



Ligand-assisted magnetic solid phase extraction for fast speciation of silver nanoparticles and silver ions in environmental water

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ABSTRACT

In this work, poly(1-vinylimidazole) functionalized magnetic nanoparticles (PVIM-MNPs) were prepared and adopted for the adsorption of silver nanoparticles (AgNPs) and silver ions (Ag ions). With the use of mercaptosuccinic acid as a ligand exchanger, both of AgNPs and Ag ions could be adsorbed on the PVIM-MNPs and the sequential desorption of Ag ions and AgNPs was easily achieved by using $\text{Na}_2\text{S}_2\text{O}_3$ and HNO_3 , respectively. Based on it, a new approach by coupling ligand-assisted magnetic solid phase extraction (MSPE) with graphite furnace atomic absorption spectrometry (GFAAS) detection was proposed for the speciation of AgNPs and Ag ions in environmental water samples. Factors affecting MSPE of AgNPs and Ag ions were investigated and the optimized conditions were established. With an enrichment factor of 100-fold, the detection limits of the proposed method were 7.5 and 8.2 ng L^{-1} for Ag ions and AgNPs with relative standard deviations of 6.4% and 7.0% ($c = 50 \text{ ng L}^{-1}$, $n = 7$), respectively. The proposed ligand-assisted MSPE-GFAAS method has the advantages of high sensitivity, low cost and easy operation, and could be used for the quantification of Ag ions and various coating modified AgNPs with a size range of 5–120 nm in environmental waters.

1. Introduction

Metal-containing nanoparticles (NPs) such as Ag-, Au-, TiO_2 - and ZnO-NPs have been widely manufactured and utilized in the fields of materials, electronics, energy, cosmetics and medicine. Because of the antimicrobial properties, AgNPs are recognized as one of the most frequently used nanomaterials in consumer products (fabric, tableware, medical disinfectant) directly associated to daily human life [1]. With the increase use of AgNPs-containing products, AgNPs were inevitably discharged into the environmental water along with the release of Ag ions [2,3], which probably posed a potential risk to living organism and human health. It has been reported that AgNPs were toxic to plants [4], fish [5] and human cell [6] and the toxicity of AgNPs is generally believed to be related with their release of Ag ions, which have toxic effects on many pathogens [7]. Additionally, the concentration, size, coating, shape and agglomeration of AgNPs, the releasing speed of Ag ions, as well as the concentration of the released Ag ions could affect the toxicity of AgNPs [7–9]. Therefore, speciation and determination of Ag ions and AgNPs with various coating and size in environment waters is crucial for evaluating the environmental pollution and toxicity properties of AgNPs.

The speciation analysis of Ag ions and AgNPs is generally achieved by combining high efficient separation/extraction methods with

different detection techniques [10–12]. Various detection techniques including flame atomic absorption spectrometry (FAAS) [13], graphite furnace atomic absorption spectrometry (GFAAS) [14], inductively coupled plasma optical emission spectrometry (ICP-OES) [15] and inductively coupled plasma mass spectrometry (ICP-MS) [16] as well as single particle ICP-MS [17,18] have been adopted for the determination of silver in different matrix. Among them, GFAAS is a fast, sensitive and low-cost method with advantages of high atomization efficiency and less sample consumption. The separation techniques for Ag ions and AgNPs include chromatographic approaches (e.g. liquid chromatography [19], field flow fractionation [20] and capillary electrophoresis [21] and non-chromatographic techniques (e.g. ultrafiltration/ultra-centrifugation [22], cloud point extraction (CPE) [14,23,24], liquid phase microextraction (LPME) [25,26], and solid phase extraction (SPE) [27–29]). In view of the low concentration of target Ag species and complex sample matrix in the real-world samples, the novel non-chromatographic separation techniques (CPE, LPME, SPE methods) are good choices for real sample analysis, which can not only separate Ag species, but also remove sample matrix and preconcentrate target species. Liu's group [23] first established the TritonX-114 (TX-114) based CPE method for thermosreversible extraction and recycling of different NPs such as Au, TiO_2 and Fe_3O_4 NPs, and the particle sizes and shapes of NPs can be efficiently preserved during the extraction. Then

