Interaction between graphene oxide nanoparticles and quartz sand

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Abstract

In this study, the influence of pH, ionic strength (I_S), and temperature on graphene oxide (GO) nanoparticles adsorption onto quartz sand were investigated. Batch experiments were conducted at three controlled temperatures (4, 12, and 25 °C) in solutions with different pH values (pH=4, 7, and 10), and ionic strengths (I_S=1.4, 6.4, and 21.4 mM), under static and dynamic conditions. The experimental results shown that GO nanoparticles were very stable under the experimental conditions. Both temperature and pH did not play a significant role in the adsorption of GO nanoparticles onto quartz sand. In contrast, I_S was shown to influence adsorption. The adsorption of GO particles onto quartz sand increased significantly with increasing I_S. Furthermore, the experimental data were fitted nicely with a Freundlich isotherm, the adsorption kinetics were satisfactorily described with a pseudo-second-order model and the thermodynamic behavior of adsorption process was examined.

Materials and Methods

GO Nanoparticles

High purity SP-1 graphite powder (Bay Carbon Inc, Bay City, MI) was used to produce graphite oxide based on the procedures reported by Hummers et al. (1958). The graphite oxide was exfoliated by sonication and centrifugation. The GO suspensions were prepared by mixing 3 mg of graphene oxide flakes with 250 mL of a phosphate buffered solution (PBS) with low ionic strength (I_S=1.35 mM). Subsequently, the suspensions were sonicated for 2 h to ensure that the dispersion is thoroughly uniform. Calibration curves were prepared, for each set of solution chemistry examined in this study, in order to establish the relationship between absorbance, A_{bs} [-], and GO concentration, C_{GO} [M/L³], in the range 0 to 30 mg/L.

Sand

Quartz sand with grain diameter ranging from 0.425 to 0.600 mm (sieve no. 30/40) was used for the GO adsorption experiments. Following the procedures reported by Chrysikopoulos and Aravantinou (2014), the particle-size distribution value determined by sieve analysis was used to calculate the coefficient of uniformity, $C_u=d_{60}/d_{10}$=1.21. The quartz sand was cleaned according to the method of Loveland et al. (1996) and Xu et al. (2008). Finally, the quartz sand was dried in an oven at 80 °C.

Batch Experiments

Both static and dynamic batch experiments were conducted under various solution chemistry conditions at 4, 12 and 25 °C. A PBS solution was used to stabilize the pH of GO dispersion (Dreyer et al., 2010). All batch experiments were performed in 20 mL Pyrex glass screw-cap tubes. Its tube contained 14 g of sand and 14 mL of GO suspension. The experiments at 4 and 12 °C were conducted in an incubator. The dynamic batch experiments were performed with the tubes attached to a rotator, operated at 12 rpm, in order to allow the sand to mix within the GO suspension.

Results

Isotherm Batch Experiments

The experimental data from the GO equilibrium adsorption onto quartz sand at three different temperatures where fitted nicely with a Freundlich isotherm:

$$C^{*}_{eq} = K_f C^{m}_{eq}$$

$$\Rightarrow \log C^{*}_{eq} = \log K_f + m \log C_{eq}$$

where C_{eq} [mg GO/Liter of solution] is the aqueous phase of GO concentration at equilibrium, C^*_{eq} [mg GO/g sand] is the GO concentration adsorbed onto the quartz sand at equilibrium, K_f [L^m/(g sand)(mg GO)$^{m-1}$] is the Freundlich constant, and m [-] is the Freundlich exponent. The Freundlich parameters m and $\log K_f$ were estimated by the slope and ordinate, respectively, of the linear plot of $\log C^*_{eq}$ versus $\log C_{eq}$.

