

**Sorption and Desorption of Synthetic Organic Chemicals (SOCs)  
to Macromolecule-Loaded Porous Adsorbents**

by

Hyung-Nam Lim

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Environmental Engineering

The original of the complete thesis is on file  
in the Rensselaer Polytechnic Institute Library

Examining Committee:

James E. Kilduff, Thesis Adviser

Chang Y. Ryu, Member

Simeon J. Komisar, Member

Lupita D. Montoya, Member

Rensselaer Polytechnic Institute  
Troy, New York

August, 2008

© Copyright 2008

by

Hyung-Nam Lim

All Rights Reserved

## ABSTRACT

In this research, sorption/desorption and desorption hysteresis of synthetic organic chemicals (SOCs) were investigated using various macromolecule-loaded porous media. Such composite materials were synthetic sorbents that can be well-characterized, offer the potential for controlled properties, and can be designed to serve as model soils and sediments. The macromolecules included synthetic polymers (e.g., polystyrene, PS and polystyrene sulfonate, PSS), and natural organic matter (NOM) (e.g., Tomhannock reservoir aquatic NOM (TMK NOM), commercial Aldrich humic acid (HA), and international humic substance society (IHSS) HA samples). The macromolecules were loaded to hydrophilic porous adsorbents such as silica, alumina, and anodized alumina membranes (AAMs), and single-walled carbon nanotubes (SWNTs) as model hydrophobic media. Size exclusion chromatography (SEC) was used to characterize the adsorption of the macromolecules to adsorbents. Continuously mixed batch reactors (CMBRs) were employed to investigate sorption and desorption of SOC (e.g., phenanthrene, naphthalene, methylbenzene, and chlorobenzene) to macromolecule-loaded adsorbents and determine phase partitioning constants.

All of tested polyelectrolytes, four types of HA, and a PSS mixture (1.8 kDa, 18 kDa and 100 kDa monodisperse PSS standards) as model NOM showed preferential adsorption of lower molecular weight ( $M_w$ ) components to alumina mesopores due to size exclusion and slow adsorption kinetics of higher  $M_w$  components. The adsorption of purified Aldrich humic acid (PAHA) to silica pores showed similar trends with size exclusion of higher  $M_w$  components but was not favorable due to electrostatic repulsion between PAHA and silica surface under neutral pH conditions. PAHA adsorption to non-porous alumina and macro-porous AAMs was opposite to the case of adsorption to porous alumina, showing preferential adsorption of higher  $M_w$  components. It was found that PAHA adsorption to porous inorganic substrates was governed by a ratio between the hydrodynamic size (radius of gyration,  $R_g$ ) of PAHA and the size of pores (radius of pore,  $R_p$ ). PAHA was separated into 6 fractions (1, 2, 4, 6, 12, 43 kDa) using SEC techniques.

The adsorption of the PAHA fractions to porous alumina showed similar trends with the whole PAHA, which was also dependent on the  $R_g/R_p$  ratio. For the fractions (4, 6, 12, 43 kDa) having presumably larger  $R_g$  than alumina pore size ( $R_p$ ), lower  $M_w$  components of the fractions adsorbed preferentially due to size exclusion of bigger components. On the contrary, the fractions with smaller  $R_g$  (1, 2 kDa) showed preferential adsorption of higher  $M_w$  components, similar to the adsorption of the whole PAHA to non-porous alumina and macroporous AAMs.

