



Separation and measurement of silver nanoparticles and silver ions using magnetic particles



Samuel K. Mwilu^a, Emily Siska^a, R.B. Nasir Baig^b, Rajender S. Varma^b, Ed Heithmar^a, Kim R. Rogers^{c,*}

^a U.S. Environmental Protection Agency, Las Vegas, NV, USA

^b U.S. Environmental Protection Agency, Cincinnati, OH, USA

^c U.S. Environmental Protection Agency, Research Triangle Park, NC, USA

HIGHLIGHTS

- Simple rapid method is reported to separate trace amounts of silver nanoparticles.
- Surface-modified magnetic particles capture and concentrate trace amounts (ppb) of AgNPs.
- Magnetic capture particles selectively separated silver nanoparticles from ionic silver.
- Recovery was better than 97% for AgNPs from tap water or environmental surface water.

ARTICLE INFO

Article history:

Received 17 September 2013

Received in revised form 22 October 2013

Accepted 22 October 2013

Available online 30 November 2013

Keywords:

Silver nanoparticles
Magnetic capture particles
Separation technique
Environmental monitoring

ABSTRACT

The recent surge in consumer products and applications using metallic nanoparticles has increased the possibility of human or ecosystem exposure due to unintentional release into the environment. To protect consumer health and the environment, there is an urgent need to develop tools that can characterize and quantify these materials at low concentrations and in complex matrices. In this study, magnetic nanoparticles coated with either dopamine or glutathione were used to develop a new, simple and reliable method for the separation/pre-concentration of trace amounts of silver nanoparticles followed by their quantification using inductively coupled plasma mass spectrometry (ICP-MS). The structurally modified magnetic particles were able to capture trace amounts of silver nanoparticles (~2 ppb) and concentrate (up to 250 times) the particles for analysis with ICP-MS. Under laboratory conditions, recovery of silver nanoparticles was >99%. More importantly, the magnetic particles selectively captured silver nanoparticles in a mixture containing both nano-particulate and ionic silver. This unique feature addresses the challenges of separation and quantification of silver nanoparticles in addition to the total silver in environmental samples. Spiking experiments showed recoveries higher than 97% for tap water and both fresh and saline surface water.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The unique chemical and physical properties associated with engineered nanomaterials (ENMs) have led to a rapid increase in nano-based products being introduced to the consumer market. The manufacturing and commercialization of these nano-based consumer products are projected to grow exponentially (PEN) and will undoubtedly have a major impact on future societies. Unique characteristics of these particles due in part to their size, structure and high surface area have yielded a myriad of benefits associated with their use. For

example, dispersions of copper carbonate nanoparticles and microparticles have recently been exploited commercially for the preservative treatment of wood (Matsunaga et al., 2009), replacing the highly toxic chromated copper-arsenate formula. Sunscreen formulations based on titanium dioxide nanoparticles are continually being advanced because of their superior UV blocking capabilities by either light absorption or scattering (Shi et al., 2012). In addition, because of its wide spectrum biocide activity, nanosilver has been incorporated into a variety of products including detergents, clothing (Falletta et al., 2008) dishwashers, water filters (Dankovich and Gray, 2011), medical appliances (Crabtree et al., 2003; Jones et al., 2004) and food packaging materials (Gottesman et al., 2011). Alongside these benefits is the concern of possible adverse outcomes due to direct or indirect human or ecosystem exposure. Given the increasing ubiquity and early acceptance of nanotechnology, the release of these ENMs into the ecosystem either in their native form, derivatives or complexed with other compounds may be inevitable. Several studies have observed toxic effects for

* Corresponding author at: U.S. Environmental protection Agency, 109 TW Alexander Dr., Research Triangle Park, NC 27711, USA. Tel.: +1 919 541 3086.
E-mail address: rogers.kim@epa.gov (K.R. Rogers).

different types of ENMs including silver (Beer et al., 2012; Hackenberg et al., 2011; Lubick, 2008; Panacek et al., 2011; Teodoro et al., 2011), gold (Cho et al., 2009; Lasagna-Reeves et al., 2010), fullerene (Lovren et al., 2007), and metal oxide (Posgai et al., 2011) nanoparticles. These effects have been demonstrated in vitro and often at elevated nanomaterial concentrations. There is, however, an urgent need to develop sensitive tools to detect and characterize ENMs at lower concentrations expected to be present in environmental matrices.

Several nanoparticle characterization techniques based on light scattering and electron microscopy have been used to determine size distributions of nanoparticles in pristine laboratory settings (Montes-Burgos et al., 2010; Ulrich et al., 2012). Current innovations such as single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) and asymmetric flow field flow fractionation with optical spectroscopic or inductively coupled mass spectrometry (AF4-ICP-MS) show considerable promise for direct detection and characterization of different forms of ENMs. Although these techniques have been demonstrated to be sensitive for nanomaterials in simple aqueous samples, there may be challenges to their direct application to low concentrations of ENMs in environmentally complex matrices. For example, AF4 may be limited by unwanted losses of nanomaterials in separation channels mainly due to non-specific particle–membrane interactions (MacCuspie et al., 2011). In addition nanoparticles smaller than 30 nm cannot be accurately detected by sp-ICP-MS (MacCuspie et al., 2011; Mitrano et al., 2012). Moreover, in a mixture of metallic particles and ions, sp-ICP-MS cannot be distinguished between the nanoparticles and other colloid-bound metal ions or precipitates (Mitrano et al., 2012) although this limitation can be ameliorated by coupling a size-separation technique with SP-ICP-MS (Pergantis et al., 2012). Consequently, there is a need for simple and effective sample preparation methods, i.e., separation and/or pre-concentration techniques for nanomaterials especially at low concentrations and in complex matrices.

A variety of approaches including chromatographic techniques, cloud point extraction, centrifugation and filtration have been developed for extraction, separation and concentration of ENMs from aqueous media (Simonet and Valcárcel, 2009; Hanauer et al., 2007; Akbulut et al., 2012; Liu et al., 2009; Maurer et al., 2013). Filtration is the most common, although often problematic due to low sample recoveries. Factors such as particle size, physicochemical properties of the particles and the filter media will determine the filtration efficiency of a specific contaminant (Kang and Shah, 1997). For the aforementioned sample preparation techniques, a basic knowledge about the particle chemistry is essential to ensure accurate measurements and minimal particle losses. Since this information is often not directly accessible, there is a need for the development of a simplified compact process that provides adequate separation/concentration while still preserving the nanoparticle integrity with minimal sample losses.

