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Chemosphere

Influence of silver nanoparticles on heavy metals of pore water in contaminated river sediments

Wei Tao [a, b], Guiqiu Chen [a, b, *], Guangming Zeng [a, b, **], Ming Yan [a, b], Anwei Chen [c], Zhi Guo [a, b], Zhenzhen Huang [a, b], Kai He [a, b], Liang Hu [a, b], Lichao Wang [a, b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] College of Resources and Environment, Hunan Agricultural University, Changsha 410128, PR China

HIGHLIGHTS

- AgNPs caused heavy metals to be transferred from surface water to sediment.
- Heavy metals were released to water phase in ionic form after sedimentation.
- Hg^{2+} was reduced to Hg^0 and formed Ag-Hg amalgam in sediment pore water.

GRAPHICAL ABSTRACT
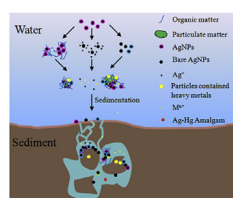
ARTICLE INFO

ABSTRACT

Despite the increasing knowledge on the discharge of silver nanoparticles (AgNPs) into the environment and their potential toxicity to microorganisms, the interaction of AgNPs with heavy metals remains poorly understood. This study focused on the effect of AgNPs on heavy metal concentration and form in sediment contaminated with heavy metals from the Xiangjiang River. The results showed that the concentration of Cu, Zn, Pb and Cd decreased and then increased with a change in form. The changes in form and concentrations of heavy metals in pore water suggested that Cu and Zn were more likely to be affected compared to Pb and Cd. The concentrations of Hg in sediment pore water in three AgNPs-dosed containers, increased greatly until they reached their peaks at 4.468 ± 0.133, 4.589 ± 0.235, and 5.083 ± 0.084 $\mu g\ L^{-1}$ in Bare AgNPs, Citrate AgNPs and Tween 80 AgNPs, respectively. The measurements of Hg concentrations in the sediment pore water, combined with SEM and EDX analysis, demonstrated that added AgNPs stabilized in pore water and formed an amalgam with Hg^0, which can affect Hg transportation over long distance.

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1. Introduction

With a significant increase in development of nanotechnology, greater attention is being paid to the pollution by engineered nanomaterials (ENMs). The latter is a new class of pollutants, and, little information is currently available on their potential environmental impacts. ENMs have unique properties that emerge at small dimensions. It has been shown that the same properties may also have adverse effects on organisms once they were released to the environment (Shoults-Wilson et al., 2013) while the magnitude of these adverse effects depends on the characteristics, concentration, bio-availability, and transformations of ENMs in the environment.

In recent years, there has been a great focus on testing the toxicity of Ag nanoparticles (AgNPs), because AgNPs are one of the

most commonly used ENMs in consumer products, serving mainly as antimicrobial agents. The widespread use of AgNPs can result in leaching of AgNPs into natural water from manufacturing and disposal of consumer products without entering wastewater treatment (Benn and Westerhoff, 2008; Jones and Hoek, 2010; Mueller and Nowack, 2008), even though municipal wastewater treatment plants have a high removal efficiency of AgNPs (Li et al., 2013).

River sediment is a main potential place ENMs would end up through spillage, discharge, atmospheric deposition, soil runoff, or STP discharge waters (Blaser et al., 2008; Boxall et al., 2007; Mueller and Nowack, 2008). The wider production and use of ENMs will inevitably result in their release into the river system. The Xiangjiang River is one of the tributaries of the Yangtze River in China, and the largest river in Hunan province, has a surface area of 94,600 km^2, and a total length of 856 km. Many large cities, such as Changsha, Xiangtan and Zhuzhou, are located in the middle and lower reaches of the Xiangjiang River. The mining and metallurgical industries are highly developed in this basin. The Xiangtan Steel Group, Zhuzhou Metallurgical Corporation and Shuikoushan Mining Bureau are distributed along the lower reaches of the river (Mao et al., 2014). The Xiangjiang River has suffered from substantial metal contaminations because of urbanization and industrialization. In some areas, the concentration of Cd, Zn, and Cu transcended the standard values of Grade III standard of China environmental quality standard for soil (GB15618-1995) by 10—170 times, 2.2—10.2 times and 1.4 times, respectively (Zhu et al., 2012).

Numerous studies have demonstrated that AgNPs can be toxic to bacteria (Jeon et al., 2003; Bosetti et al., 2002), invertebrates (Bielmyer et al., 2002), algae and plants (Lee et al., 2012; He et al., 2012), or it can stimulate the activity of microorganisms (Guo et al., 2016; Zuo et al., 2015). However, the extent of toxicity of AgNPs varies with water chemistry and sediment characteristics (Chambers et al., 2014) possibly because AgNPs interact with natural aquatic colloids after their release. This can affect the stability and subsequent environmental behavior of both AgNPs and aquatic colloids (Lin et al., 2010). Trace metals can be associated with particles and colloids, which play an important role in heavy metal transport, and can be affected by AgNPs (Vignati and Dominik, 2003).

