

Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics

TROY M. BENN* AND PAUL WESTERHOFF

Civil and Environmental Engineering, Arizona State University, Box 5306, Tempe, Arizona 85287-5306

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Manufacturers of clothing articles employ nanosilver (n-Ag) as an antimicrobial agent, but the environmental impacts of n-Ag release from commercial products are unknown. The quantity and form of the nanomaterials released from consumer products should be determined to assess the environmental risks of nanotechnology. This paper investigates silver released from commercial clothing (socks) into water, and its fate in wastewater treatment plants (WWTPs). Six types of socks contained up to a maximum of 1360 $\mu\text{g-Ag/g-sock}$ and leached as much as 650 μg of silver in 500 mL of distilled water. Microscopy conducted on sock material and wash water revealed the presence of silver particles from 10 to 500 nm in diameter. Physical separation and ion selective electrode (ISE) analyses suggest that both colloidal and ionic silver leach from the socks. Variable leaching rates among sock types suggests that the sock manufacturing process may control the release of silver. The adsorption of the leached silver to WWTP biomass was used to develop a model which predicts that a typical wastewater treatment facility could treat a high concentration of influent silver. However, the high silver concentration may limit the disposal of the biosolids as agricultural fertilizer.

Introduction

The burgeoning nanotechnology industry is quickly producing nanomaterials that are being incorporated into consumer products. As of 2007, the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars had compiled a list of more than 500 consumer products that claim to include some form of engineered nanoparticle (1). Of these products, about 20% contain silver nanoparticles. Socks, paints, bandages, and food containers incorporate nanosilver (n-Ag) to exploit its antimicrobial properties. In clothing such as socks, n-Ag may restrict the growth of odor-causing bacteria (2–10).

Despite the growing commercialization of n-Ag, little is known about the environmental effects of widespread use of products containing silver nanoparticles (11). Ionic silver is highly toxic to aquatic organisms (12–14), and the United States Environmental Protection Agency (USEPA) has set water quality criteria values for silver in salt and fresh water at 1.9 and 3.4 ppb, respectively. The USEPA has also instituted a secondary drinking water standard for silver of 100 ppb. Toxicity and exposure data for nanoparticle silver, however, is currently lacking (15–17). Studies have demonstrated the

toxicity of nanoparticle silver to bacteria (3, 5, 6, 8, 10), suggesting that the antimicrobial effects of silver may be detrimental to aquatic ecosystems. Therefore, it is important to characterize (as colloidal or ionic) and quantify the silver released from commercial products.

The ubiquitous use of commercial products containing n-Ag could potentially compromise the health of many ecosystems. For example, household washing of clothing containing n-Ag may release silver into sewer systems. Since more than 70% of the U.S. population is served by public sewers (18), most of the n-Ag from consumer products would enter a municipal wastewater treatment plant (WWTP). The n-Ag present in sewage may partition onto wastewater biomass and be removed at a WWTP, only to re-enter the environment via agricultural land application of wastewater treatment biosolids. If n-Ag proves to be difficult to remove in a wastewater treatment system, n-Ag remaining in the treated effluent stream may enter surface water environments, potentially disrupting numerous biological ecosystems.

This paper investigates n-Ag release from commercial clothing (specifically, socks) into water, as well as the form of this silver and the adsorption characteristics that determine its fate in WWTPs. The amount of n-Ag in the sock fabric was quantified before determining the concentration and form (nanoparticle or ionic) of the silver released during repeated washings of the socks with distilled water. Batch adsorption isotherm studies were conducted with wastewater biomass and two sources of silver: (1) silver released from the socks into the wash water (nanoparticle or ionic), and (2) reagent ionic silver. These isotherms were then used with a partition model for wastewater treatment to evaluate the amount of silver that could be present in the treated effluent or WWTP biosolids.