Magnetic particles as sorbents for nanoparticles can offer a valuable separation/concentration method for trace amounts of nanoparticles, prior to their determination by either spectroscopic or electrochemical techniques. Nanoscale ferro-magnetic particles are typically superparamagnetic, hence they can be readily attracted by an external magnet but do not remain permanently magnetized after the field is removed (Baig and Varma, 2013). Moreover, they can be easily tuned by structural surface modifications (Baig and Varma, 2012) to form highly effective and robust adsorbent materials. These features, combined with the high surface area of the magnetic micro-/nano-particles, make them effective tools for concentrating nanomaterial from environmental samples. Recently, magnetic particles have emerged as a new generation of adsorbent materials used for capturing environmental contaminants such as metal ions (Hu et al., 2007; Yavuz et al., 2006) and hydrophobic organic compounds (Wang et al., 2008). The strategy of chemical extraction with magnetic recovery has been demonstrated to immobilize and pre-concentrate non-magnetic molecules and ions to superparamagnetic particles by modifying these capture particles with chelators such as glutathione and dopamine (Baig and Varma,

2013). Magnetic separation using these chemically-modified particles offers simplicity and overcomes many of the problems associated with conventional separation/preconcentration techniques (Wang et al., 2008, Ashtari et al., 2009). To the best of our knowledge, magnetic particles have not been reported for the separation/concentration of silver nanoparticles (AgNPs).

In the current study, we demonstrate the use of unmodified and surface-modified magnetic particles for the capture and concentration of AgNPs in aqueous media. The physical characterization of the magnetic particles before and after exposure to AgNPs was conducted. In addition, the applicability of this technique for use with AgNPs in environmental water samples is reported. The novelties of this work include the high potential for concentration of trace levels of nanoparticles as well as selective removal of nanosilver in mixtures containing silver ions.

2. Experimental section

2.1. Chemicals

Silver nanoparticles (AgNPs) of several different sizes and with different surface coatings were obtained from Nanocomposix (San Diego, CA) (polyvinyl pyrrolidone (PVP)–stabilized 10 nm and 75 nm nominal diameter, Biopure, aqueous suspension, 1.0 mg/mL) and citrate-stabilized AgNPs 10 nm and 75 nm nominal diameter, Biopure, aqueous suspension, 1.0 mg/mL. These AgNPs are sold as standard particles commissioned by the Organization for Economic Cooperation and Development (OECD). Each OECD standard sample is provided with batch-specific characterization data describing size, morphology, zeta potential, and particle concentration. All nanoparticle dilutions were made in ultrapure water (18 M Ω , Barnstead Water Systems). Ultrapure hydrochloric acid (HCl) and nitric acid (HNO₃), silver nitrate (AgNO₃), and silver standards for ICP-MS were purchased from Fisher Scientific (USA). All chemicals were used as received without purification. Magnetic particle stock suspensions (20 mg/mL) were prepared in ultrapure water and sonicated for 10 min prior to use.

2.2. Synthesis and surface modification of magnetic particles

Magnetic particles were synthesized according to a previously published report (Baig and Varma, 2012). Briefly, FeSO₄·7H₂O (13.9 g) and Fe₂(SO₄)₃ (20 g) were dissolved in 500 mL water in a 1000 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the solution to pH 10. The reaction mixture was then continuously stirred for 1 h at 60 °C. The unmodified magnetic particles (UMPs) were magnetically separated, washed with water until the pH reached 7, and then dried under vacuum at 60 °C for 2 h.

2.3. Surface modification of magnetic particles

Surface modification was achieved by adapting previously published reports (Baig and Varma, 2012; Polshettiwar and Varma, 2010). For modification with glutathione, UMPs (0.5 g) were dispersed in 15 mL water and 5 mL of methanol and sonicated for 15 min. Glutathione (reduced form) (0.4 g) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The glutathione-functionalized magnetic particles (GMPs) were then isolated by centrifugation, washed with water and methanol, and dried under vacuum at 50 to 60 °C. Dopamine-modified magnetic particles were synthesized as follows; UMPs (2 g) were dispersed in 25 mL water by sonicating for 30 min. Dopamine hydrochloride (1 g) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The dopamine-functionalized magnetic particles (DMPs) were then precipitated using acetone, isolated by centrifugation, and dried under vacuum at 60 °C for 2 h.

2.4. Material characterization

Scanning electron microscopy (SEM) was performed using a Zeiss EVO MA SEM (Carl Zeiss SMT Ltd, Cambridge, UK) with an in-lens or SE2 arrangement at 3–10 keV working voltage and ~5 mm lens to detector distance. Carbon planchets (highly polished, 12.7 mm diameter, Ted Pella Inc., Redding CA) were mounted on the stage using double-sided carbon tape. X-ray mapping examinations were carried out using a QUANTAX Bruker energy dispersive X-ray spectrometer attached to the Zeiss microscope. The EDS mappings were carried out at a voltage of 8–10 kV under vacuum conditions.

The ability of the magnetic particles to capture AgNPs was tested by exposing 2 µg/mL AgNP solution to 2 mg/mL magnetic particles. Briefly, magnetic particle suspensions were added to AgNPs, the mixture shaken for 30 min at 100 rpm to disperse the particles then incubated for 15 min to facilitate absorption of the AgNPs. The particles were magnetically separated from the suspension using the magnetic capture flow cell design shown in Fig. 1. The total silver content of the flow cell eluate was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) after digestion in aqua regia. The difference in silver content before and after separation of the magnetic particles was indicative of the amount of AgNPs captured by the magnetic particles.

