

Interaction of Engineered Nanoparticles with Hydrophobic Organic Pollutants

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ABSTRACT

As nanomaterials become increasingly part of everyday consumer products, it is imperative to measure the potential release during production, use, and disposal, and assess their impact on human health and the ecosystem. This compels the research to better understand how the properties of engineered nanomaterials (ENM) lead to their accumulation and redistribution in the environment, whether they could become emerging pollutants or if can affect the mobility and bioavailability of other toxins. Organics pollutants that are liquid at room temperature associate with nanoparticles in an aqueous medium not only as molecules adsorbed on nanoparticles surfaces, but also as a discrete phase to form microscopic oil-nanoparticle aggregates. On the basis of our recent studies, pollutant-NP-aggregate formation is believed to be instrumental in an intended or unintended dispersion of organic pollutants. This knowledge would allow the use of environmentally friendly nanoparticles for cleanup of oil spills or other techniques such as surf washing. A better understanding of the nature and properties of pollutant-nanoparticle-aggregate will help predict the fate of pollutants in the aquatic environment. This work describes the various instruments and methods currently available for the detection and identification of pollutant-nanoparticle-aggregate.

The sorptive properties of engineered nanomaterials (ENMs) were also investigated, with polyaromatic hydrocarbons and organochlorine pesticides used as model pollutants. Linear Freundlich adsorption constants for the ENMs were correlated with the

octanol-water partitioning organic pollutants. The suspended particles from the water phase were separated, and the adsorbed substances were analyzed using a combination of thermal-chromatographic-mass spectroscopic techniques. Sorption of hydrophobic organic pollutants to nano-particles increased the concentration of contaminants in the aqueous phase as compared to the "real" partitioning due to the octanol-water partitioning. The effects water chemistry on the partitioning of hydrophobic pollutants to EMS were investigated. The effects of nano-materials on the mobility of pollutants that are commonly found at many sites have been studied. These compounds include aromatic hydrocarbons, and two and three-ring polyaromatic hydrocarbons that have relatively small water solubility. The high partitioning coefficient indicated engineered nanomaterials have the potential to increase the mobility of hydrophobic pollutants in aquatic environment.

Key words: engineered nanomaterials, pollutants, adsorption,

1. INTRODUCTION

The fate of organic pollutants released into the environment are primarily controlled by a combination of main environmental conditions, the physicochemical properties of the compound, at the point(s) of discharge, transport, interaction and subsequent residence of the compound.

Many water contaminants can sorb onto natural colloids such as humic substances, clay and metal oxides in suspension, thereby increasing their concentrations in

solution beyond thermodynamic solubilities (Kim et al., 1992). Hydrophobic organic pollutants have a tendency to avoid contact with water and to associate with a nonpolar particles containing an organic coating or the lipid-containing biomass of an organism [1]. Many of these contaminants are also transported not only in a dissolved state by water, but also sorbed to moving colloids [2-11]. The adsorption behavior of hydrophobic pollutants onto colloids and their transport may also increase their bioavailability [12,13]. Hence, mobile colloidal particles may act as carriers of strongly sorbing contaminants in surface and subsurface pollutants. Since mobile colloids often move at rates similar or faster as nonsorbing tracers, the potential of enhanced transport of colloid-associated contaminants can be very significant [14]. The increased development and production of engineered (ENP) nanoparticles in many used in many consumer products has increased the potential risk of their release into the environment. The high surface area activity of ENP may result in increased interaction with pollutant could have significant influence on their transport

2. Equations

The sorption of polyaromatic hydrocarbons and hydrophobic pesticides on different NMs were investigated Three phase partitioning of POPs are measured by partition Coefficient of pollutant between NP and dissolved phase

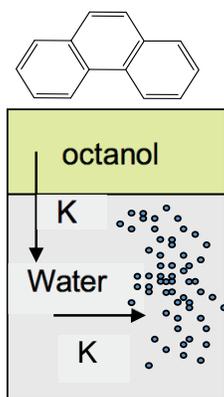


Figure 1 Schematic of three phase partitioning of pollutants between organic-water-nanoparticle phase



Mass balance of pollutant

$$K_{NP} = \frac{[Pollut]_{NP}}{[Pollut]_{Free}[NP]} \dots\dots\dots(1)$$

Rearranging equation 1

$$[pollut]_{total}[Pollut]_{Free} = 1 + K_{NP}[NP] \dots\dots\dots(2)$$

Where $[Pollut]_{total}$ and $[Pollu]_{total}$ are retentate and permeate concentration. Equation 2 is similar to Stern-Volmer relationship.