Materials and Methods

Acid Digestions of Sock Fabric. Six brands of commercially available socks were purchased (Table 1) based on the manufacturers' claims that the socks contained nanoparticles of silver. A modified digestion method was used to quantify the amount of silver in the socks (EPA SW 846 Method 3050B). An air-dry mass (100–500 mg-dry) of each sock was submerged in a solution of 5 mL of ultrapure reagent grade nitric acid (6901-05, JT Baker, Phillipsburg, NJ) and 5 mL of deionized water. After a watch glass was placed over the digestion beaker, the solution was heated to approximately 100 °C and allowed to react. Nitric acid was added in 2 mL aliquots until the bulk of the sock material was digested. The digestion solution was allowed to cool, and then 3 mL of 30% hydrogen peroxide (HX0635-2, EMD Chemicals Inc., Gibbstown, NJ) was added to complete the digestion process. Again the digestion beaker was heated to 100 °C, and hydrogen peroxide was added in 1 mL aliquots until effervescence was minimal, indicating completion of the digestion. The digestion solution was cooled, filtered through a glass fiber filter (Qualitative #2, Whatman) and diluted to 100 mL. Silver was quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES iCAP 6000, Thermo Scientific).

Washing of Socks in Water. Socks were placed in 1 L amber glass bottles with 500 mL of ultrapure water (Millipore Inc.). The bottles were agitated for either 24- or 1-h contact times on an orbital shaker table at approximately 50 rpm. The 24-h contact time was chosen to allow sufficient opportunity for the socks to leach silver. The 1-h contact time is more representative of a "real world" washing machine cycle, though the quantities of leached silver from both

* Corresponding author phone: 480-965-3589; fax: 480-965-0557; e-mail: Troy.Benn@asu.edu.

TABLE 1. Sock ID/Characterization and Silver Content

sample ID	sock company	description (color)	price per pair	acid digestion analysis		wash analysis	
				mass of silver per mass of sock ($\mu\text{g Ag/g sock}$)	average sock mass (g)	total silver in sock (μg)	cumulative silver released after 4 24-h washings (μg)
1a	Sharper Image	loungesock (green)	\$2.47	25.8	29.3	756	836
1b	Sharper Image	loungesock (blue)	\$2.47	57.8	27.3	1578	1845
2	Sharper Image	athletic (white)	\$1.65	2.1	28.6	60	bdl
3	Fox River (Xstatic)	casual (black)	\$13	1358.3	23.0	31,241	165
4	Arctic Shield (E47)	over-the-calf boot sock (green)	\$14	35.9	58.6	2104	bdl
5	Zensah	basketball (black)	\$13	bdl	24.2	bdl	bdl
6	AgActive London	casual (black)	£6.99	0.9	21.9	20	19

contact time experiments are comparable. After the specified contact time, the socks were removed, excess water was wrung out into the glass bottle, and the socks were placed in new bottles for the next washing. Each brand of sock was washed at least 3 consecutive times for either 1 or 24 hours. All 1 L glass bottles were acid washed with 10% HCl (HX0603-3, EMD, Gibbstown, NJ) or 10% HNO_3 , triple rinsed with distilled water, and air-dried prior to use.

One brand of sock (1b) was washed with City of Tempe tap water (conductance $\sim 1000 \mu\text{mhos/cm}$) using the above procedure and a single 24-h contact time. This was done for comparison with socks washed in ultrapure water.

The effect of detergents on silver released from socks into domestic wastewaters was not addressed in this research. Although it is acknowledged that most people use soaps when washing their clothes, the goal of this study was to obtain data on the interaction of n-Ag from socks with distilled and tap water. Additional research is required to identify the effect of detergents on the quantity and form of silver released from socks into domestic wastewater streams.

Separation of Nanoparticle and Ionic Silver Species.

Three approaches were employed to separate the nanoparticle form of silver from ionic silver and to quantify both forms. First, wastewater samples were centrifuged at 15 000 rpm ($F = 24\,900g$) for 20 min, but this procedure did not remove all colloidal silver from suspension. Second, the silver in the washwater samples was size-separated using membrane filters (Pall) of 0.4, 0.1, and $0.02 \mu\text{m}$ pore diameter in either a 25 mm syringe filter or a 45 mm vacuum pump apparatus. The $0.4 \mu\text{m}$ filter cleared extraneous material from clogging the smaller-pored filters. The $0.02 \mu\text{m}$ filter is the smallest pore size commercially available for a syringe filter apparatus and can be used as a rough estimate for a threshold between ionic and nanoparticle silver. Third, a silver ion specific electrode (ISE) (Accumet Silver/Sulfide, Fisher) was used in combination with a pH/mV meter (Φ 250 series, Beckman) to measure free Ag^+ ions of the unfiltered 1-h washes of socks 1b and 3.