2.5. Digestion and ICP-MS detection

AgNPs were quantified by measuring the total silver content either in the flow cell eluate or directly by digesting the magnetic particles after magnetic separation. ICP-MS instrument response curves for silver were prepared using Ag certified reference material diluted in 1% HNO₃. All ICP-MS determinations were performed on a Perkin Elmer NEXION

300D. Flow cell eluate solutions were digested by mixing 1 mL sample with 2 mL of aqua regia (1:3, HNO₃:HCL). In the case of magnetic particles 2 mL of aqua regia was added to the particles and allowed to digest completely (solution remained clear with no visible particles) before diluting for ICP-MS analysis.

3. Results and discussion

3.1. Characterization of adsorption of AgNPs to magnetic capture particles by SEM

The synthesis and characterization of magnetic particles used in the present study have been previously described (Baig and Varma, 2012; Polshettiwar et al., 2009). Suspensions of these partially dispersed particles showed spherical morphology with a size range of 10–25 nm. Functionalization of these magnetic particles with glutathione and dopamine hydrochloride for use as transition metal catalysts has also been reported (Baig and Varma, 2012; Polshettiwar and Varma, 2010). SEM analysis for each of the magnetic particle suspensions prior to exposure to AgNPs showed what appeared as particle aggregates with topological features at the sub-micron scale (Fig. 2). Due to instrument resolution, individual magnetic particles previously described for these preparations as having size distributions of 10–25 nm were not resolved (Baig and Varma, 2012). Representative EDS analysis of these magnetic particles prior to exposure to silver nanoparticles indicated the presence of iron and oxygen but no silver (Fig. 1S).

Several surface modified magnetic particles and combinations of magnetic particles were analyzed for their ability to capture various types and sizes of AgNPs. Fig. 3 shows the SEM micrographs of AgNPs (75 nm, citrate-stabilized) trapped within different magnetic sorbent materials. Elemental analysis confirmed the presence of AgNPs bound to the magnetic particles (Fig. 2S). The white spheres (shown in the red box) represent the AgNPs (Fig. 2S). EDS analysis of the background showed the presence of Fe and O but no Ag (Fig. 3S). These magnetic particles seem to form a porous framework that trapped the AgNPs. A higher magnification image better shows this framework (Fig. 4S).

3.2. Adsorption of AgNPs onto magnetic particles, separation and analysis by ICP-MS

Magnetic particles are advantageous as capture media for AgNPs in that they can be used at a high magnetic particle to silver particle ratio and then be easily separated from suspension. Although agglomerated, to some extent, these magnetic capture particles are readily dispersed by brief sonication and due to their nanoscale primary particle size, show a relatively high surface area to mass ratio (Baig and Varma, 2012).

The experimental design for capture and analysis of AgNPs using magnetic capture particles is shown in Fig. 4. After incubation of various magnetic particle types with AgNP preparations (different sizes and different coatings), the mixtures were subjected to magnetic separation and both the eluate and captured particles were extracted and analyzed for total silver by ICP-MS. Upon exposure to a neodymium magnet, the magnetic particles were easily separated from their suspension matrix (Fig. 1A). The flow cell configuration allowed an efficient means for bringing the capture particles into close proximity of the capture magnet (Fig. 1B).

AgNPs with different surface coatings (citrate and PVP) and with different sizes (10 nm and 75 nm) were incubated with different types and combinations of magnetic particles (UMP, GMP, DMP, [equal mass mixture of DMP, GMP], Mix D–G). Exposure of each type of AgNP to the magnetic capture particles (UMP, GMP and Mix D–G) removed more than 90% of the silver in the eluate (Fig. 5). The DMP particles were less efficient in capturing and recovering AgNPs (with the exception of the 75 nm PVP-coated particles) from suspension. The decrease in capture efficiency of the DMP magnetic particles may have been due

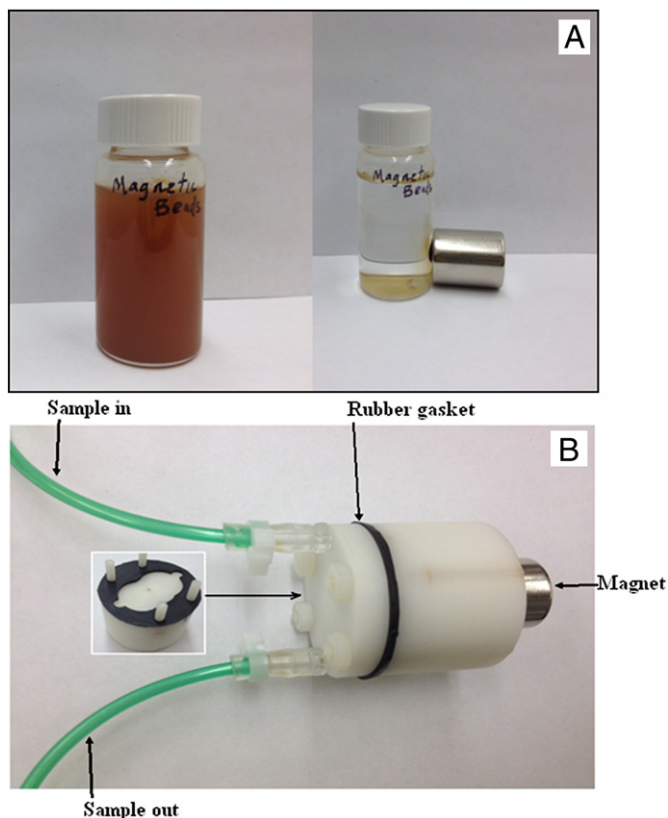


Fig. 1. (A) Magnetic particles in suspension; when a magnetic field is applied the solution becomes clear and (B) magnetic separation flow cell used for separating magnetic particles from solution.

