Short communication

Effects of surfactant type and concentration on graphene retention and transport in saturated porous media

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HIGHLIGHTS

- SDBS and CTAB effectively stabilized GR in aqueous solutions.
- SDBS- and CTAB-GR showed different retention and transport behaviors.
- SDBS-GR showed relatively high mobility in the porous media.
- CTAB-GR was almost immobile in the columns at low surfactant concentration.
- CTAB-GR was highly mobile in the columns at high surfactant concentration.

ARTICLE INFO

ABSTRACT

Knowledge of the fate and transport of graphene (GR) nanosheets in porous media is essential to understand their environmental impacts. In this work, sand column experiments were conducted to investigate the retention and transport of surfactant-dispersed GR nanoparticles under various conditions. An anionic surfactant, sodium dodecylbenzene sulfonate (SDBS) and a cationic surfactant, cetyltrimethylammonium bromide (CTAB) were used to disperse and stabilize GR in aqueous solutions. Both surfactants were effective in stabilizing the GR particles, even at low concentration (0.004% w:v) because the surfactant coating introduced negative (SDBS) or positive (CTAB) charges on the GR surfaces. As a result, the SDBS- and CTAB-GR showed different retention and transport behaviors in the saturated porous media. At low surfactant concentration, the transport of SDBS-GR was much higher than that of the CTAB-GR, which was almost immobile in the sand columns with mass recovery rate only about 4%. When the surfactant concentration increased from 0.004% to 0.4%, it reduced the transport of SDBS-GR and dramatically enhanced the mobility of the CTAB-GR (with mass recovery rate of 91%). It is suggested that the presence of 'free' SDBS ions may reduce the electrosteric repulsions between SDBS-GR and sand surfaces by compressing the electrical double layer. The 'free' CTAB ions, however, may compete with the CTAB-GR for adsorption sites on the sand surfaces. Findings from this study indicated that the dispersion method plays an important role in affecting the environmental fate and transport of GR particles.

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1. Introduction

A great deal of attention has been paid to graphene (GR) and GR-based nanomaterials recently because they have remarkable properties and a variety of applications [1–4]. While the central focus of GR is on promising potential benefits, there are also growing concerns over its potential environmental impacts. Recent studies have shown GR and GR-based nanomaterials can be toxic toward organisms including bacteria and humans [5,6]. Liu et al. [7] found that GR and GR-based materials have strong cytotoxicity toward bacteria and the antimicrobial actions are contributed by both membrane and oxidation stress. Genotoxicity of GR nanoribbons in human mesenchymal stem cells were also demonstrated as the GR-based nanomaterial can penetrate into the cells and cause DNA fragmentations as well as chromosomal aberrations [6]. With knowledge of these potential risks to the ecosystems, it is very

much needed to understand the fate and transport of GR and GR-based nanomaterials in the environment.

Many GR applications, such as solar cell [8], polymer composite [9], and conductive thin film [10], require the preparation of soluble GR (i.e., well-dispersed GR suspension), which presents challenges as pristine GR sheets are hydrophobic and tend to form agglomerates due to strong attractive van der Waals force [2]. To optimize its uses, pristine GR sheets are often modified with different chemical agents, including surfactants, to aid the dispersion [11–13]. While surface modification promotes the applications, it may also affect the fate and transport behaviors of GR once the modified GR is released into the environment. Several previous studies have investigated the retention and transport behaviors of surface modified GR, particularly graphene oxides and surface functionalized GR, in porous media under various flow and chemistry conditions and found that surface characteristics of the nanoparticles strongly affect their fate and transport [14–17]. Although surfactant modification is also a common practice to disperse GR [4,12,18], to the best of authors' knowledge, none of the previous studies has examined the transport behaviors of surfactant modified GR. In the literature, many studies have shown that surfactant modifications not only can stabilize engineered nanoparticles (e.g., carbon nanotubes and silver nanoparticles), but also enhance their mobility in porous media at both low and high surfactant concentrations [19–21].