A complete phase separation between NP and water is necessary to obtain a valid K_{NP} value. Generally, this cannot be achieved due to the fact that the very fine particles pass through the filter, or do not settle during centrifugation. As a result the concentration of contaminants in the water phase could be overestimated, and the NP-water partition coefficient is underestimated.

For octanol-water partitioning of pollutants

$$1) \quad C_w = \frac{C_o}{K_{ow}}$$

For Equilibrium process the sorption of hydrophobic pollutants to ENP

$$2) \quad C_s = K_{NP} C_w^{1/n}$$

Combining equations (1) and (2)

$$\log K_{oc} = A \bullet \log K_{ow} + \log f_{oc} + B$$

Where: C_s = Concentration in NP phase,
 C_w = Concentration dissolved in water
 C_o = con. in octanol phase
 K_{ow} = octanol water partitioning

3. EXPERIMENTAL

Materials

We tested using 2 and 3 ring PAHs for this study including anthracene, naphthalene and phenanthrene and pesticides as probe molecules to study the fate and transport of hydrophobic organic pollutants in water

streams nanoparticles. The experimental procedure for this study involves 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 Erlenmeyer flask. After stirring the flasks for 5 days the mixture is allowed to settle for 3 hours and then the aqueous and octanol layers will be separated. The aqueous suspensions were divided into three portions. One portion will be extracted with equal volumes of methylene chloride (MC) and hexane. The mixture will be centrifuged and the supernatant organic phase will be collected and injected into GC. The concentrations of PAHs in MC and hexane and water were measured by Gas chromatography analysis. The second portion will be centrifuged at 10,000 rpm for 30 min. The mixture will be decanted and the settled nanoparticles will be put in crucible to dry in oven (105 °C) for 8 hr. The mass fraction of the adsorbed organics on dried particles will analyzed using thermal gravimetric analyzer (Perken Elmer) and FTIR or TOC

4. RESULTS

Pollutant adsorption on Nanoparticles

The fate of organic compound released into the environment is primarily controlled by factors like the prevailing environmental conditions at the point(s) of discharge, transport and subsequent residence, the physicochemical properties of the compound, and the patterns of use (that is, locus and timing of introduction. The physico-chemical properties relating to the environmental behavior of hydrophobic organic compounds are mainly affected by the aqueous solubility and octanol-water partition coefficient.

Pollutants adsorbed to suspended nanoparticles were determined with thermogravimetric technique integrated with gas chromatography and mass spectrometry (Figure

Aqueous solubility (S_w) is the equilibrium

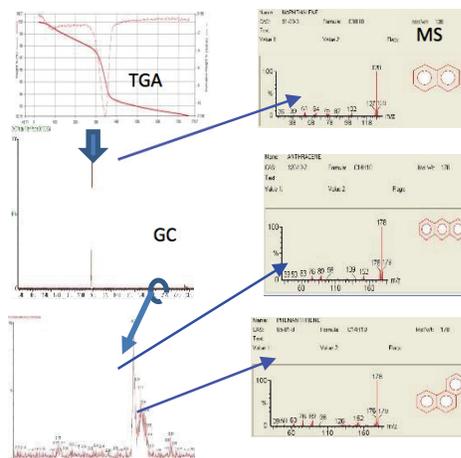


Figure 2. TGA –MS for analysis of Polyaromatic hydrocarbons adsorbed on nano-TiO₂

Adsorption isotherm of PAH on carbon-nanotube is shown in Figure 3.

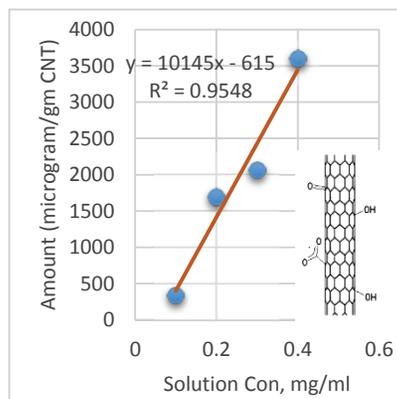


Figure 3 Adsorption isotherm

Disclaimer

The views expressed in this extended abstract are those of the author and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency

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