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

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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) respectively, were in the range of 0.016–0.023 μg/L. The repeatability and reproducibility (RSD, n=7) at a spiking level of 0.1 μg/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 μg/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].
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, Mwili 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 occurred, the use of magnetic nanoparticles as SPE adsorbents could result in incomplete desorption of AgNPs after extraction. Thus, monodisperse magnetic microspheres are prefer to nanoparticles as adsorbents. On the other hand, as AgNPs are mainly negative 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 (FeCl₃·6H₂O), iron (II) chloride tetrahydrate (FeCl₂·4H₂O), 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 (NH₄OH), 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 MΩ) 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 Fe₃O₄ nanoparticles. Briefly, 2.7 g FeCl₃·6H₂O and 1.0 g FeCl₂·4H₂O were dissolved in 50 mL of water with vigorous stirring. Then, 28 wt% NH₄OH 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 N₂ protection. Subsequently, the Fe₃O₄ 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 Fe₃O₄ nanoparticles were magnetically collected and 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 flasks 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 Fe₃O₄ 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 particles 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 (ξ) 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 PAN alytical X’Pert Pro (UK) instrument using Cu-Kα radiation. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60 (Japan) at a heating rate of 10 °C/min in N₂ 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
103.2 mg/L Ca(NO₃)₂, and adjusted to pH 4.5 with diluted HNO₃ and NaOH. The mixture was then shaken at 200 rpm at room temperature for 90 min. The resulting AgNP loaded MCMs were separated from the solution by external magnetic field. After washing three times with 10 mL water, the loaded microspheres were re-dispersed in 1 mL of 10% nitric acid containing 1% thiourea, and the mixture was then shaken at 250 rpm for 10 min for desorption. After magnetic separation, 0.5 mL of the solution was withdrawn and diluted to an appropriate volume for ICP-MS analysis.

2.4. Determination of Ag content by ICP-MS

An ICP-MS instrument (Agilent 7700cs, USA) was used to quantify Ag contents in the test solutions using Ag standard solutions prepared by diluting 1000 mg/L Ag⁺ certified reference material (National Institute of Metrology; Beijing, China) with 5% nitric acid in water. The AgNP concentration in the control AgNP suspensions was obtained by subtracting the free Ag⁺ concentration from total silver content of the same AgNP suspension determined by ICP-MS after digestion with 5% nitric acid overnight (The free Ag⁺ concentration in AgNP suspensions were determined with a pH/mV meter; details of the measurements were described in S-3).

2.5. Sample collection

Three environmental waters, river, lake and waste water samples were collected and analyzed to evaluate the proposed method for selective extraction of AgNPs in real water samples. River and lake waters were collected from Chaobai River (Beijing, China) and Weiming Lake (Beijing, China), respectively. Municipal sewage influent and effluent were collected from Qinghe wastewater treatment plant (WWTP, Beijing, China).

3. Results and discussion

3.1. Optimization of the extraction conditions

Before optimizing the extraction conditions, adsorption experiments were performed to evaluate the adsorption of AgNPs on the surface of extraction devices (for details see S-4 in the Supporting Information). It was demonstrated that adsorption of AgNPs on the surface of the extraction device was 4.6% in the presence of 0.01% (v/v) Triton X-100 (Table S1), which is negligible. The extraction efficiency in each optimization of experimental condition was calculated by the following Eq. (1).

\[
EE = \frac{C_s \times V_s}{C_e \times V_e}
\]

where \(C_s\) is concentration of Ag⁺ corresponding to AgNPs initial present in the sample solution before loading onto the microspheres, and \(C_e\) is concentration of Ag⁺ corresponding to AgNPs detected in the eluent after desorption. \(V_s\) and \(V_e\) are volume of sample solution and eluent, respectively.

3.1.1. Extraction and elution time

The effect of extraction time was investigated over various interval of time (5–300 min). At the end of each time interval, the amount of AgNPs captured was calculated by the difference between the initial and final AgNP concentration in suspension. As shown in Fig. 2, the adsorption of AgNPs rapidly increased with time and then reached an
equilibrium beyond which no more AgNPs were further removed from the suspension. The initial high extraction rate is probably due to the abundant available binding sites on the surface of the adsorbent. The adsorption efficiency increased to 74.7% with agitation time to 90 min and then level off. Therefore, a contact time of 90 min was selected for further studies.

Various eluent solutions were tested to select the best desorbing solution for the adsorbed AgNPs. Since silver is liable to form stable complex with thiourea, solutions containing thiourea is frequently chosen as eluent for silver desorption. It was found that 1 mL of 1% (w/v) thiourea in 10% (v/v) nitric acid can quantitatively elute AgNPs (Fig. S3). The effect of elution time on the recovery of AgNPs was then investigated, and the results showed that AgNPs can be quantitatively recovered within 10 min (Fig. 2). Finally, an eluent of 1 mL 1% (m/v) thiourea in 10% (v/v) nitric acid with an elution time of 10 min was employed as optimized elution conditions.