The Freundlich model and the dual-mode model (i.e., a combination of hole-filling and solid phase dissolution) described well phenanthrene sorption to PS (i.e.,  $\mu\text{g-phenanthrene/mg-PS}$ , phenanthrene uptake normalized by PS loading,) which is loaded in porous silicas with various pore sizes. The characteristics of phenanthrene sorption to PS represented by the Freundlich isotherm model parameters ( $n$  and  $K_F$ ) and the ratio of hole-filling to solid phase dissolution ( $Q^0b/K_d$ ) of dual-mode model fitting changed depending on the  $R_g$  (PS size)/ $R_p$  (silica pore size) ratios of PS-loaded porous silicas. Integrated hysteresis index (IHI) values employed for estimating phenanthrene desorption irreversibility from PS-loaded silicas were also different under various PS loading conditions (i.e.,  $R_g/R_p$  ratio). Glass transition temperature ( $T_g$ ) of each of the PS-loaded silicas was different from that of bulk phase (particulate) PS and changed depending on the  $R_g/R_p$  ratio, which indicated that the physical characteristics of macromolecules (i.e., PS) can be altered in confining inorganic geometries of porous silicas.

Phenanthrene sorption to PAHA (i.e.,  $\mu\text{g-phenanthrene/mg-C}$  (PAHA), phenanthrene uptake normalized by PAHA loading) loaded in porous aluminas (PAs) and non-porous aluminas (NPAs) decreased with increasing PAHA adsorption/loading density (PAD) ( $\text{mg-C/m}^2\text{-adsorbent}$ ). This observation was attributed to low phenanthrene accessibility to the entire PAHA adsorbed on PAs and NPAs under higher PAD conditions. In general, the Freundlich isotherm parameter “ $n$ ” values for phenanthrene sorption to PAHA loaded in PAs were lower than those for PAHA loaded in NPAs. In both cases of PAHA-loaded PAs and NPAs, phenanthrene sorption isotherms were linear or near-linear.

Phenanthrene uptake by TMK NOM-loaded SWNTs was lower than that by SWNTs without TMK NOM loading. This observation was opposite to the cases of

macromolecule (e.g., PS, PAHA)-loaded (hydrophilic) silicas and aluminas, which showed higher phenanthrene uptake by macromolecule-loaded adsorbents than neat adsorbents. Chemical treatments of SWNTs using the Peroxone advanced oxidation process (AOP) (i.e, simultaneous treatment by ozone ( $O_3$ ) and hydrogen peroxide ( $H_2O_2$ )) also decreased phenanthrene uptake by SWNTs. Gas phase nitrogen ( $N_2$ ) adsorption analysis indicated that TMK NOM loading and Peroxone AOP treatments reduced the BET (Brunauer, Emmett, and Teller) specific surface area and pore volume of SWNTs. For Peroxone AOP-treated SWNTs, amorphous carbon increased as evidenced by increase in Raman D/G (D-band/G-band) ratio. The introduction of heteroxygen moieties by Peroxone AOP treatments, verified by FT-IR (Fourier transform infrared spectroscopy) spectra, was attributed to lower phenanthrene uptake. SEC results of TMK NOM solutions before and after contacting SWNTs showed preferential adsorption of the lower  $M_w$  (smaller in size) components of TMK NOM by SWNTs, possibly leading to a reduction in pore structures available for subsequent phenanthrene uptake.  $\pi$ - $\pi$  EDA (pi-pi electron donor acceptor) interactions, size exclusion, and steric effects were suggested as mechanisms of the sorption of SOCs to SWNTs based on *n*-hexadecane normalization analyses (i.e., normalization of hydrophobic effects) of uptake data of various SOCs (e.g., benzene, cyclohexene, chlorobenzene, methylbenzene, naphthalene, and phenanthrene) by SWNTs.

The association of NOM with hydrophilic/hydrophobic and porous/non-porous adsorbents (e.g., silica, alumina, SWNTs, and activated carbon) and nano-sized silica particles changed  $T_g$  of NOM. Such observation was i) similar to the case of loaded/confined PS (i.e. synthetic macromolecule) in silica pores, of which  $T_g$  was different from that of bulk phase (particulate) PS; ii) implied that the physical characteristics of NOM can be altered by association with the pores and surfaces of soils and sediments, which can affect sorption and desorption behaviors of SOCs released in the environment.