Scanning and Transmission Electron Microscopy Analyses. Scanning electron microscopy (FEI XL30 EFSEM with EDX capabilities) and transmission electron microscopy (JEOL JEM-2010F TEM/STEM with EDX capabilities) were used to confirm the presence of silver nanoparticles in the sock material and in the washwater samples, respectively. The sock material was ashed at 550°C in a programmable muffle furnace (Fisher Scientific), then prepared on an SEM stub. Two methods of stub preparation were used: (1) the ashed sock material was lightly dusted onto the carbon tape of the SEM stub surface, and (2) the ashed sock material was suspended in distilled water and subsequently evaporated in droplets onto the carbon tape of the SEM stub. Energy-dispersive X-ray analysis (EDX) was used to confirm the elemental presence of silver in the electron micrographs.

For TEM imaging, the sock washwater was first evaporated to concentrate the nanoparticles, thus increasing the probability of identifying them on the TEM stub. Drops of the concentrated sock washwater were then evaporated on the TEM stub for analysis. EDX was used to confirm the presence of silver in the micrographs.

Adsorption Experiments with Wastewater Biomass.

Batch adsorption isotherms quantified the potential removal of silver (nanoparticle and ionic, combined) from the washwater by wastewater treatment system biomass (activated sludge). Isotherm studies were conducted on two types of silver-containing water solutions: the sock washwaters and a reagent ionic silver solution. The latter was prepared using a plasma standard solution of Ag^+ (1000 ppm Ag^+ , 5% HNO_3 , Cat. no. PAGN-100, Manchester, NH) and distilled water.

Wastewater biomass for the isotherm studies was collected and prepared in two ways. First, biomass was sampled from a bench-scale reactor. This reactor was conditioned with return activated sludge (RAS) from a local WWTP and operated without wasting of biosolids (i.e., long sludge age). Second, a fresh sample of biomass was collected from the RAS line of a local wastewater treatment facility. A 5 mM NaHCO_3 solution was used to rinse the biomass before spiking it into the batch isotherm experiments.

For each batch sample in the isotherm test, 40 mL of the silver solution of interest was spiked with a dose of the biomass stock solution, and the sample was diluted up to 50 mL with ultrapure water. The initial silver concentrations in the batch experiments ranged from 60 to 500 ppb. Doses between 0.5 and 6 mL (0.17–2.23 mg of dry biomass) of the biomass stock solution were used in the samples.

All experiments were conducted within a pH range of 5.8–7.4. The pH values of the experiments using sock washwater were not adjusted. However, the ionic silver stock solution experiment was adjusted from pH 3.5 to pH 6.1 using 1 N NaOH (7708, Mallinckrodt, Paris, KY). The samples were allowed to mix on a shaker table at 45 rpm for 1 h of contact time, making these quasi-equilibrium experiments, allowing ample time for adsorption to take place while limiting the time for the biomass to produce additional surface area for adsorption. Then they were filtered through a 0.4 or $0.45 \mu\text{m}$ membrane filter (Pall) to remove any suspended biosolids. The filtrate was then analyzed for total silver by ICP-OES.

Results

Quantification of Silver in Sock Material and SEM Confirmation of Nanoparticle Size. Acid digestion of the sock material indicated that 5 of the 6 types of socks contained detectable levels of silver ranging from 2 to $1360 \mu\text{g-Ag/g-sock}$ (Table 1). SEM confirmed the presence of silver nanoparticles in socks 1a, 3, and 4 (not shown). Figures 1 and 2 show SEM/EDX images of representative samples from

