Short Communication

NANOWASTES AND THE ENVIRONMENT: USING MERCURY AS AN EXAMPLE POLLUTANT TO ASSESS THE ENVIRONMENTAL FATE OF CHEMICALS ADSORBED ONTO MANUFACTURED NANOMATERIALS

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Abstract—Emerging nanotechnologies hold great promise for creating new means of detecting pollutants, cleaning polluted waste streams, and recovering materials before they become wastes, thereby protecting environmental quality. Studies focusing on the different advantages of nanoscience and nanotechnology abound in the literature, but less research effort seems to be directed toward studying the fate and potential impacts of wastes that will be generated by this technology. Using a combination of biogeochemical and toxicological methods, we conducted a preliminary investigation of the potential environmental fate of Hg as an example pollutant bound to nanomaterials used in treatment of gas effluents. Methylation of Hg sorbed onto SiO_2-TiO_2 nanocomposites was used as a proxy for Hg bioavailability to sedimentary microorganisms, and the FluoroMetPLATE™ assay was used to assess the toxicity of both virgin and Hg-loaded SiO_2-TiO_2 nanocomposites. Our results show that the bioavailability of Hg sorbed onto SiO_2-TiO_2 nanocomposites to sedimentary microorganisms is pH dependent, with decreasing reaction rates as the pH increases from 4 to 6. Toxicity tests conducted using liquid extracts obtained by leaching of Hg-loaded SiO_2-TiO_2 nanocomposites with the synthetic precipitation leaching procedure solution showed an average inhibition of 84% (vs 57% for virgin SiO_2-TiO_2 nanocomposites). These results suggest that Hg sorbed onto engineered nanoparticles could become bioavailable and toxic if introduced into natural systems. Accordingly, studies focusing on the environmental implications of nanomaterials should include determination of the fate and impacts of pollutants that enter the environment bound to engineered nanomaterials.

Keywords—Nanowastes   Titania-silica nanocomposites   Mercury   Trojan horse effect   Toxicity

INTRODUCTION

The environmental fate and transport of manufactured nanomaterials (MNs) as well as the fate of pollutants sorbed onto MNs through nanotechnology-based remediation processes are of growing concern. This is because nanoscience and nanotechnology are now poised to become the most important drivers of economic growth and development for the early 21st century. Most scientists and engineers are confident that nanoscience and nanotechnology will revolutionize medicinal, industrial, agricultural, and environmental research as a wide variety of MNs are produced [1]. Although in its infancy, research concerning both the environmental impacts and the health implications of MNs is growing quickly [2–7]. In contrast, the fate and potential impacts of pollutants sorbed onto MNs through nanotechnology-based remediation processes have been simply ignored. For instance, the use of MNs in the removal of pollutants from either aqueous and/or gaseous effluents will generate nanowastes that need to be either recycled or disposed of safely. So far, a reactive approach has been the most common way of dealing with emerging pollutants [8]. Unfortunately, a major disadvantage of this late corrective approach is the difficulty in dealing with well-established economic activities that generate the pollutants of concern. Therefore, a proactive approach is ideal to limit the complex ramifications associated with delayed prevention and remediation measures [8].

We assessed the fate and potential impacts of Hg sorbed onto MNs (e.g., SiO_2-TiO_2 nanocomposites) by mimicking the Trojan horse effect in a sediment matrix. Spent SiO_2-TiO_2 nanocomposites used in the removal of Hg from a simulated coal combustion effluent were used in laboratory studies to determine the bioavailability of inorganic Hg sorbed onto SiO_2-TiO_2 nanocomposites using Hg methylation as a proxy for bioavailability, and the toxicity of Hg-SiO_2-TiO_2 complexes was determined using FluoroMetPLATE™ (MetPlate, Gainesville, FL USA), a bacteria-based microbiotest.

