



Dissolution of metal and metal oxide nanoparticles in aqueous media



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ABSTRACT

The dissolution of Ag (citrate, gelatin, polyvinylpyrrolidone and chitosan coated), ZnO, CuO and carbon coated Cu nanoparticles (with two nominal sizes each) has been studied in artificial aqueous media, similar in chemistry to environmental waters, for up to 19 days. The dissolved fraction was determined using DGT (Diffusion Gradients in Thin films), dialysis membrane (DM) and ultrafiltration (UF). Relatively small fractions of Ag nanoparticles dissolved, whereas ZnO dissolved nearly completely within few hours. Cu and CuO dissolved as a function of pH. Using DGT, less dissolved Ag was measured compared to UF and DM, likely due to differences in diffusion of organic complexes. Similar dissolved metal concentrations of ZnO, Cu and CuO nanoparticles were determined using DGT and UF, but lower using DM. The results indicate that there is a need to apply complementary techniques to precisely determine dissolution of nanoparticles in aqueous media.

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1. Introduction

Metal and metal oxide nanoparticles are being used in industrial settings and have diverse applications (<http://www.nanotechproject.org>) that likely will result in release to the environment, directly, or from nanoparticle-containing products (Nowack et al., 2011). Silver nanoparticles (Ag-NPs) are used in many consumer product applications, mainly due to their antimicrobial properties. These products range from wound dressings, socks and other textiles, paints, air filters, toothpaste, baby products, vacuum cleaners, and washing machines. Zinc oxide nanoparticles (ZnO-NPs) are used for extensive application in sunscreens, cosmetics, and bottle coatings because of their ultraviolet blocking ability and the visible transparency of nanoparticulate forms. Nano sized copper particles are widely used as a bactericide, for air and liquid filtration, metallic coating, wood preservation. These NPs are very unstable in pure form, and they are used in many products as Cu stabilized (coated) with carbon, or in form of CuO. Carbon coated Cu-NPs serve as catalysts for chemical reactions (catalyst for the synthesis of methanol and glycol), electromagnetic interference (EMI) shielding and heat

sinks, replacement for more expensive noble metals for printed electronics, displays and other conductive thin film applications.

Once in the aqueous media these nanoparticles will change their physical and/or chemical properties and partly dissolve. The characterization and quantification of nanoparticles is a difficult analytical challenge since measurements are highly dependent upon (i) particle size and nature; (ii) sample concentration and solution physicochemistry (Handy et al., 2008; Klaine et al., 2008; Pourbaix, 1974; Schoonen et al., 2006).

By definition, truly dissolved metals are those with a size smaller than 1 nm (~1 kDa) (Templeton et al., 2000). From the techniques used for measurements of dissolved metal fractions in metal and metal oxide NPs suspensions, ultrafiltration (Ma et al., 2012; Navarro et al., 2008) and dialysis (Vasyukova et al., 2012; Kittler et al., 2010) are well known and commonly used. Ultrafiltration for nanoparticles is combined with centrifugation, thus includes application of a centrifugal force to separate dissolved fraction from the particulate fraction. Alternatively, the efficiency of dialysis technique is dependent on diffusion of the dissolved form through a membrane. The DGT (Diffusion Gradients in Thin films) technique has been previously used almost exclusively for *In situ* measurements of dissolved inorganic and labile organic metal species in aqueous environments (Davison and Zhang, 2012; Odzak et al., 2002; Sigg et al., 2006). In the study on toxicity of Ag nanoparticles to freshwater algae performed in this laboratory (Navarro

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et al., 2008), the DGT technique, based on the diffusion of metal ions from aqueous media through the hydro-gel was successfully used to quantify dissolved Ag fraction in simple synthetic aqueous media.

The main objective of this study was to examine the dissolution of the selected nanoparticles (Ag, ZnO, CuO, carbon coated Cu) over time (days to weeks) in aqueous media similar in chemistry to natural fresh waters. For this purpose three different techniques, DGT, dialysis membrane (DM) and ultrafiltration (UF) were used and the results compared.

2. Materials and methods

2.1. Nanoparticles

Silver nanoparticles (Ag-NPs) were produced by NanoSys, Wolfhalden, Switzerland. The particles were received as aqueous suspensions with total Ag concentration of 1 g L^{-1} and they were coated with four different coatings: citrate, gelatin, polyvinylpyrrolidone (PVP) and chitosan. General size distribution between 10 and 100 nm was given by the producer, without details regarding individual coatings.