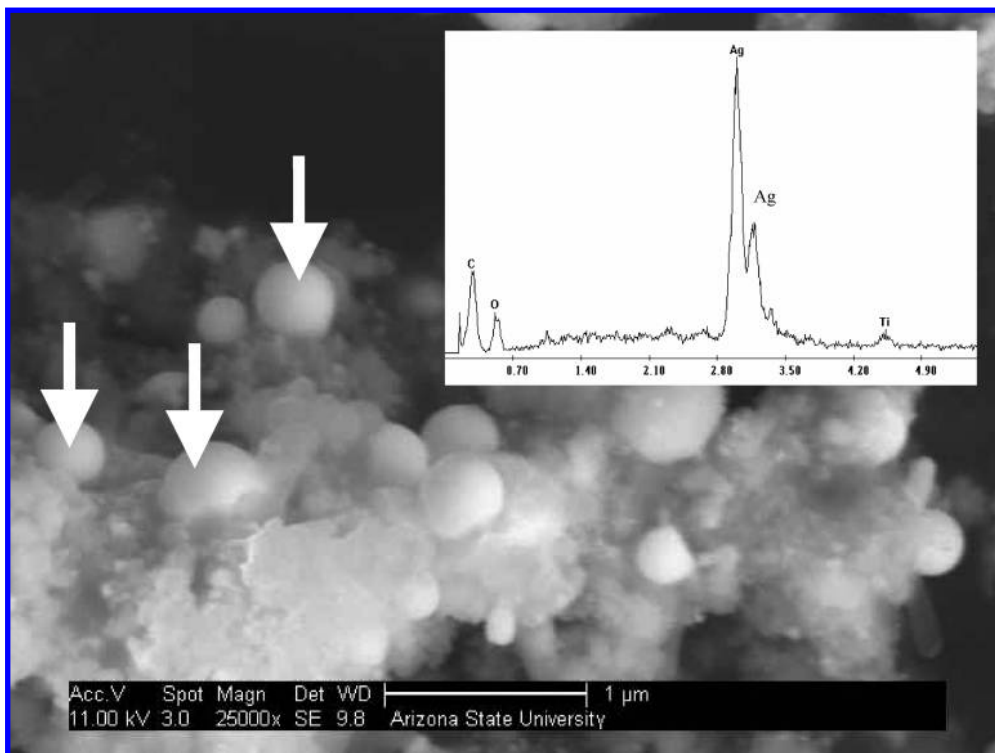


FIGURE 1. SEM image of ashed sock 3 material showing spherical silver particles on the order of 100 nm in diameter. Inset: Representative EDX analysis of the spherical silver particles marked with white arrows.

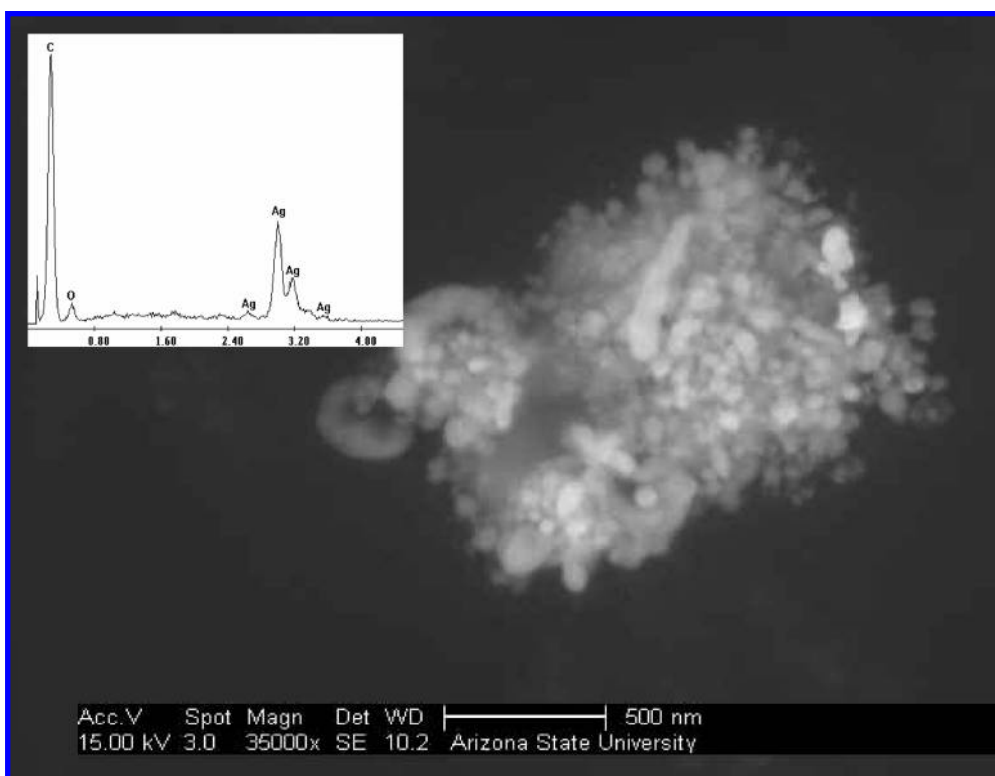


FIGURE 2. SEM image of ashed sock 1a material showing agglomerated silver nanoparticles. Inset: Representative EDX analysis of points within the mass confirms a majority of silver particles. The carbon peak is attributed to residual sock fabric and/or the carbon tape used to mount the sample.

