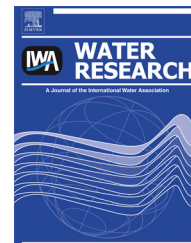


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Fate and transformation of silver nanoparticles in urban wastewater systems



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ABSTRACT

Discharge of silver nanoparticles (Ag-NP) from textiles and cosmetics, today's major application areas for metallic Ag-NP, into wastewater is inevitable. Transformation and removal processes in sewers and wastewater treatment plants (WWTP) will determine the impact of Ag-NP on aquatic and terrestrial environments, via the effluents of the WWTP and via the use of digested sludge as fertilizer. We thus conducted experiments addressing the behavior of Ag-NP in sewers and in WWTP.

We spiked Ag-NP to a 5 km long main trunk sewer and collected 40 wastewater samples after 500 m, 2400 m and 5000 m each according to the expected travel times of the Ag-NP. Excellent mass closure of the Ag derived by multiplying the measured Ag concentrations times the volumetric flow rates indicate an efficient transport of the Ag-NP without substantial losses to the sewer biofilm. Ag-NP reacted with raw wastewater in batch experiments were sulfidized to roughly 15% after 5 h reaction time as revealed by X-ray absorption spectroscopy (XAS). However, acid volatile sulfide (AVS) concentrations were substantially higher in the sewer channel (100 μM) compared to the batch experiments (3 μM ; still sufficient to sulfidize spiked 2 μM Ag) possibly resulting in a higher degree of sulfidation in the sewer channel. We further investigated the removal efficiency of 10 nm and 100 nm Ag- and gold (Au)-NP coated with citrate or polyvinylpyrrolidone in activated sludge batch experiments. We obtained very high removal efficiencies (~99%) irrespective of size and coating for Ag- and Au-NP, the latter confirming that the particle type was of minor importance with respect to the degree of NP removal. We observed a strong size dependence of the sulfidation kinetics. We conclude that Ag-NP discharged to the wastewater stream will become sulfidized to various degrees in the sewer system and are efficiently transported to the WWTP. The sulfidation of the Ag-NP will continue in the WWTP, but primarily depending on the size the Ag-NP, may not be complete. Very high removal

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efficiencies in the WWTP will divert most of the Ag-NP mass flow to the digester and only a small fraction of the Ag will be released to surface waters.

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1. Introduction

Metallic silver nanoparticles (Ag-NP) are currently used in numerous products due to the well-known antimicrobial activity of the ionic Ag⁺ (Grier, 1983; Russell and Hugo, 1994). The toxicity of various Ag compounds has been intensively studied (Ratte, 1999), but it is still debated whether there is a nanoparticle-specific toxicity, related to the physical interaction of the particle with an organism, in addition to the toxicity of ionic Ag⁺ (Levard, et al., 2012; Fabrega, et al., 2011; Marambio-Jones and Hoek, 2010). There seems to be a general consensus that the toxicity of Ag-NP is mediated by ionic Ag⁺, which is strongly supported by most recent findings of (Xiu, et al., 2012). However, Ag-NP can strongly localize the impact by bringing the source of Ag in close proximity of the biological targets (Yin, et al., 2011).

The widespread use of Ag-NP will inevitably lead to the emission of AgNP into the aquatic environment. Current production volumes of Ag-NP are still very low compared to other nanoparticle types such as nano-TiO₂ (Hendren, et al., 2011). Nevertheless, Ag-NP currently are the active agent in most nanotechnology-based consumer products (Woodrow Wilson International Center for Scholars, 2012), suggesting that industry is intensively testing and looking for new application areas for Ag-NP. The discovery of new application areas may further increase the production volumes, eventually leading to a proliferation of Ag-NP in the environment. The main applications are consumer products (cosmetics and textiles) and the release of Ag-NP from such products to the municipal wastewater has already been demonstrated experimentally in the latter case (Geranio, et al., 2009; Benn and Westerhoff, 2008; Benn, et al., 2010). Furthermore, also Ag-equipped washing machines have been reported to emit Ag-NP (Farkas, et al., 2011).

