



Development of reusable magnetic chitosan microspheres adsorbent for selective extraction of trace level silver nanoparticles in environmental waters prior to ICP-MS analysis

Tesfaye Tolessa^{a,b}, Xiao-Xia Zhou^{a,b}, Meseret Amde^{a,b}, Jing-Fu Liu^{a,b,*}

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:

Chitosan microspheres
Cross-linking technique
Selectivity
Reusability

ABSTRACT

Solid-phase extraction (SPE) based on reusable magnetic chitosan microspheres was coupled with ICP-MS for separation and quantification of silver nanoparticles (AgNPs) in the presence of silver ions in environmental water samples. The monodisperse magnetic chitosan microspheres with an average size of 2 μm were engineered using suspension cross-linking technique, and characterized and investigated for its application as SPE adsorbent. Parameters affecting the SPE were optimized, and the best performance was achieved by extracting a 20 mL sample (pH 4.5) with 10 mg adsorbent for 90 min, followed by elution with 1 mL 1% (w/v) thiourea in 10% (v/v) nitric acid for 10 min. The detection limit, calculated as 3 s (s, standard deviation for 11 blank readings), for three AgNPs coated with polyvinyl pyrrolidone (PVP), citrate and polyvinyl alcohol (PVA) and sizes of 31, 40, 46 nm, respectively, were in the range of 0.016–0.023 $\mu\text{g/L}$. The repeatability and reproducibility (RSD, $n=7$) at a spiking level of 0.1 $\mu\text{g/L}$ AgNPs were 4.2% and 8.1%, respectively. The developed method has been applied in the analysis of AgNPs in river, lake and wastewater samples, with excellent extraction efficiencies (84.9–98.8%) for AgNPs at spiking levels of 0.86 and 8.70 $\mu\text{g/L}$. The cationic chitosan microspheres showed good species selectivity and reusability for extraction of AgNPs in the presence of Ag^+ , and hence the proposed method is simple, cost effective and environmentally friendly.

1. Introduction

With the rapid development in nanotechnology, there is growing production and use of silver nanoparticles (AgNPs) in various areas such as consumer products including textiles, fabrics, personal care products, food storage containers, laundry additives, home appliances, paints, and even food supplements [1–4] as well as medical, electronic and optical devices [5,6]. On the basis of these uses, it is likely that AgNPs will be released to the aquatic environment and possibly exert toxic effect on the aquatic environment [4,7]. AgNPs may also release to the aquatic environment during the production, transport, washing or disposal of AgNPs containing products. In addition, suspended AgNPs in polluted air and runoff scouring AgNP polluted soils and landfill sewage [8], and transformation of Ag^+ into AgNPs by humic acids and microbial activities at room temperature [9,10] could finally result in AgNPs depositing on aquatic environment, giving rise to increasing human and ecosystem AgNP exposure. Recent studies

demonstrated ionic Ag^+ and AgNPs release into wastewater from stocks washing machines [11], fabrics [12], athletic, shirts toothpaste, shampoo and detergent [13,14]. Using SEM these authors confirmed that AgNPs are already present in wastewater. Some models also predicted that the concentration of AgNPs in the environmental waters will reach 80 ng/L in the near future [15,16].

On the other hand, the toxicity of AgNPs to a variety of living organisms such as plant [7], fish [17], rat [18] and human cells [19,20] has been reported. Even though the mechanism of AgNP toxicity has not been clearly elucidated, different studies show that the size and coatings of AgNPs, as well as the speciation and concentration of the corresponding ionic Ag impact the toxic properties [8,21–23]. Moreover, the release of corresponding Ag^+ from the AgNPs and the transformation of Ag^+ into AgNPs allow them to coexist in the environment [24]. Therefore, separation and quantification of AgNPs in environmental samples in the presence of Ag^+ is of great importance to evaluate its toxic-effects [25,26].

* Corresponding author at: State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China.

