

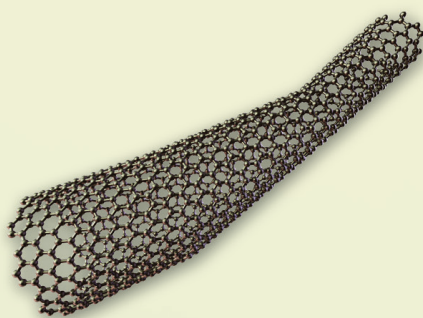
TGA-GC-MS

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Characterizing Interaction of Nanoparticles with Organic Pollutants Using Coupling Thermal Analysis with Spectroscopic Techniques

Introduction

There are more than a thousand products claiming to contain Engineered Nanoparticles (ENP) in products ranging from clothing, cosmetics, and electronics, to biomedical, chemical, energy, environmental, food, materials and optical products. The effects of ENP on environmental and human health are strongly related to their large surface-to-mass ratio and surface properties. Although the influence of natural colloids on the environment is well documented, we have limited understanding of the fate, transport, toxicity and pollutant interactions of ENP. The tools to study these interactions are being developed.

Pollutants-colloid interaction

Many nanoparticles suspended in natural water come in contact with pollutants and proteinaceous materials. The unique properties and behaviors of ENP are strongly influenced by their physical-chemical characteristics, including their high surface area relative to their volume, high interface energy and high surface-to-charge ratio density.

The partitioning and phase distribution of hazardous organic compounds (HOC) can influence the fate and bioavailability of the contaminants in aquatic systems and aquatic microorganisms significantly. There are a wide range of organic and inorganic pollutants that become associated with partitioning of HOC to the particles. This partitioning has been shown to be inversely proportional to log solubility of HOC and the log of particle concentration. Dynamics of nanoparticle-water partitioning can significantly influence the speciation, and hence, understanding the fate, transport and toxicological impact of POPs such as PAHs, PCBs is critical. The fate of organic pollutants in aquatic environment depends largely on their partitioning behavior to nanoparticles and colloids.

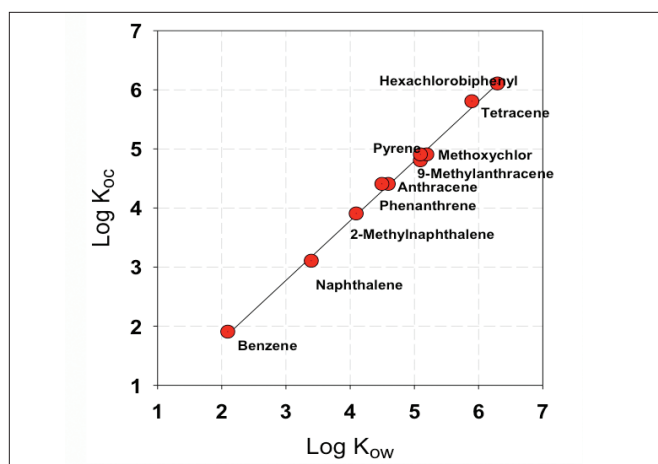


Figure 1. Suspended solid-organic carbon partitioning coefficient versus K_{ow} for polycyclic aromatic hydrocarbons and their derivatives (Karickhoff *et. al.*, Water Res., 241 (1979).

Pollutants sorbed on engineered nanoparticles

The sorption of pollutants onto nanoparticles in water phase will be the result of three phase partitioning of pollutants between organic phase, water and suspended solids.

Octanol-Water Partition Coefficient (K_{ow}) This coefficient represents the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher to K_{ow} , the more non-polar the compound. K_d is the ratio of pollutant attached onto the particle and in the water phase.

$$K_{ow} = \frac{C_o}{C_w} \quad K_d = \frac{C_p}{C_w'}$$

Where C_o , C_w and C_p are concentration of the pollutant organic compounds in the non-polar organic phase, in an equal weight of water, and concentration pollutants attached on per mass of particles. Ideally, these ratios are equilibrium partitioning of pollutants between organic phase, dissolved in water phase and particulate phases.

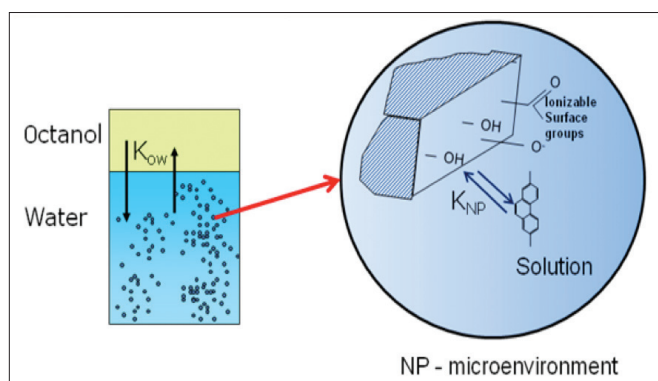


Figure 2. The influence of suspended nanoparticles on octanol-water partitioning of hydrophobic organic pollutants.