MATERIALS AND METHODS

A thorough description of the procedure used to prepare the SiO_2-TiO_2 nanocomposites as well as the mechanisms of Hg sorption onto MN surfaces has been given previously by Pitoniak et al. [9]. For measurement of Hg bioavailability using microbially catalyzed methylation as a surrogate for bioaccessibility and to minimize the Hg methylation signal associated with the sediment native Hg, we intentionally used pristine sediments with a background total Hg (THg) concentration of only 5.68 ± 0.44 ng/g wet weight (Odum Wetland, Gainesville, FL, USA). This THg value falls on the low end of the reported global background range, for which common values are mostly between 200 and 400 ng/g. Sediments were sieved (mesh size, <2 mm) to produce a homogeneous fine material and then used in laboratory experiments as a source of Hg-methylating bacteria. Mercury methylation experiments were conducted using sediment slurries prepared with Nanopure® water (Sybron-Barnsted, Dubuque, IA, USA) in a 1:5 ratio (mass/volume). The initial pH of the slurries was 4, and a 0.1 N NaOH solution was used to produce slurries with pH greater than 4. All the prepared sediment slurries were then deaerated with ultrahigh-purity N_2 to help accelerate the development of
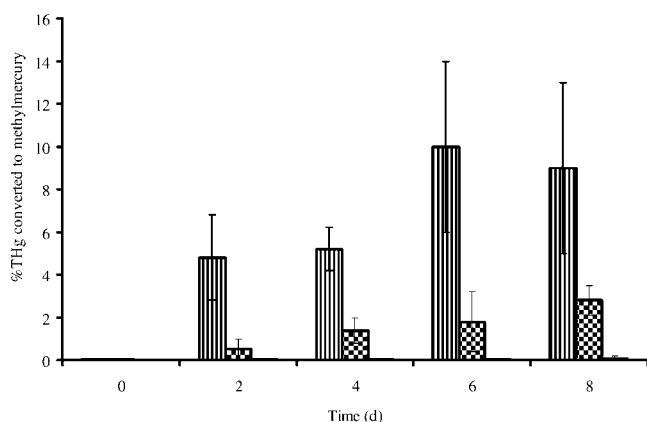
Fig. 1. Percentage of total Hg (THg) converted to methylmercury in sediment slurries spiked with Hg at different pH values. At pH 6, methylmercury concentrations were either less than or at the analytical detection limit of 0.05 ng/g. ▥ = pH 4; ▨ = pH 5; ■ = pH 6.
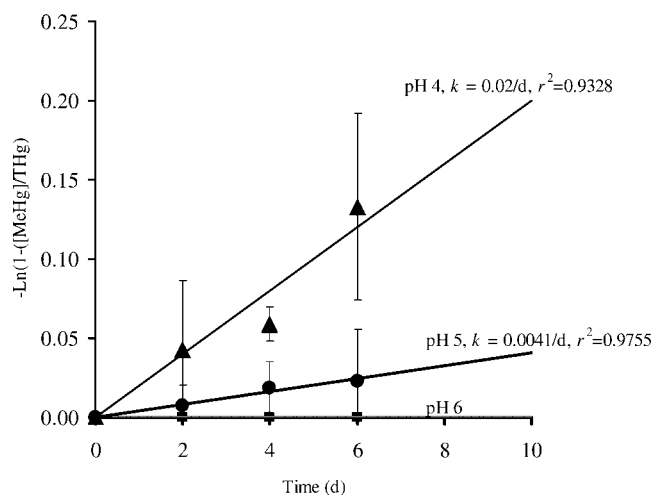

Fig. 2. Kinetics of Hg-nanocomposite methylation in sediment slurries with pH 4 (▲; native pH), pH 5 (●), and pH 6 (■). The methylation of inorganic Hg decreases with increasing pH to reach values less than the analytical detection limit (0.05 ng/g) at pH 6. MeHg = methylmercury.

anoxic conditions and favor methylmercury production. Overall, the experiment consisted of control slurries with no Hg addition and slurries spiked with Hg as Hg-SiO_2-TiO_2 complexes. In this latter treatment, Hg was added to increase the background amount of THg naturally present in sediments by approximately 40%. Tubes were then sacrificed at different time periods and analyzed for produced methylmercury. In the present study, THg and methylmercury concentrations in the aqueous phase and in sediments were determined following previously published methods [10–13].

To assess the toxicity of SiO_2-TiO_2 nanocomposites used in Hg removal from gaseous effluents, both virgin and spent SiO_2-TiO_2 nanocomposites were leached separately using the synthetic precipitation leaching procedure (SPLP) solution, which is a mixture of HNO_3 and H_2SO_4 with a final pH of 4.22 ± 0.05 [14]. Based on preliminary determinations of percentage inhibition, a 1:60 ratio (ml/mg) was used, and for each replicate, approximately 0.18 g of either single nano-oxides (i.e., SiO_2 and TiO_2), virgin SiO_2-TiO_2 nanocomposites, or Hg-loaded SiO_2-TiO_2 nanocomposites were leached with 3 ml of SPLP solution on a Roto-shaker Genie® (Scientific Industries, Bohemia, New York, USA) for 18 h. After centrifugation at 10,000 RPM for 30 min, aliquots of the supernatant were removed and used immediately for toxicity assays [15] and analysis for THg following digestion with bromine monochloride [13].

RESULTS AND DISCUSSIONS

Our results show that the treatment imposed on these slurries induces the methylation of both background Hg initially present in the sediment (control) and Hg added as Hg-nanocomposite complexes. The percentage of THg methylated from the Hg-SiO_2-TiO_2 complexes added to slurries and corrected from control samples is shown in Figure 1 as a function of pH. These results show an increasing and pH-dependent trend of methylmercury production over time, with more methylmercury produced at the lowest tested pH. This trend suggests that microbial Hg methylation could be controlled by the solubility of Hg sorbed onto MNs, which decreases with increasing pH. Although this trend also can be attributed to the effect of pH change on Hg-methylating microorganisms, the detection of methylmercury under these tested conditions, regardless of the amount produced, clearly is a strong indication for

the bioavailability of Hg-sorbed onto SiO_2-TiO_2 nanocomposites.