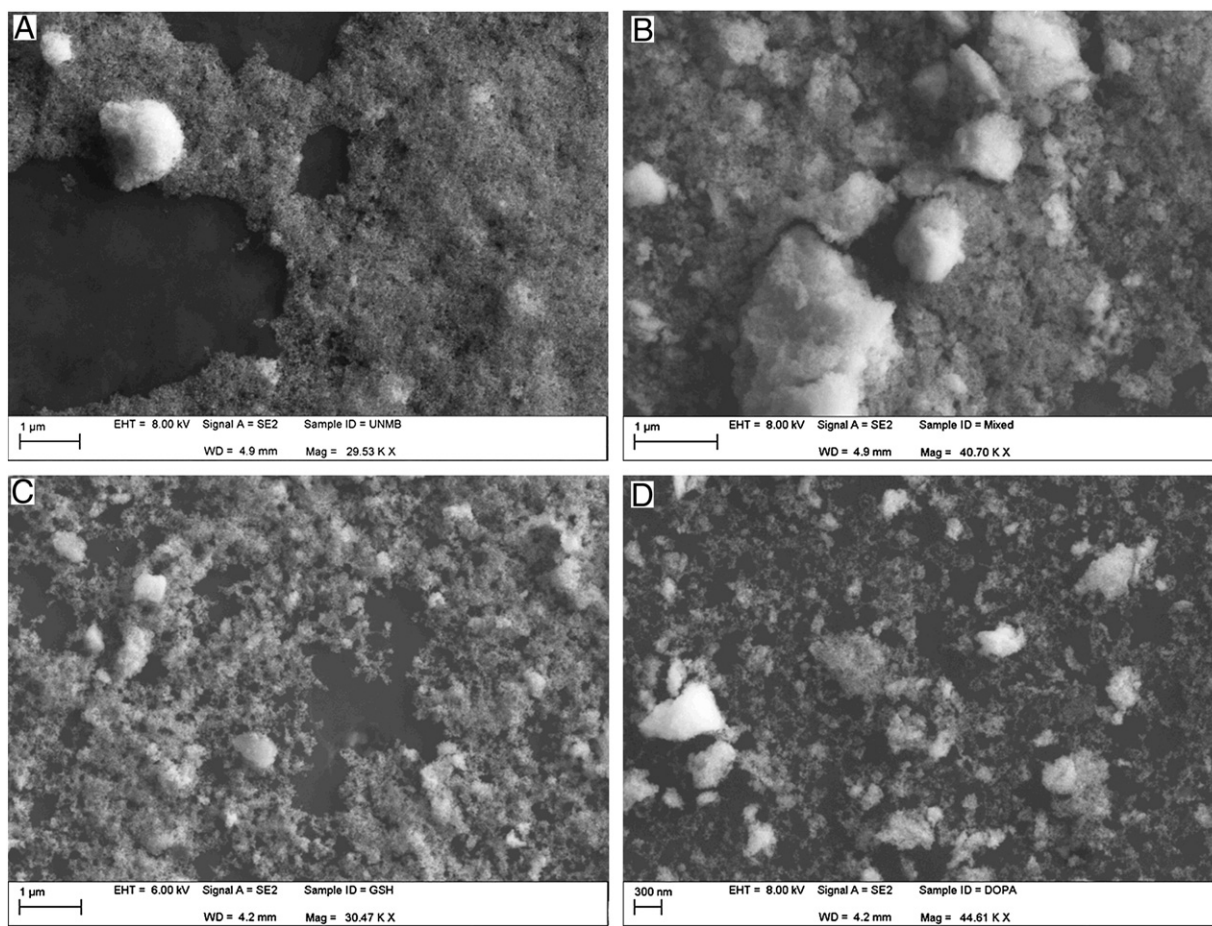


Fig. 2. SEM micrographs of magnetic particles before exposure to AgNPs; (A) UMP; (B) Mix D–G; (C) GMP; and (D) DMP.

in part to the decreased binding of AgNPs to the magnetic particles and also may have been due to the lower efficiency of magnetic capture for these particles by the flow cell as evidenced by the color of the eluate after separation indicating incomplete capture of the magnetic particles in the flow cell (Fig. 5S). The presence of GMP particles mixed with the DMP particles (i.e., Mix D–G) resulted in a visibly clear eluate after magnetic separation suggesting that the GMP particles assisted in aggregation and magnetic separation of the DMP particles (Fig. 5S).

To confirm that the AgNPs were binding to the capture particles rather than the containers and flow cell, a control experiment using AgNPs in the absence of magnetic particles showed a minimal sorption (<0.5%) of AgNPs to the separation cell and walls of the teflon vials used for incubation of the magnetic particles and AgNPs. In addition to measuring the disappearance of AgNPs from the flow cell eluate, total silver was also extracted from the magnetically separated capture particles and measured by ICP-MS. Results showed almost 100% recoveries for the 75 nm PVP-stabilized and 75 nm citrate-stabilized AgNPs as captured by the UMP and Mix D–G magnetic particles (Fig. 6S). Although the herein observed capture efficiency for AgNPs, even for the unmodified magnetic capture particles was high, it was not entirely unprecedented. Ashtari et al. (2009) observed a greater than 90% capture of beryllium ion to unmodified magnetic particles and 100% recovery for quinalzarine-modified particles.

3.3. Separation of AgNPs from ions

One of the features shown by the magnetic particle capture and separation technique was the varied ability of the magnetic particles to

bind silver ion. The DMP, GMP and Mix D–G particles captured silver ions at levels between 20% and 50%, whereas the UMP particles captured silver ions at <5% (Fig. 5).

The selectivity of UMP particles towards AgNPs was further investigated using a binary mixture containing nanoparticle suspensions and silver ions. Suspensions containing different ratios of AgNPs (from 100% Ag⁺ ions, maximum 2 µg/mL, to 100% AgNPs, maximum 2 µg/mL) were incubated with the UMP particles. The silver content was analyzed by ICP-MS after magnetic separation. Fig. 6 shows that the amount of silver detected by ICP-MS after magnetic separation is in reasonable agreement with the amount of silver expected to be recovered if only the AgNPs were bound to the magnetic capture particles. The results indicate a high degree of selectivity for the AgNP over Ag ion.

3.4. Adsorption dynamics

The adsorption of AgNPs onto the magnetic particles was investigated as a function of incubation time for 75 nm PVP-stabilized and citrate-stabilized AgNPs binding to Mix D–G particles. The initial AgNP concentration was 2 µg/mL and the concentration of magnetic capture particles was 2 mg/mL. The vials were placed on a shaker and continuously agitated at 100 rpm at room temperature (23 ± 2 °C). At the end of 5, 10, 20, 40, 60 and 120 min, one vial was taken out and the mixture passed through the magnetic separation cell. The amount of AgNPs captured was calculated as the difference between the initial and final AgNP concentration in suspension. Results showed that sorption equilibrium was reached in <20 min (Fig. 7).