3.1.2. pH of the sample solution

Since the pH of sample solution plays an important role in SPE studies, the adsorption behavior of AgNPs onto MCMs was examined in the range of pH 2–9. As shown in Fig. 3, the adsorption percentage increased rapidly with pH up to 4 and then slowly from 4 to 7. Quantitative adsorption was achieved within pH range of 7–8. However, Ag⁺ ions were notably co-extracted with AgNPs at pH > 5. Quantitative adsorption was achieved within pH range of 7 increased rapidly with pH up to 4 and then slowly from 4 to 7.

3.1.3. Sample volume and adsorbent amount

The concentration of the AgNPs lies at trace level in environmental waters. Thus, pre-concentration from large volume sample is necessary to obtain large enrichment factor and low detection limit. The effect of sample volume on the recovery of AgNPs was studied by taking different volumes (0–100 mL) containing 20 μg/L of AgNPs subjected to the specified extraction procedure. As shown in Fig. 4, quantitative recovery of AgNPs was achieved when the sample volume is less than 20 mL and adsorbent amount is 10 mg. Further increasing sorbent amount to 20 mg leads to slight reduction in extraction efficiencies, which is due to the amount of eluent is not sufficient to disperse throughout the larger amount of sorbent and quantitatively elute all the adsorbed target analytes. The extraction efficiency for AgNPs decreased abruptly with the further increase of sample volume from 20 to 50 mL and slightly decreased from 50 to 100 mL. Higher extraction efficiency still can be attained for a larger volume of sample if excessive amount of the adsorbent is added. However, this will cause unnecessary waste of adsorbents. Hence, the sample volume of 20 mL and adsorbent amount of 10 mg were selected for further studies.

3.1.4. Humic acid

Humic acid (HA), widely present in environmental samples in the concentration range of 0–20 mg/L DOC, was reported to associate with metal nanoparticles [45–47]. Experiments showed that the presence of HA at levels > 5 mg/L DOC significantly reduced the extraction efficiency of AgNPs. The possible reason is that HA contains various oxygen-containing functional groups which can effectively bind with protonated chitosan’s amines and make the active sites occupied, which was termed as “fouling” effect. To avoid the negative effect of HA on the extraction of AgNPs, Ca²⁺ in the form of Ca(NO₃)₂ was added to the sample solution to form complexes and mask the effect of HA. Results showed that the addition of 103.2 mg/L Ca²⁺ was able to efficiently eliminate the effect of HA (0–15 mg/L DOC) on the extraction of AgNPs (Fig. S4). Therefore, 103.2 mg/L Ca(NO₃)₂ was added to the sample solution to reduce the potential effect of HA in the subsequent experiments.

3.1.5. Particle size and coating

Owing to their different initial application, engineered AgNPs with different sizes and coatings were released into environmental compartments. Hence, the effect of size and coating on the extraction of AgNPs by the proposed technique should be investigated. To this effect, commercially available citrate stabilized AgNPs of different size (10, 40, 60 and 100 nm) were extracted, and the extraction efficiencies obtained were all higher than 89.9% (Fig. S5a). This reveals that the size in the range 10–100 nm has no significant effect on the extraction of AgNPs. To study the effect of coating on the extraction, AgNPs stabilized with PVP, citrate and PVA were extracted by the proposed method, respectively, and the extraction efficiencies obtained were all higher than 91.3% (Fig. S5b). This verifies that the proposed method has the application potential for separation and preconcentration of AgNPs stabilized with different capping agents with similar functional
3.2. Species selectivity

The selectivity of magnetic chitosan microspheres towards AgNPs in the presence of Ag⁺ was studied by first investigating the capacity of MCMs to bind Ag⁺. To this end, the extraction behavior of silver ions was experimentally studied and the result showed a minimal sorption (Table S2), with extraction efficiencies of less than 5% (3.82 ± 0.76), suggesting that the ionic species were efficiently excluded during extraction of AgNPs. However, in the presence of AgNPs, ionic species might be adsorbed on the surface of the AgNPs and co-extracted, giving rise to a lower apparent extraction efficiency. Therefore, the interference of silver ion species on the extraction of AgNPs was further investigated by spiking various concentration of Ag⁺ (0–40 μg/L) to 8.53 μg/L AgNPs. As shown in Fig. 5a, the calculated extraction efficiency of AgNPs resulted from the spiking of Ag⁺ is almost constant and independent on the spiked Ag⁺ concentration, indicating the adsorption capacity of silver ion towards AgNPs is minimal. The slight increase in extraction efficiency by an amount less than 5% is consistent with experimental errors that might be associated with the determination and can be neglected.