The overarching objective of this work was to determine the effect of surfactant modification on the retention and transport of GR in water-saturated porous media. Sodium dodecyl benzyl sulfonate (SDBS), an anionic surfactant, and exadecyltrimethylammonium bromide (CTAB), a cationic surfactant, were used to disperse and stabilize GR sheets in water. Laboratory column experiments were conducted to examine the transport behaviors of the surfactant modified GR in water-saturated sand media. The specific objectives were to: (1) measure the stability of GR modified with the two surfactants; (2) determine the effects of surfactant type on the retention and transport of GR in saturated porous media; and (3) determine the effects of surfactant concentration on the retention and transport of GR in saturated porous media.

2. Materials and methods

2.1. GR suspension

GR was purchased from Jcnano Technology (Nanjing, China), which was used as received in this study. According to the manufacture, the GR is high purity single layer (99.8%) with average diameter of 0.8–3 μm and thickness of 0.8–1.2 nm. Two types of surfactants, SDBS and CTAB (their structures are listed in Table 1), were used to disperse the GR. To prepare the experimental suspensions, 50 mg of pristine GR were mixed with 1000 mL of an aqueous surfactant solution (0.004% or 0.4% w:v), followed by 2 h of ultrasonication (Misonix) to aid dispersion. Subsequently, the suspension was ultracentrifuged at 500 rpm for 90 min to eliminate the aggregates and large suspensions. After keeping still for

24 h, the top 50% of the supernatant was taken as the stock solution. A fresh GR suspension was prepared for each experiment by first sonicating the stock solution for 5 min and then diluting it into the desired concentration. Concentrations of the surfactant dispersed GR suspensions were tested and calibrated through measuring their spectrum and total light adsorption at wavelength of 285 nm (SDBS-dispersed 0.004% w:v), 430 nm (SDBS-dispersed 0.4% w:v), 225 nm (CTAB-dispersed 0.004% w:v), and 270 nm (CTAB-dispersed 0.4% w:v) using an Evolution 60 UV–Vis Spectrophotometer (Thermo Scientific, Waltham, MA), respectively (Fig. S1, Supporting Information). A Zeta-Sizer Nano ZS (Malvern Instrument UK) equipped with a He–Ne laser (633 nm) was used to determine the size of surfactant-dispersed GR particles in the suspensions by monitoring the change of the hydrodynamic diameters with time. The zeta potential (ζ) of the surfactant-dispersed GR was measured by Brookhaven ZetaPlus (Brookhaven Instruments, Holtsville, NY).

2.2. GR transport

Triplicated transport experiments were conducted in acrylic columns of 2.5 cm in diameter and 16.5 cm in height. The experimental procedures are similar to Liu et al. [14]. For each experiment, the column was wet-packed with clean Quartz sand (Standard Sand & Silica Co.) with a size range of 0.5–0.6 mm and approximate average diameter of 0.55 mm. The sand was washed sequentially by tap water, 10% nitric acid (v:v), and deionized (DI) water to remove impurities followed the procedures of previous studies [15,20]. The average porosity of the packed sand porous media was about 0.44. Once the column was packed, DI water was first pumped through the saturated column for about 2 h to remove impurities followed by a surfactant (SDBS, CTAB) solution for another 2 h. A peristaltic pump (Masterflex L/S, Cole Parmer Instrument, Vernon Hills, IL) was connected to the column inlet at the top to control the flow rate at 1 mL min^{-1}. For GR transport study, 2 pore volumes (PV) of GR suspension were introduced to the sand column. After that, about two PVs of the same surfactant solution were applied to the column until the effluent GR concentration returned to the baseline level. The effluents were collected at 4-min intervals using a fraction collector. GR concentrations in the effluents were immediately measured with the UV–vis using the method described above (also see Supporting Information).

2.3. Transport model

Retention and transport of the surfactant-dispersed GR particles in the saturated sand columns were simulated with a advection–dispersion–reaction (ADR) model as described in previous studies [14,22]. The governing equation can be written as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - kC \tag{1}$$

where C is the concentration (M L^{-3}), t is time (T), D is the dispersion coefficient (L^2 T^{-1}), z is the distance traveled in the direction

Table 1
Structures of surfactants used in this study.

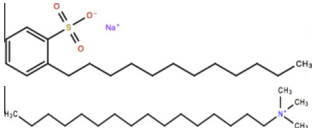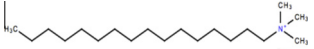| Surfactant	Linear formula	Structure	Molecular weight
SDBS	$CH_3(CH_2)_{11}C_6H_4SO_3Na$		348.48
CTAB	$CH_3(CH_2)_{15}N(Br)(CH_3)_3$		364.45

Table 2
Properties of the GR suspension used in this work.