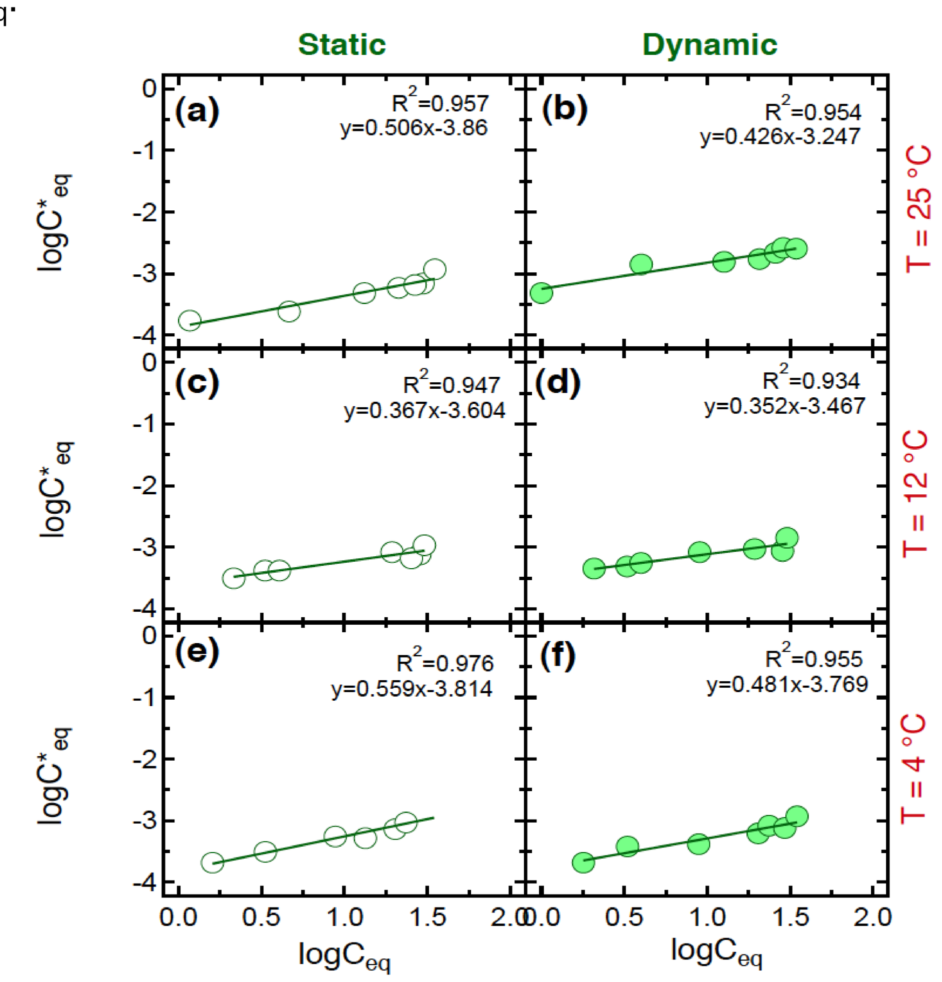

Figure 1: Linearized Freundlich isotherms for GO nanoparticles adsorption onto quartz sand at three different temperatures: (a,b) 25 °C, (c,d) 12 °C, and (e,f) 4 °C. The open circles indicate static conditions and the solid circles dynamic conditions.

Kinetic batch experiments

The experimental data from the kinetic batch adsorption experiments were fitted with the following pseudo-second-order expression:

$$\frac{dC^{*}_{t}}{dt} = k_{p2}\left(C^{*}_{eq} - C^{*}_{t}\right)^2 \quad \Rightarrow \quad C^{*}_{t} = \frac{\left(C^{*}_{eq}\right)^2 k_{p2} t}{1 + C^{*}_{eq} k_{p2} t}$$

where t [t] is time, $[M_n/M_s]$ is the GO concentration adsorbed onto quartz sand at time t, and k_{p2} $[M_s/(M_n \cdot t)]$ is the rate constant of the pseudo-second order adsorption.