socks 3 and 1a, respectively, after ashing. The carbon and oxygen peaks of the EDX analyses can be attributed to the surrounding residual sock material and/or the carbon tape used for SEM stub preparation. Particles of elemental silver

with diameters of 100–500 nm exist within the three types of socks. The silver particles in sock 1a do not appear nearly spherical like those of sock 3, but are irregularly shaped and much smaller (<100 nm). Although the melting point of pure

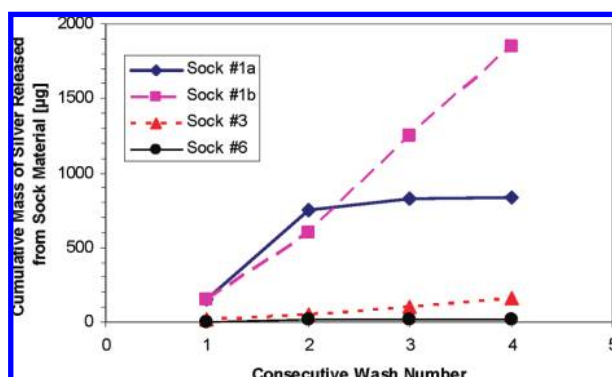


FIGURE 3. Cumulative mass of silver released from three sock types (four socks total) into four consecutive 24-h washings in distilled water.

silver is 962 °C, the ashing of the sock material at 550 °C may have sintered smaller n-Ag particles into larger diameter spheres. However, this preparatory step was necessary to remove the bulk of the sock fabric to obtain a clear image of the n-Ag.

Release of Silver into Washwater. Three of the six sock sample types (1a and 1b, 3, 6) detectably leached silver into the ultrapure wash water (1- or 24-h contact time). Figure 3 presents the cumulative mass of silver released during four sequential 24-h washes of the four sock samples. Silver was steadily released throughout the washes. Socks 1b and 3 were still releasing significant amounts of silver after four washes, whereas socks 1a and 6 had leached almost all of their silver by the fourth wash. The silver content in the 500 mL washwaters ranged from 3 to 1300 ppb (1.5–650 µg of silver). The 24-h wash simulations leached comparable (i.e., same order of magnitude) silver amounts as 1-h wash simulations. After three washes, two socks of 1b leached a total of 1245 and 1020 µg during the 24-h (Figure 3) and 1-h washes (Table 2), respectively. Similarly, two socks of 3 leached 100 and 390 µg in the 24-h (Figure 3) and 1-h washes (Table 2), respectively.

A comparison of socks based on the amount of silver leached relative to the silver content of the sock (Table 1) suggests that fundamental differences in the manufacturing processes of the socks control the amount of silver that is released into the washwater. For example, socks 3 and 4 contained relatively large amounts of silver (31 242 and 2105 µg, respectively), yet released only small percentages (<1%) of their total silver into the wash water, while socks 1a, 1b, and 6 released nearly 100% of their silver content in four consecutive washes. Additionally, the socks release their silver into the washwater at different rates. Socks 1 and 6 released the most silver during the second wash, while sock 3 steadily increased its release of silver throughout subsequent washes. These data would suggest that the various sock types have different longevities in which the silver continues to function as an antimicrobial agent. For example, because most of the silver, if not all, contained in socks 1a and 1b is leached in

the first four washes, one might assume that these socks would not perform as well as socks 3 and 4 at preventing odor-causing bacteria growth.

A fresh sock 1b sample was washed once with City of Tempe tap water (19) (conductance ~1000 µmhos/cm) for 24 h to investigate the effect of water quality on the release of silver from the sock. The potential of water to corrode metals is related to many water quality parameters, but in general, as buffering capacity and alkalinity increase, water corrosivity decreases (20). After one wash, sock 1b had released 15 µg of silver into the tap water as compared to 155 µg of silver released into the ultrapure water (Figure 3). This result may indicate that tap water is less aggressive than ultrapure water at stripping silver from the sock fabric. Therefore, these experiments in ultrapure water may be an overestimate of the amount of silver that could be leached into domestic wastewater streams. The silver in the tap water solution could not be characterized as nanoparticle or ionic because of interferences with the ISE and the probable formation of silver salts during SEM/TEM sample preparation.