	Surfactant (% w:v)	Dispersed GR (mg L^{-1})	Hydrodynamic diameter (nm)	Electrophoretic mobility (*10^{8}m^2/Vs)	Zeta potential (mV)
SDBS-GR	0.004	16.5 ± 0.5	501 ± 47	−3.32	−44.91
CTAB-GR	0.004	14.0 ± 0.8	545 ± 75	2.69	36.5

of flow (L), v is the average linear pore-water velocity (L T^{-1}), k is the particle retention constant. This model was applied to the experimental data and solved numerically with finite-difference scheme, a zero initial concentrations, a pulse-input boundary condition at the column inlet, and a zero-concentration-gradient condition at the outlet boundary [14].

3. Results and discussion

3.1. Surfactant-dispersed GR

Even at a very low concentration (0.004%), the two surfactants stabilized substantial amount of GR particles in the suspensions (Table 2), which is inconsistent with the findings in the literature that low-level of surfactants are effective in stabilizing carbon nanomaterials including carbon nanotubes in environmental media [19]. Although both were effective, the CTAB dispersed less GR particles than the SDBS. Previous studies have suggested that surfactants have different ability to stabilize GR in suspensions because they may introduce different types of energy barriers to the system [23]. Addition information about the governing mechanisms controlling the interactions between GR and the two surfactants can be found in the literature [2,23,24]. The average hydrodynamic diameters of SDBS-GR and CTAB-GR were about 501 ± 47 nm and 545 ± 75 nm, respectively. These values are similar despite the fact that the two surfactants used in this study are very different. This result indicated that surfactant modification may not have strong effects on the size and shape of the GR. A factor of 2/3 was used to convert the hydrodynamic diameters to the lateral dimension of the GR [14], the obtained average GR sheet diameter (lateral dimension) was around 349 nm, which is within the values reported by the manufactory and in the literature [23,25]. Although the pristine GR sheets are neutral, the surfactant modification introduced charges to their surfaces and the anionic and cationic surfactants made the GR particles negatively and positively charged, respectively (Table 2). As a result, the zeta potential values of the SDBS- and CTAB-GR were −44.91 and 36.50 mV, respectively.

3.2. Effect of surfactant on GR stability

At the low concentration (0.004%), surfactants stabilized the GR particles in the suspensions for a long time (Fig. 1). Both SDBS- and CTAB-GR suspensions stayed unchangeable for at least 7 h (Fig. 1a), suggesting low-level of anionic and cationic surfactants are effective in stabilizing GR sheets. Similarly, the hydrodynamic diameters of SDBS-GR and CTAB-GR showed little changes over time (Fig. 1b), further confirming the effectiveness of the two surfactants. During the dispersion, the hydrophobic groups of SDBS and CTAB were adsorbed onto GR particles through van der Waals attractions, while the effective charges of the two surfactants were disassociated and imparted on these particles by the hydrophilic groups in aqueous media [4,23], which introduced strong electrostatic repulsion to prevent the aggregations. The extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory (see Supporting Information) was applied in this work to determine the interaction profiles between surfactant modified GR particles. The estimated XDLVO energy barrier between the dispersed GR particles was
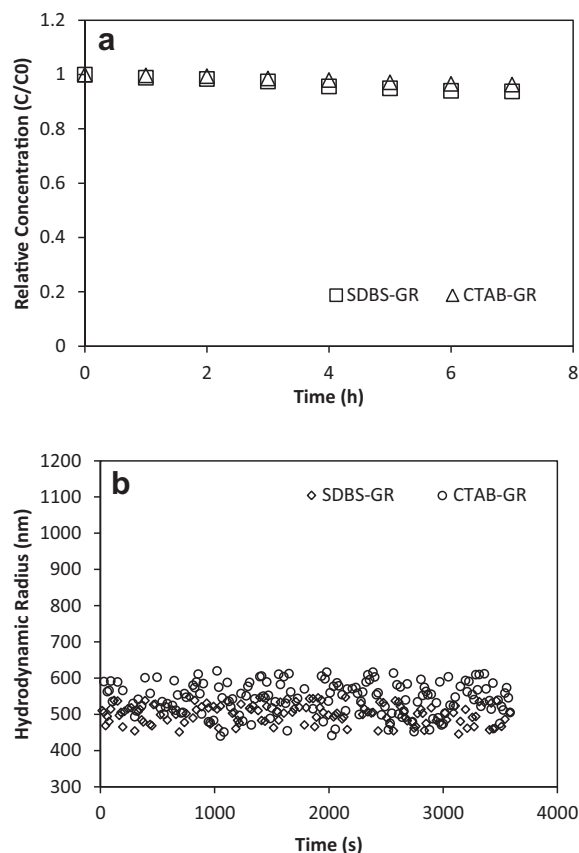