Zinc oxide (ZnO-NPs; nominal size in dry form $d = 4.5$ and 27 nm), copper oxide (CuO-NPs; nominal size in dry form $d = 7.5$ and 45 nm) and carbon coated Cu-NPs (nominal size in dry form $d = 7.5$ and 27 nm) were produced by Particle Technology Laboratory, ETH Zurich, Switzerland, using the flame-spray pyrolysis and characterized in the same laboratory. According to the producer, the nanoparticles were characterized by X-ray diffraction (XRD) on a Bruker AXS D8 Advance diffractometer (Cu $K\alpha$, 40 kV, 40 mA). The crystallite sizes were calculated using the Rietveld method and the software TOPAS3. Transmission electron microscopy (TEM) imaging of ZnO and CuO-NPs used in this study was performed in the same laboratory and as a part of their study published elsewhere (Gass et al., 2013; Waser et al., 2013). Before use in the study, ZnO, CuO and carbon coated Cu-NPs were suspended in deionized water (1 g L^{-1}) and ultrasonicated for 30 min in ultrasonic bath Bandelin Sonorex RK 52.

2.2. Techniques

The total metal concentration was measured in all the experiments using Thermo Finnigan Element 2 – High Resolution Sector Field ICP-MS with simultaneous, automatically calibrated, dual mode detector for analog and counting measurements. A linear dynamic range from $<0.2 \text{ cps}$ to $>2.5 \times 10^9 \text{ cps}$ enables quantification from ng L^{-1} to $\mu\text{g L}^{-1}$ metal concentrations. Standard Reference Material (SRM) 1640a from National Institute of Standards and Technology (NIST), containing trace elements in natural water, was used throughout the analyses to check the methods and procedures applied. Nanoparticle samples were digested before analysis by ICP-MS in a microwave unit (High Performance Microwave Digestion Unit mls 1200 mega) in concentrated HNO_3 and H_2O_2 (Merck suprapur grade).

For the determination of dissolved metal concentrations, the nanoparticles of dissolved metals were separated by DGT, dialysis membrane (DM) and ultrafiltration (UF) techniques. DGT comprises a layer of hydrogel overlying a layer of immobilized binding agent (ion-exchange resin). Hydro-gels used in this study were prepared in our laboratory. The diffusive layer was prepared from acrylamide and DGT Cross-linker (DGT Research Ltd, Lancaster) and the binding layer from the same plus ion-exchange resin Chelex-100 (Na form, 200–400 mesh size). After deployment, the resin layer is peeled off and leached in 2 M HNO_3 for 1 day before analysing the trace metal content by ICP-MS. Diffusion coefficients used to calculate the metal concentrations in aqueous media are provided by DGT Research Ltd (<http://www.dgtresearch.com/dgtresearch/dgtresearch.pdf>). The dialysis membrane used in this study is Spectra/Por Biotech Cellulose Ester (CE) Dialysis Membrane with Molecular Weight Cut Off (MWCO): 100–500 Da. The nominal flat width of dialysis membrane tubes is 24 mm, diameter 15 mm. These tubes are stable in the pH range of 5–9. After the deployment period the trace metal content inside the tube is measured by ICP-MS. Ultrafiltration was performed in Amicon Ultra Tubes, containing Regenerated Cellulose Centrifugal Filters with a cut-off of 3000 Da. Three millilitres of each sample was put in the tubes and centrifuged for 30 min at 4000 rpm (RCF = $1880 \times g$). The dissolved fraction was diluted to 10 mL and acidified to 0.1 M HNO_3 (Merck, suprapur).

Visual MINTEQ v.3.0 software <http://www2.lwr.kth.se/English/OurSoftware/vminTEQ/index.html> was used to determine equilibrium dissolution of bulk ZnO (mineral zincite, $\log K_s = 11.23$) at experimental concentration of 1 mg L^{-1} .

Size measurement was performed by Dynamic Light Scattering (DLS), using a Malvern Zetasizer ZS DLS. The same instrument was also used for the measurement of nanoparticle charge (zeta potential). Three measurements were taken per sample and the autocorrelation function was analysed using the cumulant analysis algorithm resulting in a mean size (z-average) and a standard deviation (polydispersity index, PDI). Nanoparticle Tracking Analysis (NTA) uses a NanoSight LM10 microscope equipped with a LM14 temperature controller. Based on laser-illuminated

optical microscopy, nanoparticles are seen as light-scattering centers moving under Brownian motion. A video of the movement of each particle was analysed on a frame-by-frame basis and the particle size was calculated from the measured diffusion coefficient. Each sample was measured three times.