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the method was successfully extended to the species-selective extraction of trace AgNPs from different matrix [24,30–32] with appropriate complexing agent to mask ionic Ag species. Extraction of hydrophobic NPs into an organic solvent is an alternative way for the separation/preconcentration of NPs in real samples, and some researchers have employed the liquid-liquid microextraction method for direct extraction of hydrophobic polyvinylpyrrolidone (PVP) capped AgNPs [33] and indirect extraction of hydrophilic citrate capped AgNPs with a preliminary hydrophobization step [26]. SPE is also a widely-used sample preparation technique for the extraction of AgNPs due to its high extraction efficiency, little consumption of organic solvent, low cost and easy operation. Li et al. [27] proposed a SPE-based method to effectively extract Ag-, Au-, and Pd-NPs at the ng L^{-1} level from environmental water by using an ionic exchange resin as the sorbent, while a long time (> 42 h) was needed for the elution of adsorbed NPs from the resin. With a polytetrafluoroethylene (PTFE) knotted reactor as an SPE device, Su et al. [28] achieved the selective extraction of total Ag (AgNPs + Ag^+) and Ag^+ at different pH, and the detection limits of total Ag and Ag^+ were 0.006 and $0.234 \mu\text{g L}^{-1}$, respectively. Mwilu et al. [34] reported the use of magnetic nanoparticles (MNPs) for selectively capturing AgNPs in the presence of Ag ions from aqueous media, and the magnetic sorbent loaded with the AgNPs was digested by aqua regia and diluted before ICP-MS quantification. However, there are some drawbacks associated with these reported methods: 1) most of these methods mentioned above can only extract and preconcentrate particulate species, but cannot provide the information of ionic species which may coexist in the real-world samples; 2) some of the reported methods need long operation time or tedious digestion step; 3) various coating stabilized NPs with different size would coexist in the real-world samples, which need to be simultaneously identified and quantified. Hence, it is extremely essential to develop fast and simple extraction methods for the separation and preconcentration of Ag ions and AgNPs with different size and coatings simultaneously.

By adding a suitable organic ligand (dodecanethiol) in chloroform, Li et al. [25] achieved a ligand-assisted liquid extraction of various coating stabilized AuNPs that were pre-extracted by solid phase C-18 material. Based on efficient ligand exchange and ion pair formation, Majedi et al. [26] achieved a preliminary hydrophobization of AgNPs and TiO_2 NPs and developed a solvent microextraction method for efficient extraction of the particulate species from natural water samples into organic phase. The hydrophobization and solvent microextraction process enable various coated NPs to be extracted through effective ligand exchange with the thiol group in mercaptoundecanoic acid (MUA) and ion pair formation between MUA and octadecylamine. In our previous work [29], sequential analysis of Au ions and AuNPs in water samples was realized by MSPE-ICP-MS in the presence of mercaptosuccinic acid (MSA), which probably acted as a ligand exchanger. With the addition of MSA, various coating stabilized AuNPs would transform into MSA modified AuNPs by ligand exchange method, and be further quantitatively extracted. However, the Al^{3+} immobilized $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{iminodiacetic acid}$ (IDA) magnetic sorbent exhibited a narrow quantitative adsorption pH range (2–4) toward AuNPs, which is unsuitable for the extraction of AgNPs that would tend to dissolve in acidic solution ($< \text{pH } 3.5$) [35].

Based on the sequential analysis strategy and ligand exchange method, a new method by coupling ligand-assisted MSPE with GFAAS detection was proposed herein for speciation analysis of trace AgNPs and Ag ions in environmental water samples with the addition of MSA. As the imidazole groups could form stable complexes with Ag ions due to the heterocyclic nitrogen ligands [36], poly(1-vinylimidazole) functionalized magnetic nanoparticles (PVIM-MNPs) were prepared and the adsorption/desorption behavior of AgNPs and Ag ions on the prepared PVIM-MNPs was investigated. It was found that Ag ions and AgNPs could be simultaneously adsorbed on PVIM-MNPs, then the ionic and nano-particulate Ag species retained on the PVIM-MNPs could be sequentially desorbed by $\text{Na}_2\text{S}_2\text{O}_3$ and HNO_3 , respectively. The

application potential of the proposed method of MSPE-GFAAS was evaluated by the speciation of trace AgNPs and Ag ions in environmental water samples.