Fig. 1. Changes of relative concentration (a) and hydrodynamic diameter (b) of surfactant-dispersed GR particles.

greater than 10 mJ/m^2 (Fig. 2), which is almost impossible to be overcome by the nanoparticles to enter the primary minima. The XDLVO calculations thus confirmed the experimental observations that the tested experimental conditions were unfavorable for particle aggregations. When the surfactant concentration increased from 0.004% to 0.4%, the XDLVO profiles only changed slightly for both SDBS- and CTAB-GR particles (Fig. 2), which is consistent with the findings from previous studies that high-level of surfactants are also effective in stabilizing nanoparticles [4,20].

3.3. GR retention and transport

Column experiments were conducted with GR suspensions dispersed by two surfactants at low (0.004%) and high (0.4%) concentrations and the resulting breakthrough curves are presented in Fig. 3. Mass recovery rates of SDBS-GR and CTAB-GR from the columns are shown in Table 3. At low surfactant concentrations, the breakthrough curve of the SDBS-GR was much higher than that of the CTAB-GR, which showed almost no transport through the column. Mass balance calculations showed that about 85% of SDBS-GR passed through the column, while only less than 5% of the CTAB-GR particles were found in the effluents (Table 3). High mobility of SDBS-dispersed nanoparticles including carbon
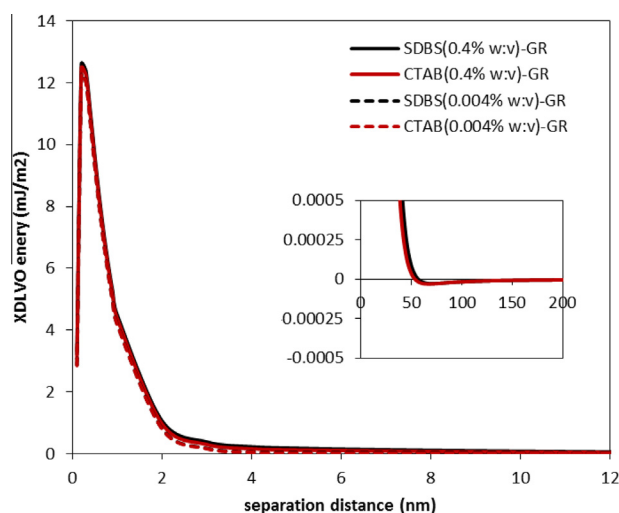
Fig. 2. XDLVO energy between surfactant-dispersed GR particles under different experimental conditions.
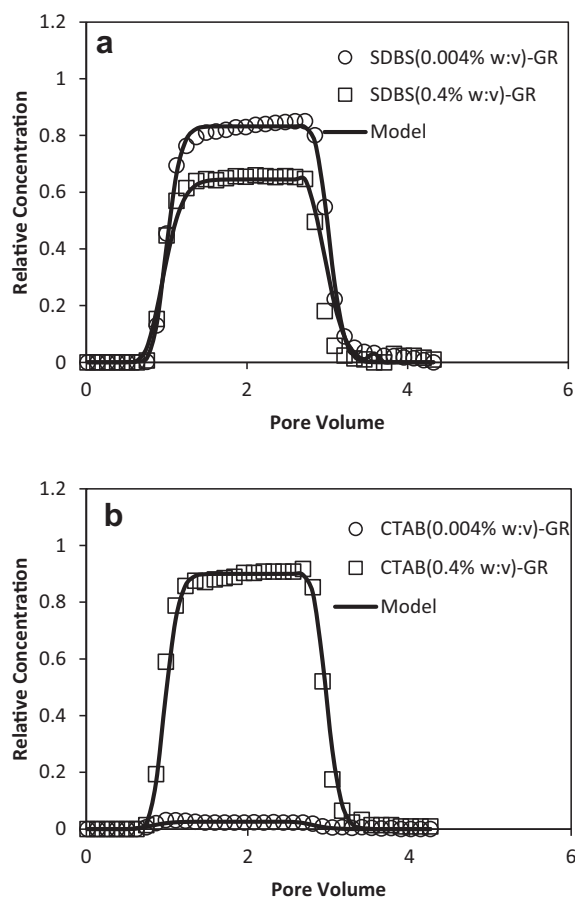