Silver Characterization of the Sock Wash Solutions. TEM and EDX analysis of the colloids in the wash water of sock 1a (Figure 4) indicated the presence of silver material with diameters from one to a few hundred nm. These particles are in the same size range and are irregularly shaped like the particles in the SEM image of the sock 1a material. Thus, at least some of the n-Ag is released into the washwater as nanoparticles; not just as dissolved ionic silver.

Table 2 summarizes the colloidal and ionic characterization of the silver leached into the washwaters. Very little silver was separated by filtration into the size range of 20–100 nm. For sock 1b, about 70–90% of the silver was characterized as ionic by the ISE depending on the number of washings, which suggests that 75–100 µg/L of n-Ag may be present in the washwaters. Therefore, it should not be assumed that all of the silver initially released from socks is in the dissolved ionic form.

The first wash of sock 3 released nearly all silver as colloidal, as confirmed by the agreement of the filtration and ISE data. Subsequent washes of sock 3 contained increasing amounts of ionic silver. Thus, the ultrapure water in which these experiments were conducted may be corrosive. In experiments using commercial n-Ag (Aldrich) in ultrapure water, the ionic silver in solution increased over time as measured by ISE. This suggests that n-Ag is oxidized into a dissolved ionic form when subjected to prolonged exposure in water.

Partitioning of Ionic and Nanoparticle Silver to Wastewater Biomass. Quasi-equilibrium batch adsorption isotherm experiments were conducted using various sock wash solutions or reagent ionic Ag⁺ solution. Silver partitioned onto the biomass and was fit with the Freundlich isotherm equation ($q = KC^{1/n}$), where C is the equilibrium silver concentration after exposure to wastewater biomass (Figure 5). The values for the Freundlich adsorption capacity parameter, K , ranged from 3.4 to 17 (µg-Ag/g-biomass)(L/

TABLE 2. Nanoparticle and Ion Separation for Silver in 1-hr Washes via Filter Analysis and Ion Selective Electrode

sock ID	total silver in wash water (µg)	percent of total silver			
		passing 0.4 µm filter	passing 0.1 µm filter	passing 0.02 µm filter	[Ag ⁺] from ISE
1b, first 1-hr wash	145	93	93	86	72
1b, second 1-hr wash	275	98	91	85	76
1b, third 1-hr wash	600	83	83	81	86
3, first 1-hr wash	80	7	3	2	5
3, second 1-hr wash	160	53	53	53	25
3, third 1-hr wash	150	97	90	87	69