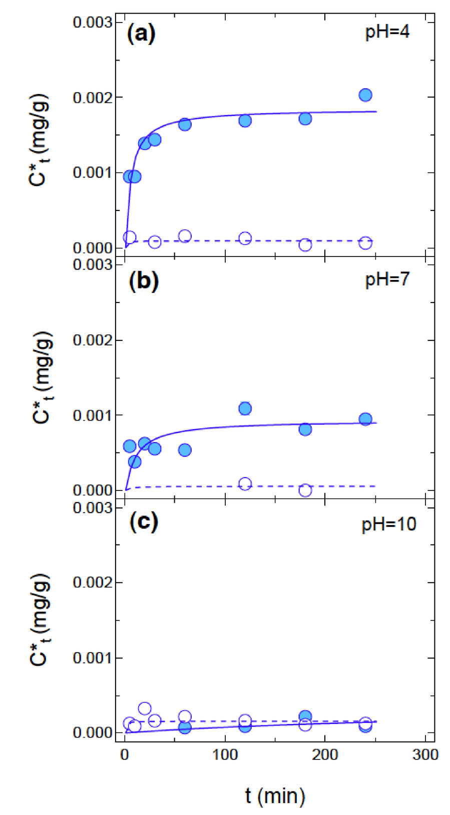

Figure 2: Effect of pH, on GO kinetic adsorption onto quartz sand. The symbols (circles) represent the experimental data, and the curves the fitted model simulations. The open and solid circles correspond to static and dynamic conditions, respectively.

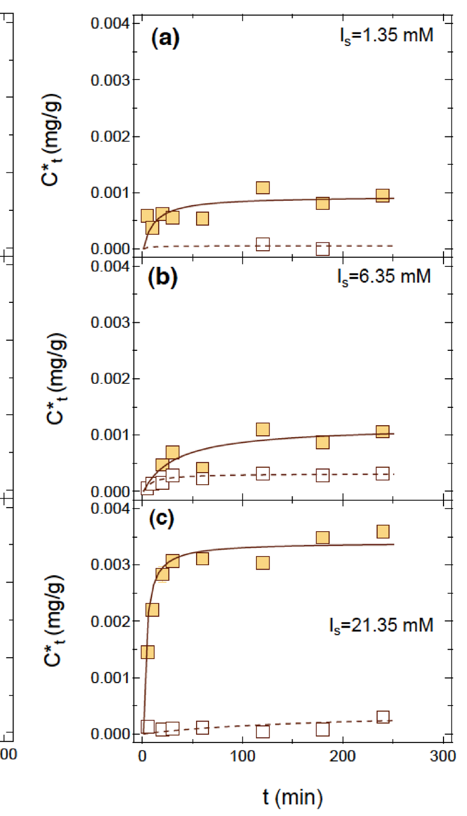

Figure 3: Effect of ionic strength, on GO kinetic adsorption onto quartz sand. The symbols (squares) represent the experimental data, and the curves the fitted model simulations. The open and solid squares correspond to static and dynamic conditions, respectively.

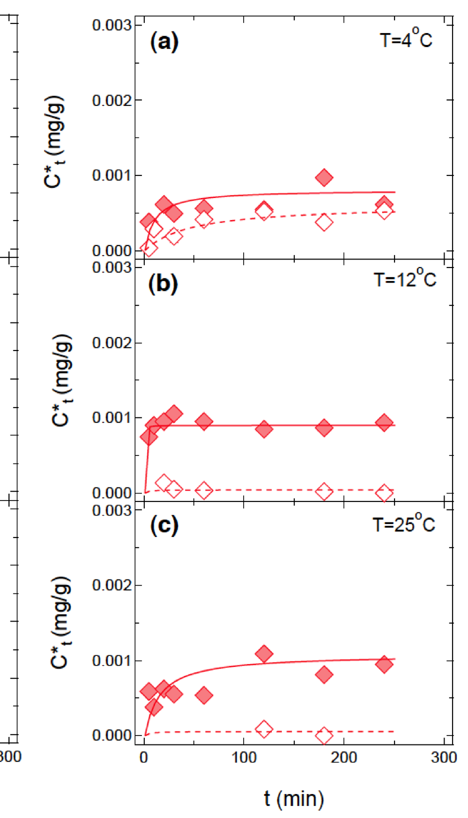

Figure 4: Effect of temperature on GO kinetic adsorption onto quartz sand. The symbols (diamonds) represent the experimental data, and the curves the fitted model simulations. The open and solid diamonds correspond to static and dynamic conditions, respectively.