Fig. 3. Breakthrough curves of SDBS (a) and CTAB (b) dispersed GR particles in saturated sand columns under different experimental conditions. Symbols are experimental data and lines are model results.

Table 3
Model results from column experiment.

GR suspension	K (min^{-1})	Mass recovery (%)	R^2
0.004% SDBS	0.0051	84.60	0.99
0.004% CTAB	0.1273	4.07	0.90
0.4% SDBS	0.0136	71.2	0.98
0.4% CTAB	0.0023	90.6	0.99

indicated that the surfactant type, particularly its charge, can affect the surface charge of GR sheets to control their retention and transport in porous media.

When the surfactant concentration increased from 0.004% to 0.4%, it showed different effects on the breakthrough behaviors of the SDBS- and CTAB-GR particles (Fig. 3). On one hand, high SDBS concentration reduced the mobility of the GR in the sand column and the mass recovery rate reduced about 14%. This is because the presence of extra SDBS ions in the system also increased solution ionic strength, which can compress the electric double layers to reduce the electrostatic repulsions between the SDBS-GR and the negatively charge quartz sand surfaces to promote the deposition [20,26]. On the other hand, high CTAB concentration greatly enhanced the mobility of the GR in the sand column and the mass recovery rate increased dramatically from 4% to 91%. This is probably because the competition between 'free' CTAB cations and the CTAB-GR in the solution for the adsorption sites on the negatively charged sand surfaces. Because both CTAB and CTAB-GR are positively charged, they can both attach onto the negatively charged sand surface. At a high concentration, the 'free' CTAB may dominate the adsorption process to reduce the retention of CTAB-GR in the sand columns.

Simulations from the ADR model matched all the experimental breakthrough curves very well with R^2 values larger than 0.9 (Fig. 3 and Table 3). The best-fit k values of SDBS- and CTAB-GR retention in the sand columns ranged from 0.0023 to 0.1273 min^{-1}. These k values were similar to the results of the retention of surfactant-dispersed carbon nanotubes in saturated sand media as reported by Bouchard et al. [19]. As anticipated, the best-fit k for SDBS-GR at high concentration (0.0136 min^{-1}) was higher than that at low concentration (0.0051 min^{-1}); while the best-fit k for CTAB-GR at high concentration (0.0023 min^{-1}) was almost two orders of magnitude lower than that at low concentration (0.1273 min^{-1}). These results confirmed that both surfactant type and concentration play important roles in controlling the fate and transport of dispersed GR particles in saturated porous media.

4. Conclusions

Two types of surfactants were used to disperse GR particles and the retention and transport of the dispersed GR in water-saturated sand columns were investigated. The experimental results showed that: (1) the two surfactants were effective in dispersing and stabilizing GR particles in aqueous solutions even at low concentration; (2) surfactant type strongly affected the retention and transport of GR in porous media because it introduced charges to the GR surfaces; (3) surfactant concentration also showed strong effects on the retention and transport of GR and increase in surfactant concentration reduced the mobility of SDBS-GR but dramatically promote the transport of CTAB-GR in saturated porous media. Findings from this work indicated that although it is mainly used as a dispersion agent, surfactant also plays important roles in controlling the environmental fate and transport of GR particles. Special attentions thus need to be paid to their environmental impacts when surfactants are selected for the optimal use of GR or other manufactured nanomaterials.

nanotubes has also been observed in previous studies [20,21]. This is mainly because both the surfaces of SDBS coated nanoparticles and the quartz sand are both negatively charged, making it hard for surface deposition. In this work, the surface charge of the CTAB-GR is positively charged; therefore, the nanoparticles can easily attach onto the negatively charged sand surfaces. This result

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.10.032.

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