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Organic matter induced mobilization of polymer-coated silver nanoparticles from water-saturated sand

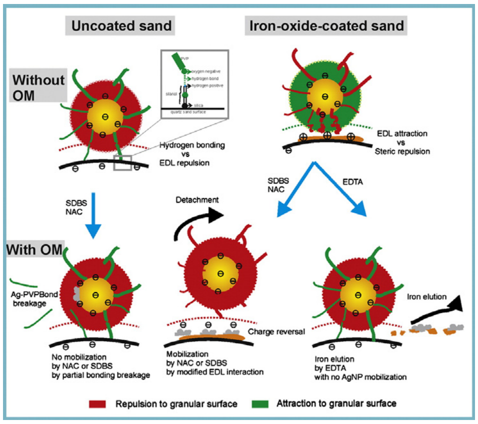
Xinyao Yang [a,*], Ziyi Yin [b], Fangmin Chen [b], Jingjing Hu [b], Yuesuo Yang [a]

[a] *Ministry of Education Key Lab for Eco-restoration of Contaminated Environment, Shenyang University, No. 21, South Wanghua Street, Shenyang 110044, China*
[b] *College of Resources and Environment, Sichuan Agricultural University, No. 211, Huiming Road, Chengdu 611130, China*

HIGHLIGHTS

- PVP coating dominates over the Ag core in governing the particle mobility.
- Both organic sulfide and sulfur-free chelate could elute PVP from AgNP.
- Organic-induced PVP detachment did not mobilize AgNP from uncoated sand.
- SDBS and NAC mobilized AgNP from iron-oxide coated sand by enhanced electrical double layer effect.
- EDTA dissolved iron-oxide coating but mobilized no AgNPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Mobilization of polymer-coated silver nanoparticles (AgNPs) by anionic surfactant (sodium dodecylbenzenesulphonate: SDBS), amino acid derivative (N-acetylcysteine: NAC), and chelate (ethylenediaminetetraacetic acid: EDTA) in water-saturated sand medium was explored based on carefully designed column tests. Exposure experiments monitoring the size evolution of polyvinylpyrrolidone (PVP) coated AgNPs in organic solutions confirm the capacity of SDBS, NAC and EDTA to partly displace PVP. Single Pulse Column Experiment (SPCE) results show both the PVP polymer and the silver core controlled AgNP deposition while the effect of the PVP was dominant. Results of Co-injected Pulse Column Experiments (CPCEs) where AgNP and SDBS or NAC were co-injected into the column following a very short mixing (<1 s) disprove our hypothesis that coating-alternation by particle associated organic would mobilize irreversibly deposited particles from the *uncoated sand*, while surface charge modification by adsorbed NAC was identified as a potential mobilizing mechanism for AgNP from the *iron-oxide-coated sand*. Triple Pulse Column Experiment (TPCE) results confirm that such a charging effect of the adsorbed organic molecules may enable SDBS and NAC to mobilize AgNPs from the iron-oxide-coated sands. TPCE results with five distinct levels of SDBS indicate that concentration-stimulated change in the SDBS format from an individual to a micelle significantly increased the mobilizing efficiency and site blockage of SDBS. Although being an electrolyte, EDTA did not mobilize AgNPs, as the case with SDBS or NAC, as it dissolved the iron oxides which in turn prevented EDTA adsorption on sand. The findings have implications for

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* Corresponding author.
E-mail address: yangxinyao@hotmail.com (X. Yang).

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better understanding the behavior of polymer-coated nanoparticles in organic-presented groundwater systems, i.e., detachment-associated uncertainty in exposure prediction of the nanomaterials.

1. Introduction

The antimicrobial properties of silver nanoparticles (AgNPs) have made these particles one of the most frequently used nanomaterials in consumer products (Kang et al., 2011). However, aggregation may reduce the specific area (surface area to volume ratio) of these tiny particles and thus weaken their antimicrobial effect (Liang et al., 2013). Therefore, AgNPs are often embedded with macromolecular polymers or polyelectrolyte like polyvinylpyrrolidone (PVP), citrate or gum Arabic (GA) to maintain a good stability, via steric effect, electrical double layer (EDL) effect or electrosteric effect, respectively (Lin et al., 2012; Thio et al., 2012). Benn and Westerhoff (2008) reported that AgNPs incorporated into textiles and fabrics are readily released during washing and AgNPs can be introduced into terrestrial environments by applying sewage sludge to landfills (Coutris et al., 2012). In groundwater environment, AgNPs may inhibit the growth of local microorganisms with their antimicrobial effect, breaking the balance of the ecosystem and degrading water quality.

Column transport studies suggested that the surface coating layer on the silver nanoparticles played an important control on the particle deposition in porous media, acting as a bridge between the silver core and the granular surface (Lin et al., 2012; Thio et al., 2012; Cornelis et al., 2013; Liang et al., 2013; Neukum et al., 2014). On the other hand, several other studies suggested that organic sulfide, i.e., cysteine, might be able to displace the coating from AgNP surface and such a coating-alternation process might have profound effect on the changed behavior of the particles in subsurface environment (Gondikas et al., 2012; Levard et al., 2012). For instance, the tailored mechanisms for the coating to manipulate AgNP transport may be lost should the particles enter environmental solutions containing organic matter which may elute the polymer coating from the silver core. An immediate question related to this phenomenon then is: will the loss of AgNP coating lead to particle mobilization from porous media?

