Sorption and Desorption Characteristics of Phenanthrene in Nano-Confined Polystyrene

Hyung-Nam Lim[1], James (Chip) Kilduff[1], Chan Su Kim[2], and Chang Yeol Ryu[2]
(1) Civil and Environmental Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180, (2) Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180

Soil/sediment organic matter plays a major role in the sorption and desorption of polyaromatic hydrocarbons (1-2). Such organic matter may coat mineral surfaces and may be adsorbed in nanometer-sized pore spaces (3). The role of such confinement on sorption and desorption equilibrium is not well understood. This is a problem that has broad application; examples include developing advanced materials such as functional adsorbents and catalyst substrates (4). In this research, the sorption/desorption characteristics of phenanthrene in polystyrene (PS)-loaded mesoporous silicas were studied as model system for soils or sediments to test whether confinement alters the physical properties of the adsorbed organic matter (and, by analogy, natural soil organic matter (SOM) present in soils and sediments).

Monodisperse glassy PS samples (polydispersity < 1.05) with various mass average molecular weights (M_w) were chosen as surrogates for aromatic functionalities in natural macromolecules. These were loaded in fairly uniform pore silicas using two schemes: (i) the fixed R_g (the radius of gyration) system, where PS, with the R_g of 8nm (M_w = 58 kDa (kg/mole)), was loaded in each of five types of porous silicas (R_p (average pore radius) = 3.9 - 51.2 nm), resulting in various R_g/R_p ratios (representing the degree of PS confinement in pore geometries) from 2.1 to 0.2; (ii) the fixed R_p system, where each of five types of PS samples (M_w = 6 - 300 kDa) was loaded in a porous silica with the R_p of 3.9 nm (the resulting R_g/R_p ratio varied from 0.7 to 4.7).

From gas phase nitrogen (N_2) isotherm measurements, it was indirectly confirmed that PS is evenly loaded inside the silica pores without pore blockage when loaded under $R_g/R_p < 1$ conditions (i.e., $R_g < R_p$). Silica pore blockage increases as the R_g/R_p ratio approaches unity (i.e., $R_g \cong R_p$), at higher ratios, PS loading is mainly present on the outer surfaces of silicas.

All phenanthrene sorption/desorption isotherms, normalized by the adsorption amounts of PS per unit mass, can be described with both the Freundlich model and the dual-mode (a combination of hole-filling and solid phase dissolution) model (Figure

1). The Freundlich isotherm parameters (*n* and K_f), the ratio of hole-filling to solid phase dissolution ($Q^o b/K_d$) (5), integrated hysteresis index (IHI) (employed for estimating sorption/desorption irreversibility), and glass transition temperature (T_g) for each of the PS-loaded silicas, prepared using the fixed R_g and fixed R_p systems, change depending on the R_g/R_p ratio, which indicates that the physical characteristics of bulk phase (particulate) macromolecules can be altered in confining geometries of porous silicas.

For the fixed R_g (M_w) system (Figure 2), in the vicinity of the R_g/R_p ratio ≅ 1 (i.e., $R_g \cong R_p$), where the degree of PS confinement is expected to be maximum, the hardness (glassy characteristics) of PS is maximized as evidenced by minimum Freundlich *n*, and maximum $Q^o b/K_d$ and T_g. Similar trends were noted for the fixed R_p system, where sorption capacity increased and molecular mobility decreased with increasing PS M_w.

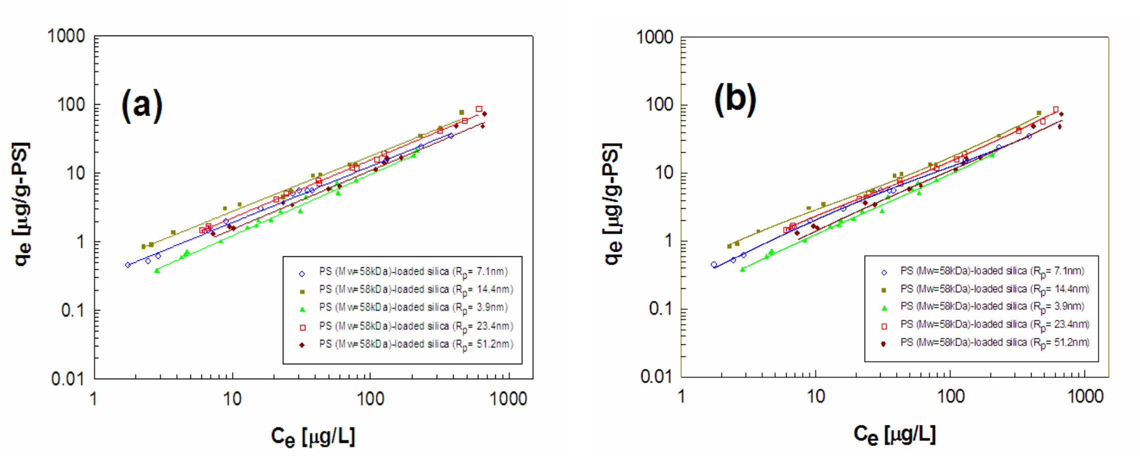

FIGURE 1. Sorption isotherms for the fixed R_g (M_w = 58 kDa) system: polystyrene (PS)-loaded silicas (R_p = 3.9 - 51.2 nm), (a) fitted with Freundlich model, (c) fitted with the dual-mode model. q_e values are normalized by the adsorption amounts of PS.

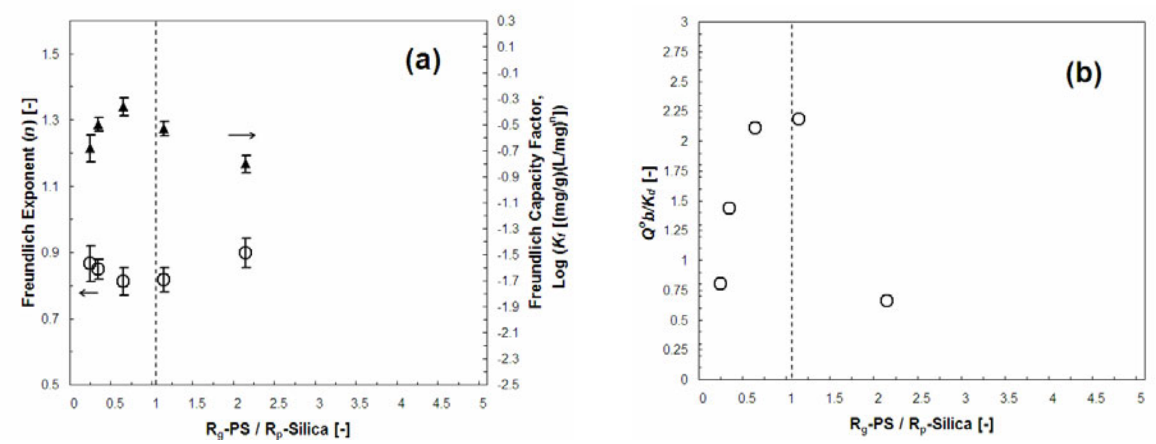

FIGURE 2. Correlation between the degree of confinement (R_g/R_p ratio) and (a) Freundlich model parameters (n, K_f), and (b) the ratio of hole-filling to solid phase dissolution (Q^ob/K_d) from dual-mode model fitting for the fixed R_g (M_w = 58 kDa) system. Error bars indicate 95% confidential intervals.

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