To assess the potential risk of ENMs entering the river system, we need to understand the role that water chemistry and sediment characteristics play on ENMs stability, mobility and toxicity. The transformation and toxicity of ENMs have been widely studied in both laboratory and field experiments (Unrine et al., 2012a, 2012b; Lowry et al., 2012). While these studies have provided a valuable insight into the mechanisms that control the transformation and toxicity of ENMs, the influence of ENMs on heavy metals in natural river systems were ignored, even in systems that are severely contaminated with heavy metals.

To better understand the influence of AgNPs on river sediments that have been contaminated with heavy metals, AgNPs with three different kinds of coatings were synthesized in the laboratory and characterized by ultraviolet—visible (UV—vis) spectrophotometry, dynamic light scattering (DLS). Hollow fiber membranes were used to collect sediment pore water, without disturbing the sediment environment. In order to analyze the change of heavy metal concentration and morphology induced by AgNPs in contaminated sediments, the total and colloidal concentrations of different heavy metals in pore water at different times were determined. These data together with the results from scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis facilitated clarification of the mechanisms involved in the concentration and morphology change of heavy metals in sediment pore water.

2. Materials and methods

2.1. Synthesis and characterization of AgNPs

Three types of AgNPs were prepared in this study. The preparation followed the method of previous studies (Kvitek et al., 2008), with some minor modifications. 4 mL of 10 mM $AgNO_3$ and 20 mL of 20 mM $NH_4 \cdot OH$ were mixed in a 100 mL beaker and were vigorously stirred with a magnetic stir bar. Then 2 mL of 0.1 M NaOH was added to adjust the pH value of the solution to 12 and 16 mL of 25 mM D-maltose was added into the mixture to form silver nanoparticles. Citrate AgNPs and Tween 80 AgNPs were prepared by adding pre-calculated volumes of the bare silver nanoparticle stock suspension and either trisodium citrate or Tween 80 into a 50 mL polycarbonate centrifuge tube in order to achieve 1 mM trisodium citrate or 10 mM Tween 80. NaCl, Na_2CO_3 and NaOH were added to adjust the ionic strength to 1 mM and pH at 7.0 ± 0.3, respectively. The tubes were sealed and shaken for 24 h in the dark at room temperature (22 °C). Dialysis was conducted using cellulose ester membranes (Spectra/Pro® Biotech) with a molecular weight cut off of 8—10 kDa for Bare AgNPs and Citrate AgNPs and 50 kDa for Tween 80 AgNPs. The Ag concentrations of AgNPs stock solutions were measured by flame atomic absorption spectrometry (AAS700, PerkinElmer, USA), after HNO_3 digestion. The dissolved fraction of the AgNPs stock solution was less than 1%, as determined by analyzing the filtrate of ultrafiltration centrifuged stock suspension (Amicon Ultra-0.5 3 K centrifugal tube, Millipore), using ICP-OES (IRIS Intrepid II XSP, Thermo Electron Corporation, USA). The UV absorption spectrum of the stock AgNPs suspensions was measured using a UV—visible light spectrophotometer at wavelength between 300 and 600 nm (Model UV-2550, Shimadzu, Japan). AgNPs size distributions were determined using a Zetasizer Nanoseries (Malvern Instruments) with a 633 nm laser source and a detection angle of 173°.

2.2. Sediment source and characterization

Laboratory experiments were performed with sediments contaminated with heavy metals and surface water from the Xiangjiang River. Sediments and surface water were collected from the Xiangjiang River under the forth bridge on the river as shown in Fig. 1. Sediments were processed with a 2 mm sieve, in order to remove large debris. Porosity was determined by drying 5 cm^3 sediment samples at 80 °C for 48 h. Total organic carbon (TOC) was measured with a TOC analyzer (TOC-VCPH, Shimadzu, Japan), after acidifying 0.1 g of dried sediment with 2 mL of 4 M HCl (non-oxidizing acid which has little influence on organic materials), in order to remove inorganic carbon (Rawlins et al., 2008; Edmondson et al., 2015). TOC of sediment was measured for soil background check, the deviation won't affect our experiment. Total bulk sediment metal concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, PS-6, BAIRD) after microwave-assisted acid digestion following USEPA method 3051 A. Sediment characteristics and element concentrations are shown in Table S1.

2.3. Experimental setup

The experiments were performed in plastic containers with two rows of holes in the wall equipped with pore water collection equipment. The pore water collection equipment consisted of a PVDF hollow fiber membrane (pore size 1 μm) with both ends in a plastic hose of 3 mm diameter, forming a closed circle, and a plastic needle stuck through the container wall into the other end of the plastic hose. All joints were sealed with 707 silicone rubbers. All