A scrutinization of this question is important since most current studies on AgNP transport focused on aggregation and deposition (Lin et al., 2011; Akaighe et al., 2013; Yang et al., 2014), while literature on mobilization as another important transport process was largely unavailable. This study aims to systematically investigate the mobilizing effect of three types of representative organic matter which include amino acid derivative, anionic surfactant, and organic chelate. The first two, modeled respectively with N-acetylcysteine (NAC) and sodium dodecylbenzenesulphonate (SDBS), both have organic sulfur but in different functional groups (–SH vs $-SO_3$). Moreover, NAC and SDBS have different functional groups and structures: NAC is hydrophilic with additional functional groups (–COOH and $-NH_2$) other than the thiol ligand while SDBS is a linear anionic surfactant with both hydrophilic and hydrophobic (dodecylbenzene) moieties (Chen et al., 2012; Zhai et al., 2004). Although organic sulfide has strong affinity with silver, the sulfur–silver interaction might differ and be specific to the organic molecule containing the sulfur (Levard et al., 2011; Gondikas et al., 2012). Kunz et al. (2014) also noted the interaction mechanisms with metal differed notably between NAC and cysteine, both containing organic thiol but having different molecule structures. Ethylenediaminetetraacetic acid (EDTA), a representative organic chelate, although containing no sulfur, may potentially have similar effect as the organic sulfide due to its exceptional capacity in coordinating and dissolving metals (Hauser et al., 2005; Finzgar and Lestan, 2007). Besides the scientific significance, the three organic molecules all have strong environmental relevance as they have been reported to occur in sewage sludge, plant root zone, seawater and sewage polluted groundwater (Bell and Kramer, 1999; Hauser et al., 2005; Wang et al., 2014).

Based on this research we seek to answer the following questions: (1) Can the organic sulfur, as part of other molecules rather than cysteine, and the sulfur-free organic molecules displace the PVP coating also? (2) Will such a coating separation process incur detachment of AgNP from depositing surfaces? (3) Can typical environmental organic matter in natural (i.e., NAC) and sewage-impacted environment (i.e., SDBS and EDTA) mobilize AgNP, and how? Exploration of the organic–PVP interaction was achieved with exposure experiments where AgNPs were exposed to the three types of the organic molecules and the dynamic evolution of the particle size with time was monitored. The effect of coating alternation on particle mobilization was studied with Co-injected Pulse Column Experiments (CPCEs) where the organic was adsorbed on AgNPs prior to column entry and the coating-alternation occurred following deposition of the particle-OM entity. Triple pulse experiments (TPCEs) where an organic pulse was introduced into the column following the deposition of AgNPs allow the mobilizing effect of solution organic matter at a short time-scale to be assessed. The findings of this work are expected to be useful to uncertainty reduction during exposure and pathway prediction of polymer-coated silver nanoparticles in organic matter-impacted groundwater environment.

2. Materials and methods

2.1. Preparation and characterization of silver nanoparticles

The polyvinylpyrrolidone (PVP) coated silver nanoparticles were prepared using a polyol method described in Yang et al. (2014). This permits PVP to bind covalently on AgNP via N, O or both N and O atoms (stability constant about $\sim 10^6$: Mdluli et al., 2011). The particle size was characterized by both dynamic light scattering (DLS, 90 Plus, Brookhaven, NY) and transmission electron microscopy (TEM, Tecnai G2 Twin, OR). The coated AgNP has a hydrodynamic diameter of 130 nm and a core diameter measured by TEM to be 40 nm. The TEM imaging confirmed that AgNP has a uniform size and spherical shape. TOC measurement confirmed the mass concentration of the free unattached PVP to be about 2% of the total AgNP. Two concentration levels, 15 ppm and 1.5 ppm AgNPs, were used respectively for column experiments and exposure experiments. The selected concentration was in the range as those used in other transport studies on AgNP (i.e., Cornelis et al., 2013; Liang et al., 2013; Neukum et al., 2014). A UV–vis spectrophotometer (Hitachi, Fisher, and Chengdu), set at 425 nm, was arranged to measure continuously online the AgNP levels in column effluent. Control experiments confirmed that the particle levels were proportional to the optical absorbance and that the added organic molecules did not affect the signal at this wavelength.

2.2. Organic compounds

Sodium dodecylbenzenesulphonate (SDBS, $C_{18}H_{29}NaO_3S$, MW = 348.48), N-acetylcysteine (NAC, $C_5H_9NO_3S$, MW = 163.19), and ethylenediaminetetraacetic acid (EDTA, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, MW = 372.27), ordered from Kelong Chemicals (Chengdu), were used to represent anionic surfactant, amino acid derivative, and organic chelate, respectively. SDBS, with a negatively-charged hydrophilic head and a hydrophobic tail, may form micelles at concentrations above the critical micelle concentration (CMC), with the hydrophobic tails aggregating into an inner core while the hydrophilic heads projecting outward to the solution. NAC is an acetylation derivative of cysteine, with an acetyle