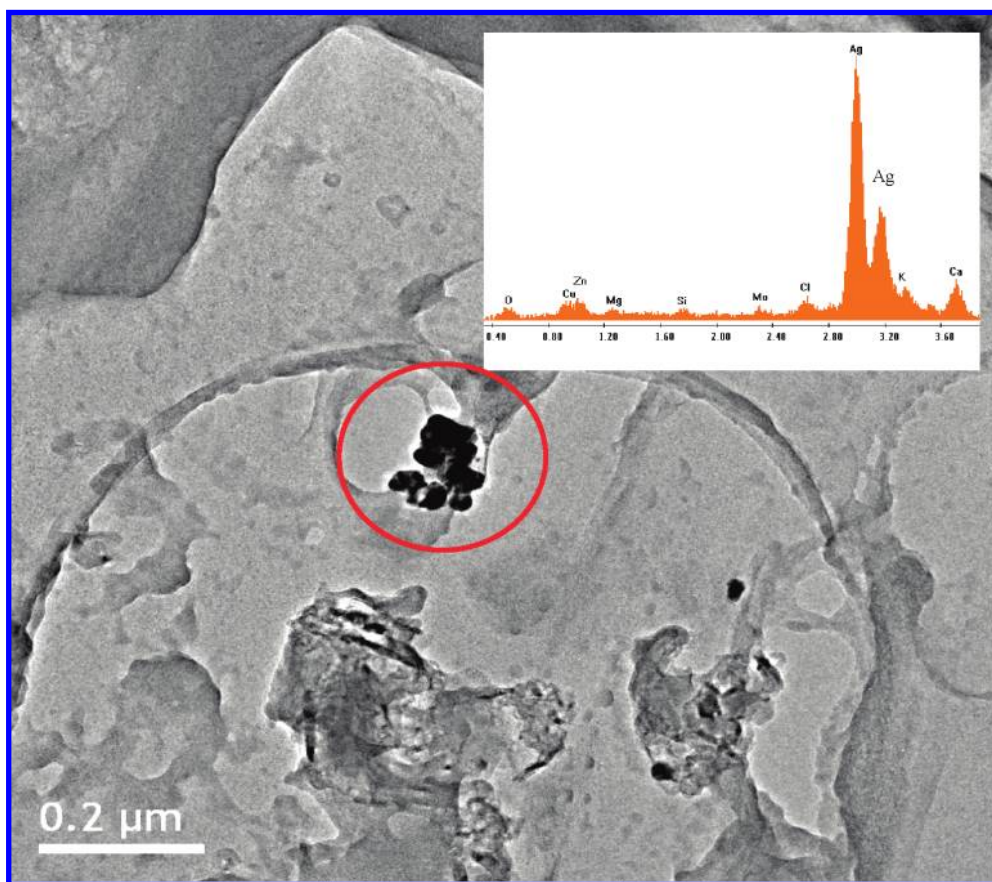


FIGURE 4. TEM image of colloidal material from sock 1a washwater. Inset: EDX confirmation that the dark particles within the circle are predominantly silver.

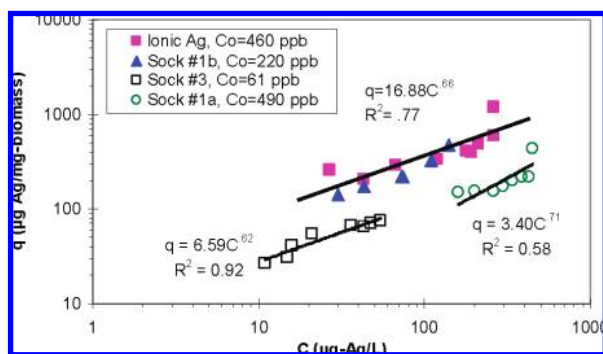


FIGURE 5. Batch adsorption isotherms for the wash solutions of three socks (1b, 3, 1a) and an ionic silver solution (Ionic Ag). Initial silver concentrations varied from 61 to 490 ppb, and pH values ranged from 5.8 to 7.4.

$\mu\text{g-Ag})^{1/n}$. The slopes of all of the isotherms are very similar, yielding an average Freundlich adsorption intensity parameter, $1/n$, of 0.66 (unitless).

Although the presence of colloidal silver was confirmed in washwater samples, the isotherm experimental data suggest that the silver leached from the socks adsorbs to biomass in a manner similar to that of ionic silver. The isotherm of reagent ionic silver solution overlaid that of sock 1b wash water, which contained mostly Ag^+ based on the ISE measurement (Table 2). Sock 3 leached low percentages of Ag^+ in washes 1 and 2, but the isotherm experiment for this sock was conducted with washwater that had been stored for 4 weeks, possibly giving the colloidal silver time to solubilize into ionic silver. Removal of Ag^+ from wastewater can be attributed mainly to precipitation with chloride and

adsorption to biomass, which can be hindered by complexation with dissolved organic matter (21).

Two wastewater biomass preparations were used for the isotherm experiments. Figure 5 presents data for isotherms conducted with biomass from a full-scale WWTP and a laboratory-scale bioreactor, which are represented by closed and open data points, respectively. Since the isotherm studies conducted on wash water from socks 1b and 1a used full-scale WWTP and laboratory-scale biomass, respectively, the difference between the closed and open data points is most likely related to the different biomass samples. However, the difference in isotherm results could also be attributed to interactions between dye from the socks and the leached silver because socks 1b and 1a differ in color.

Although adsorption characteristics may change in real environmental matrices (i.e., WWTP mixed liquor, municipal sewage, etc.), this adsorption data can be used to estimate the performance of a WWTP. The Freundlich isotherm nonlinear relationship was applied to the general fate model for sorption (22) to determine the amounts of silver contained in wastewater biomass or in treated effluent. A steady-state mass balance of a WWTP with nonlinear sorption of an adsorbate can be expressed as

$$C = C_0 - \left(\frac{X\tau KC^{1/n}}{\theta} \right) \quad (1)$$

where C is the effluent concentration of silver, C_0 is the influent silver concentration, K and $1/n$ are the Freundlich adsorption parameters, and X , τ , and θ are operational parameters of a WWTP (mixed liquor suspended solids, hydraulic and solids retention time, respectively). The common values used for these model parameters are provided as Supporting Information. Figure 6 presents