The physio-chemical properties relating to the environmental behavior of hydrophobic organic compounds are mainly affected by the aqueous solubility and octanol-water partition coefficient. Aqueous solubility (S_w) is the equilibrium distribution of a solute between water and solute phases. In other words, it is the maximum solute concentration possible at equilibrium, and it can function as a limiting factor in concentration dependent (for example, kinetic) processes. The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium. Octanol is an organic solvent that is used as a surrogate for natural organic matter. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment, such as predicting the extent to which a contaminant will bioaccumulate in fish. The octanol-water partition coefficient has been correlated to water solubility; therefore, the water solubility of a substance can be used to estimate its octanol-water partition coefficient. The presence of nanoparticles can influence the octanol-water partitioning of hydrophobic organic water contaminants.

Measurement techniques

We selected low molecular weight poly-aromatic hydrocarbons (PAHs) for this study including anthracene, naphthalene and phenanthrene as probe molecules to study the fate and transport of hydrophobic organic pollutants in water streams nanoparticles. The experimental procedure for this study involved the addition of 0-20 mg/L of PAHs in 200 mL of octanol to 900 mL of DI water containing different concentrations of nanoparticles (ranging from 0-20 mg/L) in an Erlenmeyer flask. After stirring the flasks for 5 days the mixture was allowed to settle for 3 hours and then the aqueous and octanol layers were separated. The aqueous suspensions were divided into three portions. One portion was extracted with equal volumes of methylene chloride (MC) and hexane. The mixture was centrifuged and the supernatant organic phase was collected and injected into the Clarus 600 GC from PerkinElmer. The concentrations of PAHs in MC and hexane and water were measured by gas chromatography analysis. The second portion was centrifuged at 10,000 rpm for 30 min. The mixture was decanted and the settled nanoparticles were put in a crucible to dry in an oven at 105 °C for 8 hr. The mass fraction of the adsorbed organics on dried particles was analyzed using a thermal gravimetric analyzer (PerkinElmer) and FT-IR or TOC.

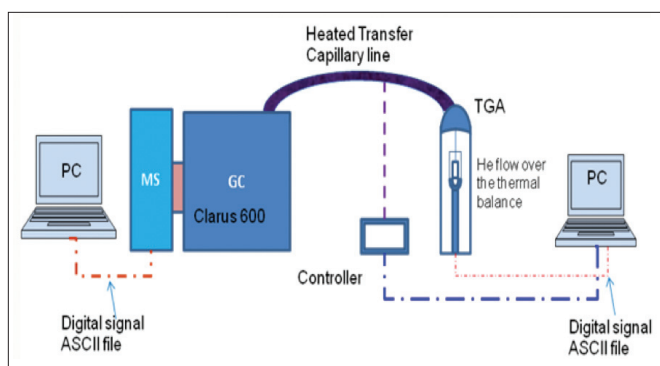


Figure 3. Schematic of PerkinElmer TGA-GC-MS set up with a heated transfer capillary line.

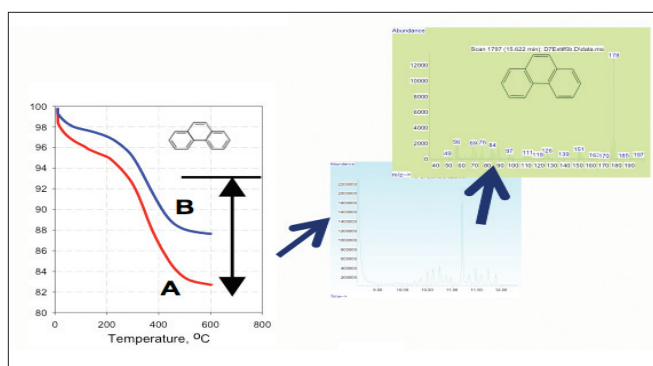


Figure 6. TGA of phenanthrene adsorption on nano-TiO₂ at pH of 10 (curve A) and 6.6 (curve B).



Figure 4. Photograph of PerkinElmer TGA-GC-MS System.