E-mail address: jfliu@rcees.ac.cn (J.-F. Liu).

<http://dx.doi.org/10.1016/j.talanta.2017.03.064>

Received 28 January 2017; Received in revised form 15 March 2017; Accepted 20 March 2017

Available online 24 March 2017

0039-9140/ © 2017 Elsevier B.V. All rights reserved.

Analysis of AgNPs in the presence of ionic species of Ag is a key challenge to quantify the AgNPs, and few strategies have been developed for this purpose. One is based on the difference between the total Ag concentration and the free Ag^+ concentration, in which the total concentration is usually determined by ICP-MS [7] or ICP-OES [12,14,27] after sample digestion, whereas the free Ag^+ concentration is detected before digestion using an ion selective electrode (ISE) [7,12,27]. Another strategy is speciation analysis based on selective extraction. Our group reported a convenient method [10,28] for the separation and preconcentration of AgNPs based on cloud point extraction (CPE) with Triton X-114, and the developed method was efficiently applied for speciation analysis of Ag ions and AgNPs. The limitation with this method is that the metal nanoparticles extracted into the Triton X-114-rich phase should be digested before ICP-MS determination [10,28,29]. Recently, to overcome this limitation, asymmetric flow field-flow fractionation (FFF) [30–32] liquid chromatography (LC) [9,33] and capillary electrophoresis (CE) [34] were coupled with ICP-MS for speciation test of AgNPs and Ag^+ .

SPE has also been proposed for separation and quantification of some noble metal nanoparticles and the corresponding ionic species [35–37]. Given the column could be clogged by the particles in the samples when the packed column-based SPE procedure was used, it is of interest to develop magnetic SPE procedure for extracting and separating AgNPs and Ag^+ . Recently, Mwilu et al. [38] reported the use of magnetic nanoparticles coated with either dopamine or glutathione for the SPE of trace amounts of AgNPs with assistance of flow cell for separation of magnetic particles from sample matrices. Since heterogeneous aggregation/agglomeration of AgNPs with magnetic nanoparticles and natural organic macromolecules in complex samples might occur, the use of magnetic nanoparticles as SPE adsorbents could result in incomplete desorption of AgNPs after extraction. Thus, monodisperse magnetic microspheres are preferred to nanoparticles as adsorbents. On the other hand, as AgNPs are mainly negatively charged in the aqueous environment due to the coating of ubiquitous natural organic matter on the surface, coating the magnetic microspheres with positively charged agents like chitosan is helpful for improving the extraction efficiency and selectivity of AgNPs.

In this work, magnetic chitosan microsphere (MCM) was developed as a reusable adsorbent for selective separation and quantification of AgNPs from environmental waters. The adsorption-desorption behavior of AgNPs on the as-prepared magnetic chitosan microspheres (MCMs) were thoroughly studied and an efficient method for separation and quantification of AgNPs by the magnetic SPE was established. Finally, the developed method was validated by the separation and preconcentration of AgNPs in environmental waters.

2. Experimental part

2.1. Chemicals and reagents

Chitosan was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), and aqueous dispersion of citrate stabilized AgNPs with nominal particle sizes of 10, 40, 60 and 100 nm were purchased from Sigma-Aldrich (St. Louis, MO). Another commercial AgNPs with PVP coating (31.02 ± 2.02 nm) was purchased from Shanghai Huzheng Nanotechnology Co., Ltd. (Shanghai, China). The stock suspension of PVP stabilized AgNPs (100 mg/L) were prepared by re-dispersing the commercial AgNPs (10,000 mg/L) in water and kept in refrigerator. The working suspensions of AgNPs were prepared by diluting the stock suspension with water and quantified by ICP-MS routinely before use. Standard solution of Ag^+ (1000 mg/L) used for ICP-MS determination was purchased from National Institute of Metrology (Beijing, China). High purity nitric acid (65%) was obtained from Merck (Darmstadt, Germany). Span-80 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The

other reagents including ammonia solution (NH_4OH), acetic acid, toluene and sodium hydroxide (NaOH) were from Beijing Chemicals (Beijing, China). All the reagents were used as obtained without further purification. Ultrapure water (18.3 M Ω) produced with a Milli-Q gradient system (Millipore, Billerica, MA, USA) was used throughout the experiments.