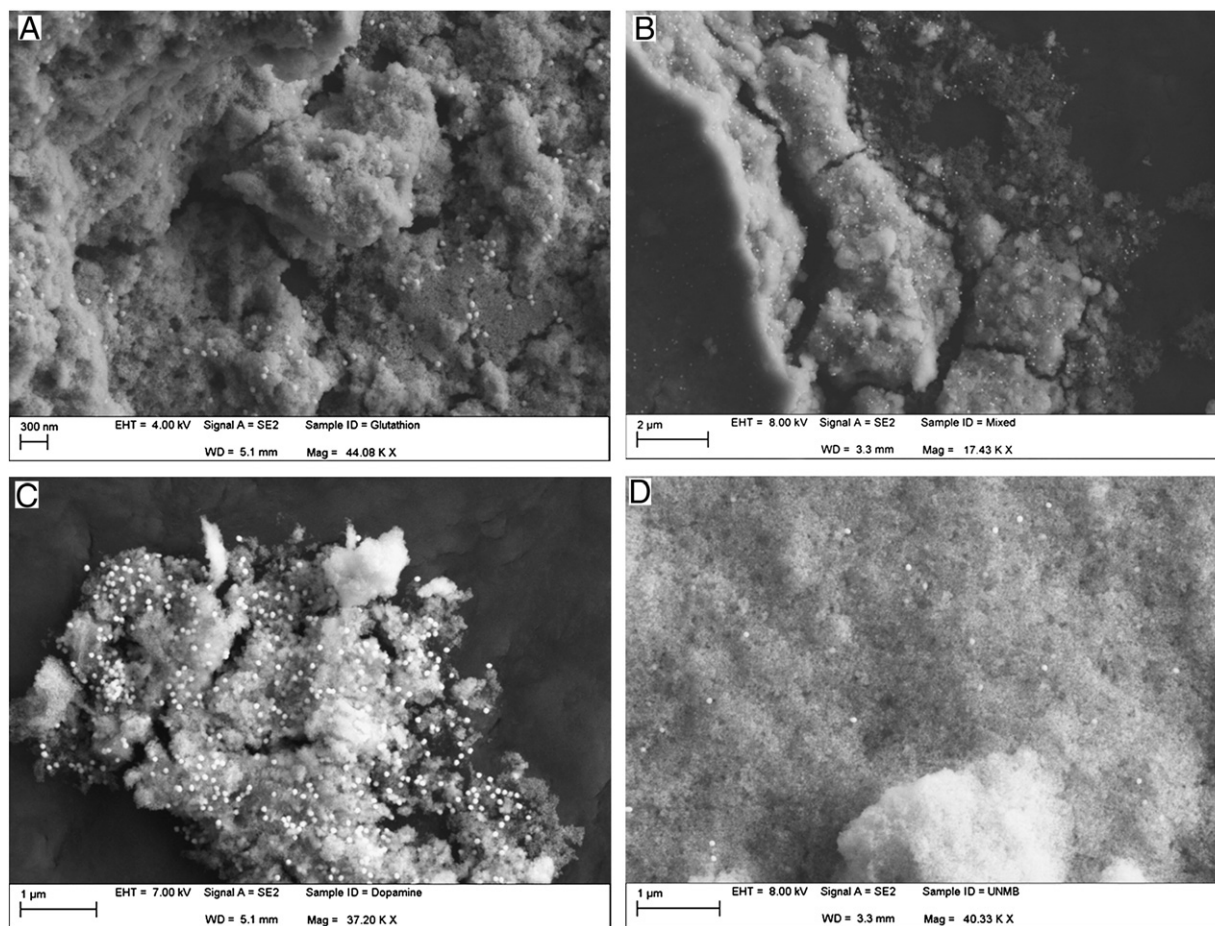


Fig. 3. SEM micrographs of magnetic particles after exposure to AgNPs (75 nm citrate). (A) GMP; (B) Mix D-G; (C) DMP; and (D) UMP.

3.5. Trace analysis

The effectiveness of the magnetic particles (Mix D-G) in capturing trace amounts of AgNPs (75 nm citrate-stabilized), at ng/mL

concentration levels was tested over a 30 min exposure time. The particles were separated using the magnetic separation cell, digested with aqua regia and analyzed for silver content by ICP-MS (Fig. 8). The method showed a high degree of correlation between the expected and recovered AgNPs.

Experimental Flow Diagram

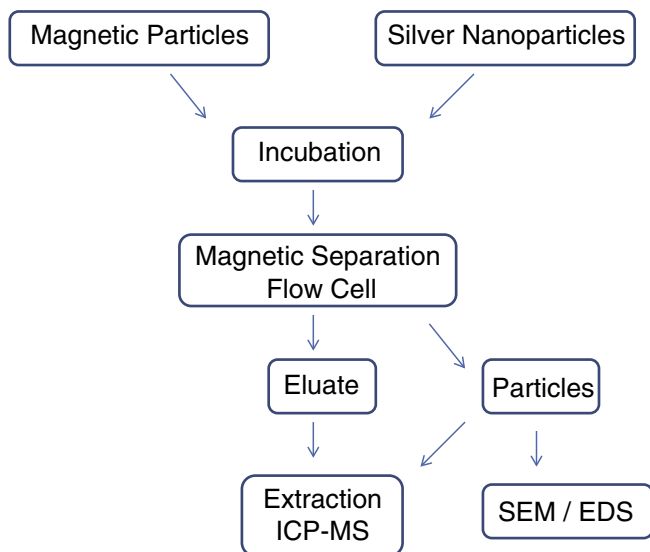


Fig. 4. Experimental flow diagram for capture and analysis of AgNPs using magnetic capture particles.