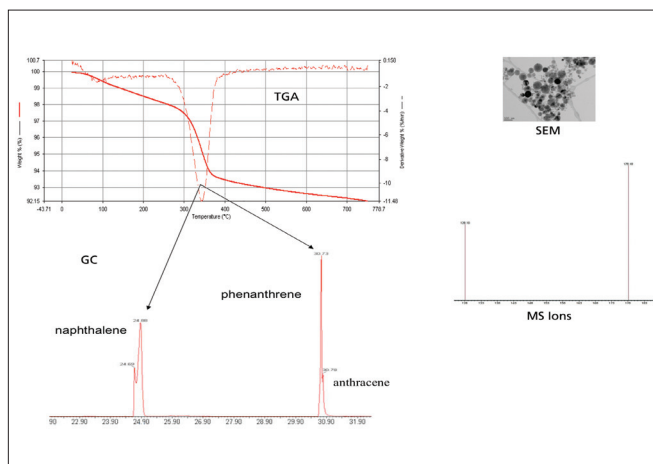


Figure 7. TGA-GC-MS data with SEM image.

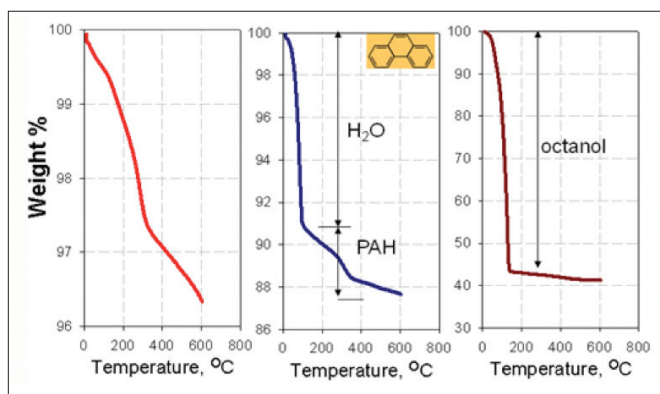


Figure 5. Thermal Analysis of nano-TiO₂, a) conOrganic pollutants adsorbed on nanoparticles: O-W Partitioning.

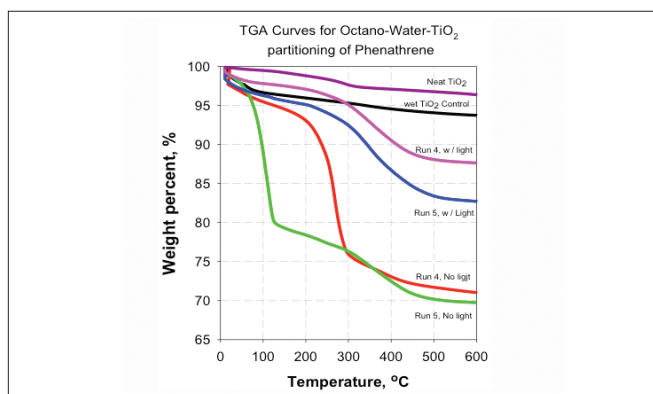


Figure 8. Absence of light made the nanoparticles less hydrophilic and increased the distribution to the organic phase.

Summary

- TGA-GC-MS is a useful technique to study nanoparticle influence on adsorption and partitioning PAHs.
- Presence of nano-TiO₂ increased the partitioning of PAHs to water phase.
- Nanoparticles resulted in increased partitioning of PAHs; six to ten times more than in water-octanol equilibrium conditions.
- Naphthalene and phenanthrene have low water solubility but differing partitioning.
- Partitioning influence increased at higher pH.
- Absence of light made the nanoparticles less hydrophilic and increased the distribution to the organic phase.
- Study suggested that the environmental risk of NP should include their transformation and influence in the transport of other pollutants.

Additional Reading

1. PerkinElmer, Inc. Nanotechnology and Engineered Nanomaterials – A Primer, www.perkinelmer.com/nano
2. PerkinElmer, Inc. Nanomaterials Reference Library www.perkinelmer.com/nano

References

1. Bom, D., Andrews, R., Jacques, D., Anthony, J., Chen, B., Meier, M.S., Selegue, J.P., Thermogravimetric Analysis of the Oxidation of Multiwalled Carbon Nanotubes: Evidence for the Role of Defects Sites in Carbon Nanotube Chemistry, NanoLetters, 2002, 2, 6, 615-619.
2. Pinault, M., Mayne-L'Hermite, M., Reynaud, C., Beynaud, C., Beyssac, O., Rouzaud, J.N., Clinard, C., Carbon nanotube produced by aerosol pyrolysis: growth mechanisms and post-annealing effects, (2004) 13, 1266-1269.
3. Penn, S.G., He, L. and Natan, M.J., Nanoparticles for bioanalysis. *Current Opinion in Chemical Biology* 2003, 7, 609-615.