The selectivity of MCMs was further investigated using binary mixtures containing AgNPs and Ag⁺. Suspensions containing different ratios of AgNPs and Ag⁺, 100% of 10 μg/L Ag⁺ ions to 100% of 10 μg/L AgNPs, were subjected to the specified extraction procedure. After magnetic separation, the silver contents of the mixtures were analyzed by ICP-MS. As shown in Fig. 5b, the amount detected are in reasonable agreement with the amount of silver expected to be extracted if only the AgNPs were bound to the MCMs, indicating a high degree of selectivity of the microspheres for AgNPs over silver ions. Thus, the proposed method has the potential to selectively extract AgNPs even from an aqueous mixture containing Ag⁺ ions.

3.3. Sorbent regeneration and reusability

To test the reusability of the MCMs, adsorption–desorption experiments were carried out under optimized experimental parameters for different cycles of use. As shown in Fig. S6, the extraction efficiency was 89.6% in the first use. The MCMs were collected and rinsed three times with eluent solution and ultrapure water. The MCMs were regenerated by soaking in 5 mL of 0.5 M NaOH for 1 h, followed by washing with ultrapure water until the pH of filtrate reached near neutral for consecutive reuse. In the consecutive three times of reuse, the microspheres remained undamaged, indicating the stability of the microspheres during the consecutive extraction processes. The decrease of adsorption efficiency in the first reuse might result from the loss of chitosan molecules which were not bind tightly to the surface of magnetic microspheres.

3.4. Analytical performance

The analytical performance of the proposed method was validated under the optimized conditions for quantification of AgNPs in ultrapure water as summarized in Table 1. Good linearity was obtained for all AgNPs stabilized with different coatings and sizes, with correlation coefficients in the range 0.994–0.999. The method repeatability (in the same day) and reproducibility (between days), both expressed in RSD, for seven measurements of 0.1 μg/L AgNPs were less than 4.2% and 8.1%, respectively. The limit of detection (LOD) of the method, which were calculated as 3 s (s is the standard deviation of blank measurements in 11 runs) were 0.023, 0.016, 0.021 μg/L for PVP, citrate and PVA stabilized AgNPs, respectively.

Compared with the previous established CPE-based methods [9,10,28], in which the AgNPs preconcentrated in the Triton X-114 should be digested with microwave digestion in the presence of concentrated acid before final determination which makes the determination tedious and time consuming, the proposed method required no sample digestion, making the method simple and fast. In addition, in comparison with previous published studies, comparable or lower LOD was obtained, which can be stated as another potential of the current method (Table 2).

3.5. Application to environmental water samples

To validate the optimum conditions and investigate matrix effects on the proposed extraction method, the developed procedure was used for the determination of AgNPs in water samples of river, lake, and effluent and influent of a WWTP. All samples were used as collected without filtering except for the influent water. The AgNPs in all the tested samples were below the detection limit of the proposed method.

![Figure 5](image-url)

**Fig. 5.** (a) Effect of Ag⁺ on the extraction efficiency of AgNPs; (b) Selectivity of MCMs for AgNPs in the presence of Ag⁺. Error bars represent the standard deviations for three replicate experiments.

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### Table 1

| Target Analytes      | Linear range (μg/L) | r²       | LOD (μg/L) | RSD (%) (n=7) |
|----------------------|---------------------|----------|------------|---------------|
| PVP-AgNPs(31 nm)     | 0.1–10              | 0.994    | 0.023      | 4.2           |
| Citrate-AgNPs(40 nm) | 0.1–10              | 0.999    | 0.016      | 3.4           |
| PVA-AgNPs(46 nm)     | 0.1–10              | 0.998    | 0.021      | 3.7           |
levels of 0.86 and 8.70 μg/L, respectively. As shown in Table 3, the extraction efficiency of AgNPs were in the range of 84.9–98.5%. Due to the excellent adsorption capacity of magnetic sorbents, satisfactory extraction efficiencies were obtained.

4. Conclusions

MCMs were prepared and used as a potential sorbent for selective extraction and quantification of trace AgNPs from environmental water samples. It was found that AgNPs with different size and coating can be separated and quantified from complex aqueous medium in the presence of their corresponding ions. Micro-level size of MCMs increases the surface of contact and stability of adsorbed analytes resulting in high adsorption efficiency. At the same time, the chitosan coating improves the dispersibility of magnetic sorbents in aqueous solution making active/binding sites of the biosorbents accessible for analytes and reduces the interference of natural organic macromolecules in complex samples which might be caused by size exclusion that frequently encountered as a result of aggregation. Water samples of different complexity such as river water, lake water, treated and untreated municipal wastewater were spiked with different concentrations of AgNPs and a high recovery was found in all cases. The advantage of this method over other frequently used separation techniques is fast, simple and easy of separation by the use of external magnetic field from complex environmental matrices. In addition, in comparison with previous published studies, comparable or lower LOD was obtained because no sample digestion was required after extraction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2017.03.064.

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