2. Experimental

2.1. Instrumentation

Constant temperature heating magnetic stirrer (DF-101S, Shanghai, China), vacuum drying oven (DZG-6020, Shanghai, China) and electromotor stirrer (RW 20 digital, IKA, Germany) were employed for the preparation of the PVIM-MNPs. Fourier transform infrared spectroscopy (FT-IR, Nicolet iS10, Thermo, USA), vibrating sample magnetometer (VSM, PPMS-9T, Quantum Design, USA) and transmission electron microscopy (TEM, JEM-2010 HT, JEOL, Japan) were utilized for the characterization of the self-prepared PVIM-MNPs. The pH values of the sample solution were adjusted by using a pH meter (Mettler Toledo 320-S, Shanghai, China) supplied with a combined electrode. Numerical control ultrasonic apparatus (KQ5200DE, Kunshan, China) was used for ultrasonic dispersion of the mixture solution and ultrasound-assisted extraction/desorption of target analytes. Several Nd-Fe-B magnets ($8.0 \text{ mm} \times 6.0 \text{ mm} \times 1.6 \text{ mm}$) were used for magnetic separation. Polarized Zeeman Graphite Furnace Atomic Absorption Spectrometer (GFAAS, Z-2000, Hitachi, Japan) was utilized for the determination of Ag and the optimum operation conditions are listed in Table S1 in Supplemental information (SI).

2.2. Reagents and standard solutions

All the silane coupling agents including tetraethoxysilane (TEOS) and methacryloxy propyl trimethoxyl silane (MPS) were purchased from Organic Silicon Material Company of Wuhan University (Wuhan, China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, AgNO_3 , La_2O_3 , sodium borohydride, polyvinyl pyrrolidone (PVP, MW = 40,000, k30), sodium dodecyl sulfate (SDS), humic acid (HA), sodium bicarbonate, ammonium persulfate (APS), NaOH, HNO_3 , 28% (m/v) aqueous ammonia were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Mercaptosuccinic acid (MSA), mercaptoundecanoic acid (MUA), trisodium citrate and 1-vinyl imidazole (VIM) were purchased from Aladdin Biological Technology Co., LTD (Shanghai, China). The purity of all reagents was at least of analytical reagent grade.

The stock solution of Ag^+ (1 mg mL^{-1}) was prepared by dissolving corresponding amount of AgNO_3 in 2% (V/V) HNO_3 . The stock solution of La^{3+} (10 mg mL^{-1}) was prepared by dissolving corresponding amount of La_2O_3 with concentrated HNO_3 and diluting with ultrapure water. Working solutions were prepared by stepwise dilution of the stock solution with 2% (V/V) HNO_3 . The ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) obtained from a Milli-Q water purification system (Millipore, Molsheim, France) was used throughout this work. Diluted HNO_3 and aqueous ammonia were used to adjust the pH of the solution. All glass wares were cleaned by soaking in aqua regia for 2 h, and washed several times with ultrapure water prior to use.

2.3. Synthesis of PVIM-MNPs

The synthesis procedure of PVIM-MNPs is illustrated in Scheme 1 and the details of the preparation steps are described in SI.

2.4. Preparation of AgNPs

AgNPs with different sizes (5–8 nm, 30–50 nm, 80–120 nm) were prepared by reducing of AgNO_3 with trisodium citrate or ethylene glycol, and the details are described in SI. The citrate stabilized AgNPs (AgNPs-Cit) with particle size of 5–8 nm were employed to perform the feasibility experiments and optimize the MSPE procedure.

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