2.3. Experimental conditions

All experiments were performed in an artificial solution which simulates natural water and contains: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} . The salts used for preparation of the solution and their concentrations are given in Supporting information (Supporting information, Table S1). MOPS buffer (N-morpholino-3 propanesulfonic acid, Sigma–Aldrich; $\text{pK}_a = 7.20$) was used to stabilize pH. The solution had an ionic strength of 0.029 M . Experimental suspensions were prepared by adding NPs from stock of 1 g L^{-1} . Total metal/metal oxide concentrations were: 0.2 mg L^{-1} in Ag-NPs experiments and 1.0 mg L^{-1} in the experiments with ZnO, Cu and CuO-NPs. The selection of these concentration was a compromise between environmentally relevant and the values sufficiently high to perform the measurements. In the experiments with Ag-NPs the pH was 7.5 and in the experiments with ZnO, Cu and CuO-NPs two different pHs were used: 7.6 and 6.1.

The particles were exposed to aqueous media with the composition described above in 2-L plastic bottles (HDPE) for a maximum of 19 days (Ag, ZnO-NPs), or 8 days (CuO, Cu-NPs). Based on several other studies and smaller experiments performed in this laboratory (data not published) it was expected that major changes in nanoparticles characteristics will occur within the selected experimental times. All experiments were run in duplicate. In each bottle DGT devices and DM were deployed in order to measure dissolved metal concentrations. The experimental bottles were kept in dark at $23 \text{ }^\circ\text{C}$ and shaken (100 rpm) to ensure equilibration of metal concentration between the solution inside and outside the dialysis membrane tube and supply of dissolved metal to the DGT devices. During the experiments, the pH was measured and samples were taken for DLS (size and zeta potential), NTA (size), UF (dissolved metal) and total metal concentration measurements. The sampling was performed using a pipette with a plastic tip, within 1 min after removal of experimental bottles from the shaker in order to minimize loss of larger agglomerates.

Dialysis membrane (DM) performance was tested in absence of NPs in solutions of $500 \mu\text{g L}^{-1}$ Zn (prepared by dissolution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{(\text{s})}$), $510 \mu\text{g L}^{-1}$ Cu (prepared by dissolution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{s})}$), at $23 \text{ }^\circ\text{C}$ and pH 6.1 (MOPS buffer).

The efficiency of DGT technique to quantify dissolved silver concentrations was tested in 2-L plastic bottles (HDPE) containing different Ag^+ concentrations (dissolved AgNO_3) in 0.01 M NaNO_3 . The DGT devices were deployed for 24 h at $23 \text{ }^\circ\text{C}$.

3. Results and discussion

3.1. Silver nanoparticles

The suitability of the DGT technique for dissolved Ag measurements had to be investigated, as it has so far not often been used for silver. As seen in Table 1, there was a very good correlation between total and DGT measured Ag concentrations in ionic silver solution, indicating that this technique can be used to measure dissolved silver fractions.

Total silver concentrations measured in the supernatant strongly decreased from nominal value of $200 \mu\text{g L}^{-1}$ due to agglomeration and sedimentation, and/or adsorption onto the bottles walls (Fig. 1). Among the four examined coatings, after 19 days only citrate coated Ag-NPs stayed in the suspension with more than 50% ($120 \mu\text{g L}^{-1}$). Ag-NP with gelatin, chitosan and PVP decreased to 10–30% of their total concentrations (Fig. 1). The average size of the particles suspended in the artificial aqueous media increased slightly when compared to the original suspensions (Table 2a). Citrate coated Ag-NPs were the smallest and PVP

Table 1
DGT measurements ($n = 6$) of dissolved Ag in 0.01 M NaNO_3 . Standard deviation is given in the brackets.

Total Ag ($\mu\text{g/L}$)	DGT ^a Ag ($\mu\text{g/L}$)
3.01 (0.01)	2.66 (0.66)
5.99 (0.01)	6.49 (0.57)
11.85 (0.21)	12.07 (1.19)
23.15 (0.35)	22.93 (0.90)

Correlation coeff. r^2 : Total Ag/DGT Ag = 0.9993.

^a Deployment time of DGT devices was 24 h at $23 \text{ }^\circ\text{C}$.

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