Adsorption Thermodynamics

The thermodynamic behavior of GO nanoparticle adsorption onto quartz sand was investigated from the temperature dependent adsorption isotherms by estimating the standard Gibbs free energy change, ΔGº [kJ/mol], the standard enthalpy change, ΔHº [kJ/mol], and the standard entropy change, ΔSº [J/mol·K], which can determine whether the adsorption process is spontaneous, and endothermic or exothermic.

$$\Delta G^{\circ} = -R_a T \ln K_o$$

R_a=8.3145 [J/(mol·K)] is the universal gas constant, and T [K] is the absolute temperature, and K_0 [L/g] is the thermodynamic adsorption equilibrium constant, also known as the thermodynamic distribution coefficient, which can be obtained from the intercept with the vertical axis of the linear plot of $\ln[C^*_{eq}/C_{eq}]$ versus C^*_{eq}. Furthermore, the values of ΔH° and ΔS° can be obtained from the following thermodynamic relationship:

$$\ln K_o = \frac{\Delta S^{\circ}}{R_a} - \frac{\Delta H^{\circ}}{R_a T}$$

The estimated values of K_0, ΔG°, ΔH°, and ΔS° are presented in Table 1. K_o increased with temperature suggesting that the adsorption process was endothermic. The positive values of ΔG° indicated that the adsorption process was non-spontaneous. The positive values of ΔH° indicated that the adsorption process was endothermic. Finally, the value of ΔS° for static experiments was negative indicating that the adsorption process was enthalpy driven, whereas for the dynamic experiments was positive indicating high affinity of the quartz sand for GO nanoparticles and increased randomness at the solid/liquid interface.