3.6. Volume effects

We also investigated the capture of AgNPs from relatively large sample volumes (500 mL). The water samples were spiked with 75 nm citrate-stabilized AgNPs (100 μg/mL) and magnetic capture particles (Mix D-G) were added at 1 mg/mL. The suspension was shaken for 30 min before magnetic separation. The separated magnetic particles laden with AgNPs were resuspended into 2 mL of water before digestion with aqua regia and analysis by ICP-MS; this represents a theoretical 250-fold increase in AgNP concentration. Recovery of total silver extracted from magnetically captured particles was $99.0 \pm 0.6\%$ ($n = 4$). Capture of the magnetic particles required ~30 min to pass the 500 mL sample through the flow cell.

3.7. Environmental samples

The efficiency of this method in capturing AgNPs from aqueous environmental matrices containing varying amounts of diverse ions was evaluated using 3 water samples. In addition to laboratory DI water and local tap water, two environmental water samples were evaluated, i.e., Lake Hancock (central Florida) water and San Francisco Bay water. Prior to addition of AgNPs, these samples did not contain detectable silver at a LOD of 400 ng/L. Each of these samples was spiked with 2 μg/mL AgNPs (75 nm PVP-stabilized) prior to adding magnetic

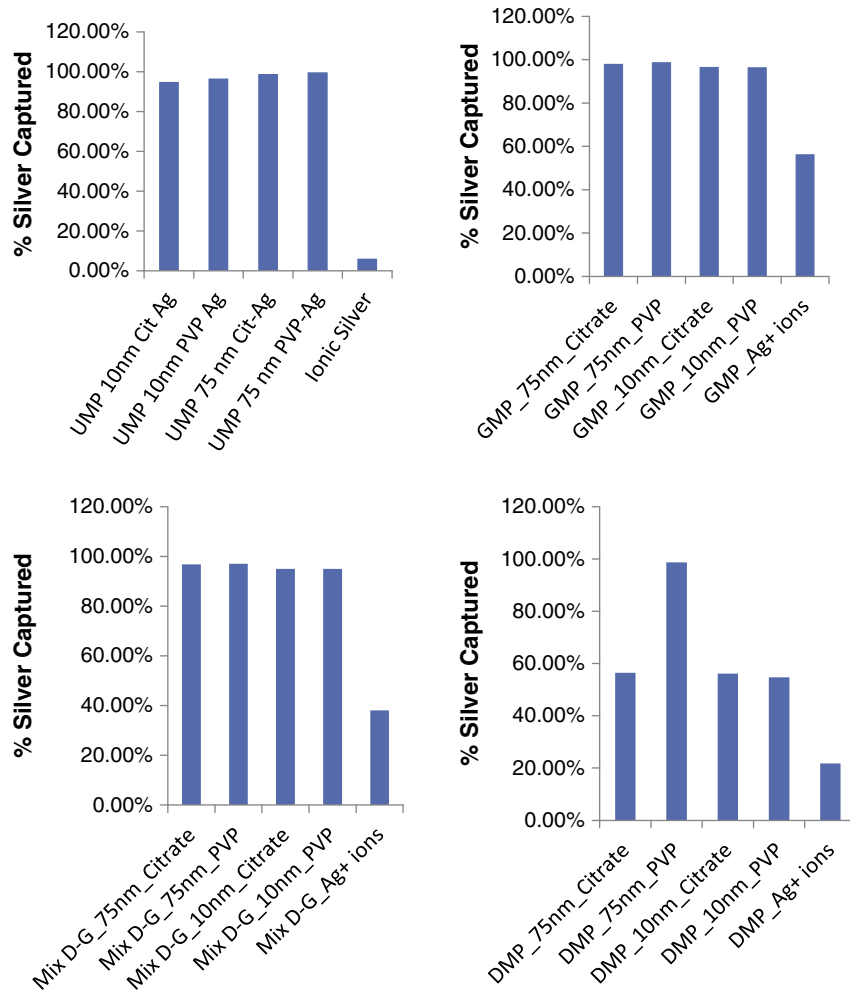


Fig. 5. Capture efficiency of magnetic particles (UMP, GMP, Mix D-G, DMP) for AgNPs (10 nm citrate, 10 nm PVP, 75 nm citrate, 75 nm PVP) and Ag⁺.

capture particles (Mix D-G, 2 mg/mL). AgNPs were most efficiently captured in the DI water as compared to the local tap water, lake water or bay water. Results, however, indicate that the recovery of

spiked AgNPs was >96% in each of these matrices (Table 1). To ensure that AgNPs did not stick to the container walls during shaking, 0.1% Triton X-100 was added to the experimental controls. It was determined experimentally that the Triton X-100 did not affect the capture of AgNPs by the magnetic particles. Representative properties of the

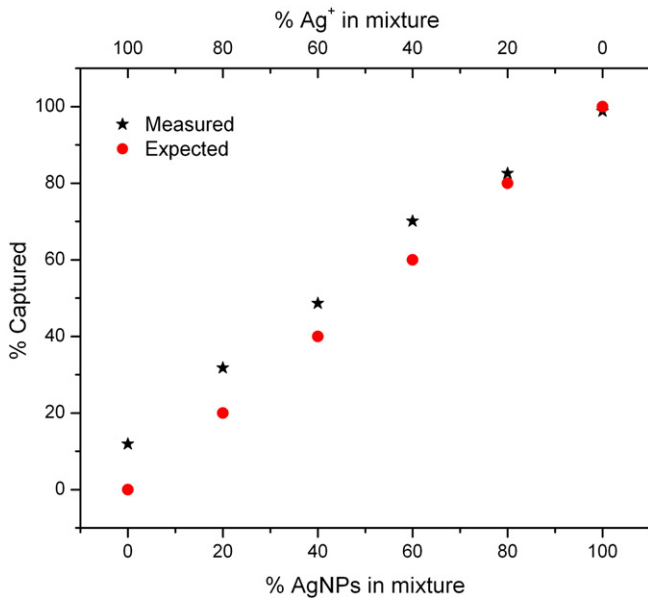


Fig. 6. Efficiency for capture of AgNP (75 nm citrate) by UMP from suspensions containing different mass ratios of Ag⁺ ions and AgNPs.

