns were then flushed with background electrolyte solution until the absorbance of effluent returned to the background values.

To quantify the potential remobilization of previously deposited GO particles due to chemical perturbation (i.e., decrease in ionic strength), following the injection experiments using 100 mM NaCl, the 1 mM NaCl solution free of GO particles was injected to the columns at 6 PV. The quantity of the remobilized GO particles in the column effluent was similarly monitored using the spectrophotometer until the absorbance returned to background values. The remobilization experiments lasted for ~8 PV.

The transport of GO particles within the saturated sand packs was described using a second-order deposition model which assumed that the number of GO deposition sites was limited and the deposition rate decreased as the GO deposition sites were progressively occupied by the retained GO particles. The mathematical form of this Langmuir-type model was:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - k_d \left(1 - \frac{S}{S_0}\right) C + k_r \frac{\rho}{n} S \quad (2)$$

$$\frac{\rho}{n} \frac{\partial S}{\partial t} = k_d \left(1 - \frac{S}{S_0}\right) C - k_r \frac{\rho}{n} S \quad (3)$$

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