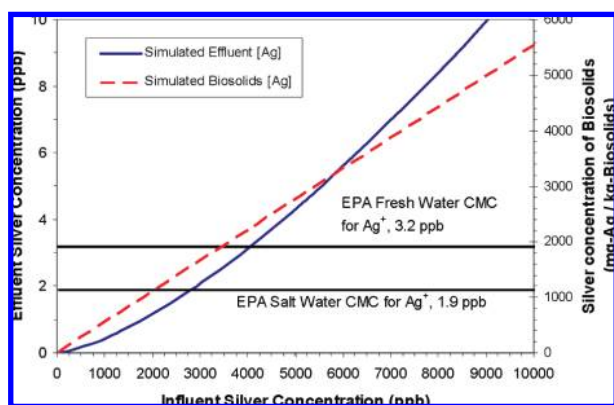


FIGURE 6. Model results illustrating the removal of influent silver for a typical WWTP (model parameters: Freundlich K and $1/n = 9.0, 0.7$; $\tau = 0.5$ d; $\theta = 5$ d; $X = 2000$ mg/L). The silver concentration in the treated effluent would exceed the USEPA salt and fresh water Criteria Maximum Concentrations (CMCs) at influent concentrations of 2900 and 4250 ppb, respectively. The concentration of silver in the waste activated sludge flow is represented by the dashed line and the secondary y -axis.

simulations of the silver concentrations exiting an activated sludge reactor using common WWTP design conditions and average values for K and $1/n$ (9.0 and 0.7, respectively). Using a common municipal WWTP influent silver concentration of $5 \mu\text{g/L}$, the model results in an effluent silver concentration of $0.01 \mu\text{g/L}$, and the wasted biosolids silver concentration is $2.8 \text{ mg-Ag/kg-biosolids}$. The effluent from the wastewater treatment facility would exceed the USEPA water quality criteria for salt water and fresh water at influent silver concentrations of about 2900 and 4250 ppb, respectively. These influent concentrations are 3 orders of magnitude higher than those commonly observed for municipal WWTPs (21). The treated effluent would not exceed the 100 ppb secondary drinking water standard for silver until the influent concentration reached approximately 45 400 ppb (not shown graphically).

Based upon the existing water quality criteria for silver, the model suggests that wastewater treatment plants are capable of removing a much higher silver load from a wastewater stream than should be reasonably expected from an increased number of consumer products containing silver nanoparticles. Model simulations were conducted by varying two WWTP operation parameters: the MLSS concentration was varied from 2000 to 4000 mg/L and the ratio of $\theta:\tau$ was varied from 5 to 20. Using the 1.9 ppb salt water CMC as the maximum allowable effluent concentration, a MLSS concentration of 2000 mg/L with an $\theta:\tau$ of 20 would treat an influent silver concentration of $1460 \mu\text{g/L}$. Similarly, a MLSS concentration of 4000 mg/L with an $\theta:\tau$ of 5 would treat an influent silver concentration of $11\,600 \mu\text{g/L}$ (a table of the model results can be found in the Supporting Information). However, the concentration of silver in the biosolids is worthy of some consideration. The model suggests at an influent silver concentration of $180 \mu\text{g/L}$, the silver concentration in the biosolids would exceed the 5 mg/L Toxicity Characteristic Leaching Procedure (TCLP) by the USEPA. An increase in consumer use of n-Ag could therefore restrict municipal wastewater treatment facilities from exporting their biosolids as fertilizer for agricultural lands.

Additional Implications

New analytical techniques that distinguish between nanomaterials (metal, metal-oxide, quantum dots, etc.) and dissolved ionic species at relevant concentrations in environmental matrices are important for the advancement of

nanotechnology. Methods such as capillary electrophoresis (23) and size-exclusion chromatography (24) have the potential to separate nanomaterials from ionic species, but detection methods suited for environmental matrices and relatively low concentrations are limited. With the capability to separate and quantify nanomaterials, exposure data can be obtained during ecotoxicity studies to facilitate environmental risk assessment studies. The unknown environmental risks are currently preventing scientists and the public from fully supporting the advancement of nanotechnology (25), but new analytical techniques can answer these questions, thus allowing nanotechnology to develop at a pace acceptable to all stakeholders.

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Supporting Information Available

WWTP model parameters and a table summarizing the multiple simulations of the model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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