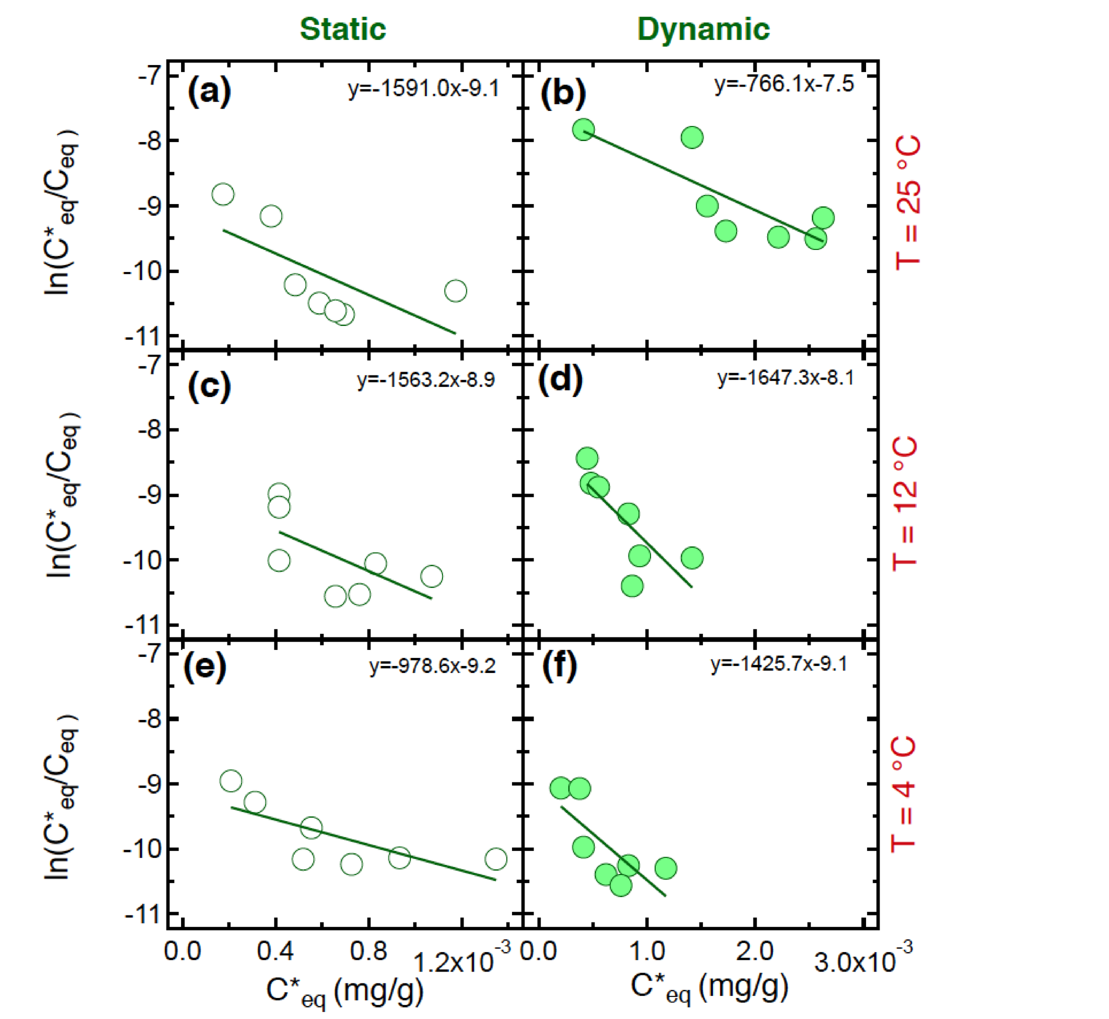

Figure 5: Linear plots of $\ln[C^*_{eq}/C_{eq}]$ versus C^*_{eq} at three different temperatures: (a,b) 25 °C, (c,d) 12 °C, and (e,f) 4 °C. The open circles indicate static conditions and the solid circles dynamic conditions.

Table 1: Calculated thermodynamic values for GO adsorption onto quartz sand

T (˚C)	K_0 (L/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
Static				
4	1.06×10^{-4}	21.1	1.9	-69.1
12	1.12×10^{-4}	21. 6		
25	1.13×10^{-4}	22.5		
Dynamic				
4	1.19×10^{-4}	20.8	47.8	98.5
12	3.10×10^{-4}	19.1		
25	5.37×10^{-4}	18. 7		

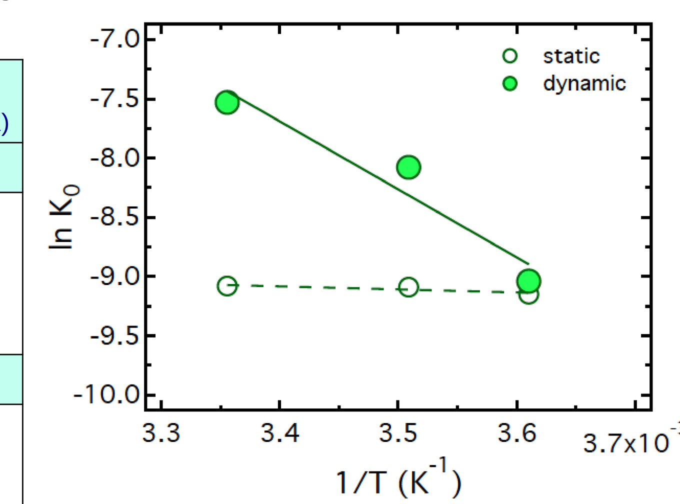

Figure 6: Linear plot of $\ln K_o$ versus 1/T.

Conclusions

- The Freundlich isotherm equation described well the adsorption of GO nanoparticles onto quartz sand.
- The adsorption process was endothermic and non-spontaneous.
- Temperature did not affect significantly the adsorption of GO nanoparticles onto quartz sand.
- The adsorption of GO nanoparticle onto quartz sand increased with increasing I_S and decreasing pH.
- The results of this study suggest that GO nanoparticles are expected to migrate easily through water saturated porous media under typical groundwater conditions.

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In this study, the influence of pH, ionic strength (IS), and temperature on graphene oxide (GO) nanoparticles adsorption onto quartz sand were investigated. Batch experiments were conducted at three controlled temperatures (4, 12, and 25 °C) in solutions with different pH values (pH=4, 7, and 10), and ionic strengths (IS=1.4, 6.4, and 21.4 mM), under static and dynamic conditions. The surface properties of GO nanoparticles and quartz sand were evaluated by electrophoretic mobility measurements. Derjaguin-Landau-Verwey-Overbeek (DLVO), and extended-DLVO (XDLVO) potential energy profiles were constructed for the experimental conditions, using measured zeta potentials. The experimental results shown that GO nanoparticles were very stable under the experimental conditions. Both temperature and pH did not play a significant role in the adsorption of GO nanoparticles onto quartz sand. In contrast, IS was shown to influence adsorption. Increasing the IS, dramatically increased. The adsorption of GO particles onto quartz sand increased dramatically with increasing IS, mainly due to secondary-minimum deposition, as indicated by the XDLVO interaction energy profiles. Furthermore, the experimental data were fitted nicely with a Langmuir type sorption isotherm, and the adsorption kinetics were satisfactorily described with a pseudo-second-order model.