2.2. Preparation and characterization of MCMs

The co-precipitating method reported in the work of Zang et al. [39] was used to synthesize Fe_3O_4 nanoparticles. Briefly, 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.0 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50 mL of water with vigorous stirring. Then, 28 wt% NH_4OH was added to the mixture under vigorous stirring at 40 °C until the pH of the mixture reached 9–10. The reaction was performed at 80 °C for 2 h under N_2 protection. Subsequently, the Fe_3O_4 nanoparticles were washed with water until the pH of the wash solution was neutral and clean wash solution was obtained.

MCMs were prepared according to the suspension cross-linking technique [40,41] with slight modification. In this typical procedure, the prepared Fe_3O_4 nanoparticles were magnetically collected and re-suspended in 50 mL of 1% (m/v) chitosan solution prepared in 2% aqueous acetic acid. The suspension was vigorously shaken and ultrasonicated for 15 min to allow the adsorption of polymer on the magnetic nanoparticle surface. Twenty mL of the mixture was then added dropwise into 80 mL of toluene containing 3 mL of Span-80 as an emulsifier in a 200 mL three necked flask at room temperature, while the mixture was stirred with a mechanical overhead stirrer at 500 rpm for 30 min. Two mL 50% glutaraldehyde was added into the suspension and the mixture was stirred for another 30 min at 40 °C. Then, drops of 1 mol/L NaOH solution was gradually added to the flask until the pH of the mixture reached 9–10, and the stirring continued for a further 2 h at 60 °C to form the chitosan coated Fe_3O_4 microspheres. The MCMs were separated with external magnetic field and washed consecutively with acetone and ethanol, and finally with water for several times until clear wash solution was obtained and the pH of the wash was nearly neutral. The as-prepared MCMs were magnetically collected and dried under vacuum at 40 °C for two days.

The as-prepared MCMs were characterized by various techniques (See Fig. S1 and S2a–d with detailed description). The transmission electron microscopy (TEM) images were recorded by a Hitachi H-7500 (Japan) at an accelerating voltage of 80 kV. The TEM image of MCMs (Fig. S1) shows that it had a spherical shape with an average diameter of about 2 ± 0.2 μm . About 50 microspheres in three micrographs were evaluated to determine the average size. The second smaller particles in each of micrographs were less populated and then removed by threshold of size counting. The average particle size of the MCMs was computed with the Nano Measurer 1.2 software (Fudan University, Shanghai, China) from the TEM images. The microspheres were dispersed in deionized water at pH 4.5, at which the surface charge (ζ) measured by a Malvern Nano ZS (Malvern Instruments, UK) was 33.6 ± 4.3 mV. The functional groups in the microspheres were confirmed by Fourier transform infrared spectroscopy (FT-IR, IRT-7000, Jasco, Japan). The X-ray diffraction (XRD) measurements were carried out with a PANalytical X'Pert Pro (UK) instrument using Cu-K α radiation. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60 (Japan) at a heating rate of 10 °C/min in N_2 atmosphere. A vibrating sample magnetometer (VSM, Riken Denshi Co. Ltd., Japan) was used to obtain the magnetization curve.

2.3. Extraction procedure

A schematic representation for the developed SPE is shown in Fig. 1. In the extraction process, adsorption was first conducted by adding 10 mg of MCMs into 20 mL of sample solution in a 25 mL polypropylene vial, which was spiked with 0.01% Triton X-100 and

Download English Version:

<https://daneshyari.com/en/article/5140945>

Download Persian Version:

<https://daneshyari.com/article/5140945>

[Daneshyari.com](https://daneshyari.com)