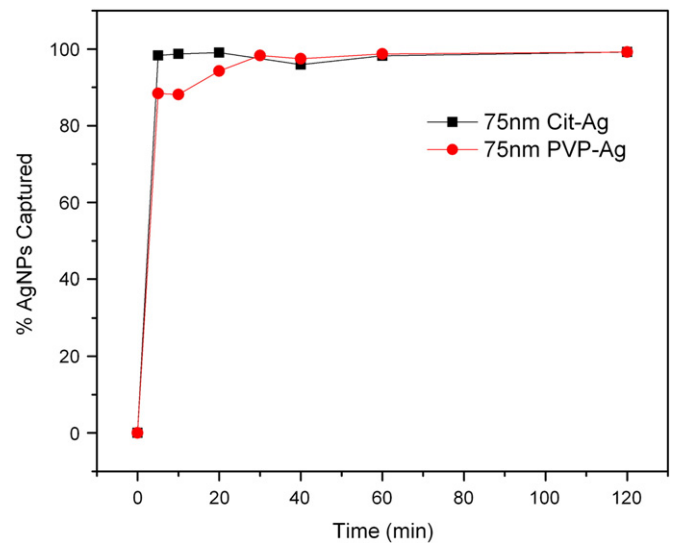


Fig. 7. Time course for capture of AgNPs (75 nm citrate) by magnetic particles (Mix D-G).

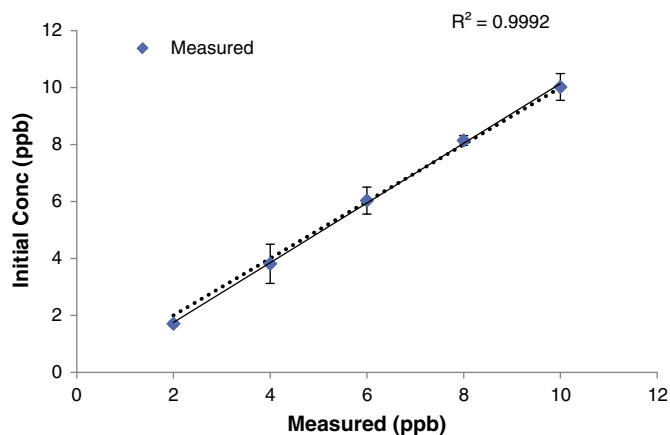


Fig. 8. Detection of trace concentrations of AgNPs (75 nm citrate captured by magnetic particles (UMP)); $r^2 = 0.9992$.

environmental water samples (San Francisco Bay and Lake Hancock water) are shown in Table 1S.

4. Conclusions

We have described a novel method for the separation of AgNPs in aqueous systems. The AgNPs were captured and concentrated using magnetic capture particles and quantified by ICP-MS. Physical characterization by SEM/EDS confirmed the presence of AgNPs captured by the magnetic particles. We then demonstrated the ability of the magnetic particles to selectively capture and concentrate (up to 250-fold concentration factor) the trace levels of AgNPs in water. The advantage of this method over commonly used separation techniques is its ease of separation by the use of an external magnetic field. Experiments with spiked environmental samples revealed that AgNPs can be recovered in complex matrices; hence, this method has the potential as an analytical tool for concentrating and detecting nanoparticles from the environment.

Conflict of interest

We are not aware of any financial or professional conflicts of interest concerning this study.

Acknowledgments

The United States Environmental Protection Agency through its Office of Research and Development has provided administrative review of this article and approved it for publication. This work was performed while S.K. Mwilu held a National Research Council Fellowship at US-EPA, Las Vegas.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.10.077>.

Table 1
Capture efficiency of AgNPs spiked into environmental water samples.

Sample	% AgNPs captured by magnetic particles
Distilled water	99.0 ± 0.2
Tap water (Las Vegas)	98.1 ± 0.3
Lake Hancock Water	98.2 ± 0.3
San Francisco Bay Water	96.1 ± 1.2

Magnetic capture particles, Mix D–G were added at 2 mg/mL. AgNPs (75 nm PVP-stabilized) were spiked at 2 µg/mL (n = 3).