Using the linear portion of the above-described Hg methylation trends and assuming that the methylation rates of inorganic Hg would be far in excess of the rates of demethylation of produced methylmercury (i.e. $K_m \gg K_d$, where K_m and K_d are reaction constant rates for the methylation of inorganic Hg and the demethylation of methylmercury, respectively), a pseudo–first order kinetics assumption would then allow determination of the reaction rates at different pH values (Fig. 2). The determined constant rates for Hg methylation in slurries spiked with Hg-SiO_2-TiO_2 complexes were $K_m = 0.02$ and 0.004/d at pH 4 and 5, respectively. The reaction constant rate approached zero at pH 6, as methylmercury levels in sediment slurries became barely detectable. Additionally, the rate determined at pH 4 was approximately one order of magnitude lower than the reaction rate observed in sediments slurries spiked with free ionic Hg added as $HgCl_2$. Although the experiment with $HgCl_2$ additions was used at the native sediment pH only (pH 4), the obtained results suggest that Hg sorption onto nanocomposites delays its bioaccessibility. Overall, Hg sorbed onto MNs and introduced into sedimentary environments could quickly become bioavailable and, therefore, toxic in more acidic systems.

The concentration of THg bound onto the SiO_2-TiO_2 nanocomposites averaged 639.04 ± 366.31 ng/g nanomaterial, whereas THg concentrations on plain materials were at or less than our analytical detection limit (0.05 ng/g). The SPLP extraction procedure was comparatively applied to SiO_2 and TiO_2 nanoparticles; ultraviolet-irradiated, virgin SiO_2-TiO_2 nanocomposites; and the Hg-contaminated, ultraviolet-irradiated nanocomposites [9]. Obtained leachates were then used for toxicity testing with FluoroMetPLATE, which is specific to heavy metal toxicity [15]. The toxicity results expressed as percentage inhibition are presented in Figure 3. Based on this toxicity test, SiO_2 and TiO_2 nanoparticles are rather nontoxic, despite the 4% inhibition response obtained with SiO_2 leachate. In contrast, both the virgin and Hg-contaminated nanocomposites show a much higher toxicity, with an average inhibition of 57 and 84%, respectively. It appears that both the support
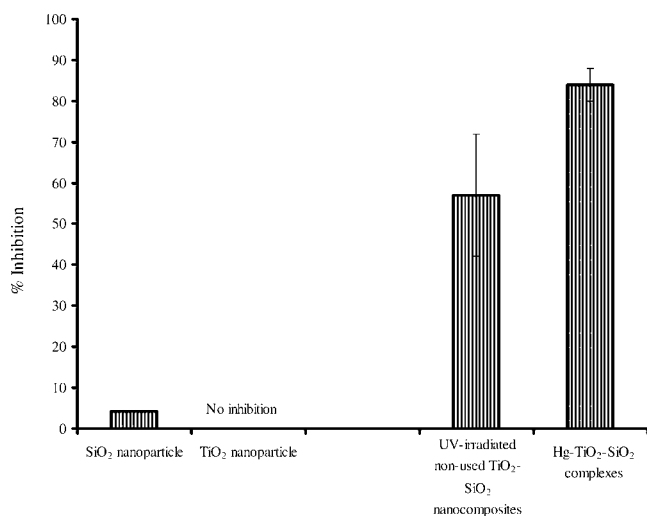
Fig. 3. Toxicity effect of the synthetic precipitation leaching procedure solutions obtained from leaching of virgin and Hg-loaded SiO_2-TiO_2 nanocomposites in a 1:60 ratio (ml synthetic precipitation leaching procedure solution/mg nanomaterial). Results are expressed as the percentage inhibition. UV = ultraviolet light.

material (i.e., SiO_2-TiO_2 nanocomposites) and Hg adsorbed onto it contribute to the recorded inhibition. The toxicity of virgin SiO_2-TiO_2 nanocomposites (57% inhibition) likely results from its physicochemical characteristics, whereas the much higher inhibition recorded with the Hg-contaminated SiO_2-TiO_2 nanocomposites indicates an additional toxicity effect from the adsorbed toxic Hg. In sediment slurries spiked with SiO_2-TiO_2 nanocomposites, the above-observed toxicity could translate into reduced Hg methylation as bacteria involved in Hg biotransformation become affected. Consequently, the detection of methylmercury in these methylation experiments points to the potential bioavailability of Hg sorbed onto SiO_2-TiO_2 nanocomposites.

In summary, pollutant-loaded MNs from nanotechnology-based remediation processes could result in potential concerns related to the environmental fate of adsorbed pollutants as they ultimately enter natural (e.g., waterways) or engineered (e.g., landfills) systems as waste streams. Compared to sediments spiked with free $HgCl_2$, the addition of MN-adsorbed Hg to sediment slurries resulted in slower rates of methylmercury production and near-total inhibition of Hg methylation at pH 6 or greater. Overall, these results point to the potential for bioaccessibility of MN-adsorbed pollutants as a function of certain key environmental parameters, such as acidic pH.

These preliminary results clearly illustrate the need for further research that could lead to guidelines for the handling and disposal of nanowastes.

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