Depending on the environmental conditions and the properties of the AgNP (e.g. coating, size), Ag(0) is transformed into different species, such as ionic Ag, Ag₂O and Ag₂S. The oxidative dissolution of Ag-NP of different sizes and coatings/stabilizing agents in aqueous suspensions has been addressed in several studies (Zhang, et al., 2011; Kittler, et al., 2010; Liu and Hurt, 2010). The increased solubility of Ag-NP with decreasing particle size was explained by the modified Kelvin equation (Ma, et al., 2012). The sulfidation of Ag-NP under laboratory conditions was subject of several studies (Reinsch, et al., 2012; Levard et al., 2011a,b; Liu, et al., 2011) revealing that the sulfidation/corrosion of polyvinylpyrrolidone (PVP) – and citrate-coated Ag-NP was not hampered by the coating, but that the formation of a passivating surface layer may slow down the kinetics of the corrosion process. Detailed microscopic investigations revealed Ag₂S in the sludge of a full-scale wastewater treatment plant (WWTP) (Kim, et al., 2010) and Kaegi, et al. (2011) demonstrated that the sulfidation of Ag-NP can occur during the anaerobic stages of the wastewater treatment process.

Results about the removal efficiencies of NP in WWTP are still controversial. Based on lab-scale experiments, Limbach et al. (2008) estimated a transmission of about 6% for CeO₂ nanoparticles through a WWTP. Slightly lower values for Ag-NP, roughly corresponding to the fraction of sludge that is lost via the secondary clarifier, were obtained in a study conducted on a pilot WWTP (Kaegi, et al., 2011). Kiser et al. (2010) suggest that functionalized NP may be pass the WWTP to a higher degree than non-functionalized NPs. Most recently, Hou et al. (2012) reported almost complete removal of citrate-coated Ag-NP from a simulated sequential batch reactor. On the other hand, very poor removal efficiencies of NP during primary wastewater treatment are reported (Jarvie et al., 2009; Hou et al., 2012).

The behavior of Ag-NP, or NP in general along their transport in sewer systems has not been addressed so far, although physical and chemical transformation will already start in the sewer system, especially as high sulfide levels are reported in sewers (Nielsen et al., 2008). In addition to transformation occurring in the sewer, the role of the sewer biofilm that might retain and accumulate Ag-NP is yet unknown. Sheng and Liu (2011) provide evidence that although wastewater biofilms are rather tolerant to Ag-NP, Ag-NP can attach on or penetrate into the biofilm. Fabrega et al. (2009) report that the presence of fulvic acid favored the uptake and bioaccumulation of Ag NPs to biofilms. The sewer biofilm could therefore act as a temporary sink for Ag-NP that are accumulated during dry water conditions, but on the other side could act as a source of Ag-NP during rain events when parts of the biofilm are eroded. It is conceivable that under such conditions, the Ag-NP could bypass the WWTP and directly enter into the aquatic environment via stormwater discharge.

Due to the enormous dilution of the Ag-NP in the wastewater or the activated sludge, the collision between an Ag-NP and a 'foreign' collector (e.g. TSS of the wastewater, activated sludge) is much more likely than the collision between two Ag-NP and thus, heteroaggregation and/or deposition determine the fate and transport of the Ag-NP in urban wastewater systems. Lin et al. (2011) investigated the affinities of Ag-NP for different surface compositions (bare glass beads vs. hematite coated glass beads) and revealed considerable higher attachment efficiencies of Ag-NP for the hematite coated surfaces. Hydrophobic interactions not included in the classical DLVO theory were used to explain experimentally determined attachment efficiencies of Ag-NP (gum Arabic or PVP coated) to variously hydrophobic surfaces (Song et al., 2011). Furthermore, (Lin et al. (2012) revealed that an organic coating can even favor the attachment of NPs to uncoated surfaces. Ag-NPs are generally stabilized against autoaggregation by an organic coating, most popular, citrate or PVP. However, a high stability of the Ag-NP in stock suspensions does not necessarily imply a high mobility of the Ag-NP in the environment. On the other hand, a low stability of NP (high deposition efficiency) does not imply a low mobility of the NP,

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