References

- Ashtari P, Wang K, Yang X, Ahmadi SJ. Preconcentration and separation of ultra-trace beryllium using quinalizarine-modified magnetic microparticles. *Anal Chim Acta* 2009;646:123–7.
- Akbulut O, Mace CR, Martinez RV, Kumar AA, Nie Z, Patton MR, et al. Separation of nanoparticles in aqueous multiphase systems through centrifugation. *Nano Lett* 2012;12(8):4060–4.
- Baig RBN, Varma RS. A highly active magnetically recoverable nano ferrite-glutathione-copper (nano-FGT-Cu) catalyst for Huisgen 1,3-dipolar cycloadditions. *Green Chem* 2012;14:625–32.
- Baig RBN, Varma RS. Organic synthesis via magnetic attraction: benign and sustainable protocols using magnetic nanoferrites. *Green Chem* 2013;15:398–417.
- Beer C, Foldbjerg R, Hayashi Y, Sutherland DS, Autrup H. Toxicity of silver nanoparticles—nanoparticle or silver ion? *Toxicol Lett* 2012;208(3):286–92.
- Cho W-S, Cho M, Jeong J, Choi M, Cho H-Y, Han BS, et al. Acute toxicity and pharmacokinetics of 13 nm-sized PEG-coated gold nanoparticles. *Toxicol Appl Pharmacol* 2009;236(1):16–24.
- Crabtree JH, Burchette RJ, Siddiqi RA, Huen IT, Hadnott LL, Fishman A. The efficacy of silver-ion implanted catheters in reducing peritoneal dialysis-related infections. *Perit Dial Int* 2003;23(4):368–74.
- Dankovich TA, Gray DG. Bactericidal paper impregnated with silver nanoparticles for point-of-use water treatment. *Environ Sci Technol* 2011;45(5):1992–8.
- Falletta E, Bonini M, Fratini E, Lo Nostro A, Pesavento G, Becheri A, et al. Clusters of poly(acrylates) and silver nanoparticles: structure and applications for antimicrobial fabrics. *J Phys Chem C* 2008;112(31):11758–66.
- Gottesman R, Shukla S, Perkas N, Solovoyov IA, Nitzan Y, Gedanken A. Sonochemical coating of paper by microbicidal silver nanoparticles. *Langmuir* 2011;27(2):720–6.
- Hackenberg S, Scherzed A, Kessler M, Hummel S, Technau A, Froelich K, et al. Silver nanoparticles: evaluation of DNA damage, toxicity and functional impairment in human mesenchymal stem cells. *Toxicol Lett* 2011;201(1):27–33.
- Hanauer M, Pierrat S, Zins I, Lotz A, Sönnichsen C. Separation of nanoparticles by gel electrophoresis according to size and shape. *Nano Lett* 2007;7(9):2881–5.
- Hu J, Lo IMC, Chen G. Performance and mechanism of chromate (VI) adsorption by δ-FeOOH-coated maghemite (γ-Fe₂O₃) nanoparticles. *Sep Purif Technol* 2007;58(1):76–82.
- Jones SA, Bowler PG, Walker M, Parsons D. Controlling wound bioburden with a novel silver-containing Hydrofiber dressing. *Wound Repair Regen* 2004;12(3):288–94.
- Kang PK, Shah DO. Filtration of nanoparticles with dimethyldioctadecylammonium bromide treated microporous polypropylene filters. *Langmuir* 1997;13(6):1820–6.
- Lasagna-Reeves C, Gonzalez-Romero D, Barria MA, Olmedo I, Clos A, Sadagopa Ramanujam VM, et al. Bioaccumulation and toxicity of gold nanoparticles after repeated administration in mice. *Biochem Biophys Res Commun* 2010;393(4):649–55.
- Liu J-f, Chao J-b, Liu R, Tan Z-q, Yin Y-g, Wu Y, et al. Cloud point extraction as an advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters. *Anal Chem* 2009;81(15):6496–502.
- Lovern SB, Strickler JR, Klaper R. Behavioral and physiological changes in daphnia magna when exposed to nanoparticle suspensions (titanium dioxide, nano-C60, and C60HxC70Hx). *Environ Sci Technol* 2007;41(12):4465–70.
- Lubick N. Nanosilver toxicity: ions, nanoparticles or both? *Environ Sci Technol* 2008;42(23):8617.
- MacCuspie RI, Rogers K, Patra M, Suo Z, Allen AJ, Martin MN, et al. Challenges for physical characterization of silver nanoparticles under pristine and environmentally relevant conditions. *J Environ Monit* 2011;13(5):1212–26.
- Matsunaga H, Kiguchi M, Evans P. Microdistribution of copper-carbonate and iron oxide nanoparticles in treated wood. *J Nanopart Res* 2009;11(5):1087–98.
- Maurer EI, Sharma M, Schlager JJ, Hussain SM. Systematic analysis of silver nanoparticle ionic dissolution by tangential flow filtration: toxicological implications. *Nanotoxicology* 2013:1–32.
- Mitrano DM, Leshner EK, Bednar A, Monserud J, Higgins CP, Ranville JF. Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry. *Environ Toxicol Chem* 2012;31(1):115–21.
- Montes-Burgos I, Walczyk D, Hole P, Smith J, Lynch I, Dawson K. Characterisation of nanoparticle size and state prior to nanotoxicological studies. *J Nanopart Res* 2010;12(1):47–53.
- Panacek A, Prucek R, Safarova D, Dittrich M, Richtrova J, Benickova K, et al. Acute and chronic toxicity effects of silver nanoparticles (NPs) on *Drosophila melanogaster*. *Environ Sci Technol* 2011;45(11):4974–9.
- <http://www.nanotechproject.org/cpi/browse>. [accessed 10/2013].
- Polshettiwar V, Baruwati B, Varma RS. Magnetic nanoparticle-supported glutathione: a conceptually sustainable organocatalyst. *Chem Commun (Camb)* 2009;14:1837–9.
- Polshettiwar V, Varma RS. Nano-organocatalyst: magnetically retrievable ferrite-anchored glutathione for microwave-assisted Paal-Knorr reaction, aza-Michael addition, and pyrazole synthesis. *Tetrahedron* 2010;66(5):1091–7.
- Posgai R, Cipolla-McCulloch CB, Murphy KR, Hussain SM, Rowe JJ, Nielsen MG. Differential toxicity of silver and titanium dioxide nanoparticles on *Drosophila melanogaster* development, reproductive effort, and viability: size, coatings and antioxidants matter. *Chemosphere* 2011;85(1):34–42.
- Shi L, Shan J, Ju Y, Aikens P, Prud'homme RK. Nanoparticles as delivery vehicles for sunscreen agents. *Colloids Surf A Physicochem Eng Asp* 2012;396:122–9.
- Simonet BM, Valcárcel M. Monitoring nanoparticles in the environment. *Anal Bioanal Chem* 2009;393(1):17–21.

- Pergantis SA, Jones-Lepp TA, Heithmar EM. Hydrodynamic chromatography on-line with single particle inductively coupled plasma-mass spectrometry for ultratrace detection of metal-containing nanoparticles. *Anal Chem* 2012;84(15):6462–5.
- Teodoro JS, Simões AM, Duarte FV, Rolo AP, Murdoch RC, Hussain SM, et al. Assessment of the toxicity of silver nanoparticles in vitro: a mitochondrial perspective. *Toxicol in Vitro* 2011;25(3):664–70.
- Ulrich A, Losert S, Bendixen N, Al-Kattan A, Hagendorfer H, Nowack B, et al. Critical aspects of sample handling for direct nanoparticle analysis and analytical challenges using asymmetric field flow fractionation in a multi-detector approach. *J Anal At Spectrom* 2012;27(7):1120–30.
- Wang P, Shi Q, Shi Y, Clark KK, Stucky GD, Keller AA. Magnetic permanently confined micelle arrays for treating hydrophobic organic compound contamination. *J Am Chem Soc* 2008;131(1):182–8.
- Yavuz CT, Mayo JT, Yu WW, Prakash A, Falkner JC, Yean S, et al. Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals. *Science* 2006;314(5801):964–7.