Dispersive liquid–liquid microextraction of silver nanoparticles in water using ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate

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ABSTRACT

Using the ionic liquid (IL) 1-octyl-3-methylimidazolium hexafluorophosphate as the extractant and methanol as the dispersion solvent, a dispersive liquid–liquid microextraction method was developed to extract silver nanoparticles (AgNPs) from environmental water samples. Parameters that influenced the extraction efficiency such as IL concentration, pH and extraction time were optimized. Under the optimized conditions, the highest extraction efficiency for AgNPs was above 90% with an enrichment factor of >90. The extracted AgNPs in the IL phase were identified by transmission electron microscopy and ultraviolet–visible spectroscopy, and quantified by inductively coupled plasma mass spectrometry after microwave digestion, with a detection limit of 0.01 μg/L. The spiked recovery of AgNPs was 84.4% with a relative standard deviation (RSD) of 3.8% ($n = 6$) at a spiked level of 5 μg/L, and 89.7% with a RSD of 2.2% ($n = 6$) at a spiked level of 300 μg/L, respectively. Commonly existed environmental ions had a very limited influence on the extraction efficiency. The developed method was successfully applied to the analysis of AgNPs in river water, lake water, and the influent and effluent of a wastewater treatment plant, with recoveries in the range of 71.0%–90.9% at spiking levels of 0.11–4.7 μg/L.
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Introduction

Silver nanoparticles (AgNPs) have been applied in various products, such as plastics, household textiles, medicine, and cosmetics, due to their excellent antimicrobial properties (Benn and Westerhoff, 2008; Blaser et al., 2008; Emam et al., 2013; Meyer et al., 2011; Quadros and Marr, 2011; Sondi and Salopek-Sondi, 2004; Shahverdi et al., 2007; Sallum et al., 2014; Tolaymat et al., 2010). As a result, AgNPs can be released into

the environment, and result in potential risk to human beings and other biological organisms (Li et al., 2012; Khan et al., 2011; Losert et al., 2014; Sharma et al., 2014; Tian et al., 2013; Yu et al., 2012). It was reported that orally delivered AgNPs induced deleterious effects on the liver and heart for mammals (Elle et al., 2013). Additionally, AgNPs could accumulate and transport along the food chain (Zhao and Wang, 2010). However, the mechanism of AgNP toxicity is not clear, although it was reported that the morphological

characteristics such as surface charge, particle size and shape were related to their toxicity (Badawy et al., 2011; Burkowska-But et al., 2014; Carlson et al., 2008; Pal et al., 2007). This lack of knowledge could be ascribed to the complexity of nanoparticles themselves, as well as the lack of methods that are capable of monitoring the trace AgNPs from complex environmental and biological samples without disturbing their characteristics (Farré et al., 2011).

To date, several methods have been developed for the separation and determination of AgNPs such as field flow fractionation, anodic particle coulometry, and hydrodynamic chromatography, but these methods have limitations to varying extents, for example, poor resolution, time consuming and overly elaborate procedures (Liu et al., 2012; Bednar et al., 2013; Stuart et al., 2012; Tiede et al., 2009). Liu et al. first established the Triton X-114-based cloud point extraction method for analysis of trace AgNPs in river water, which was then used to detect AgNPs in samples from wastewater treatment plants (WWTP) (Liu et al., 2009a; Chao et al., 2011; Li et al., 2013) and in lixiviates obtained from sticking plasters and cleaning cloths (López-García et al., 2014).

Because of their unique properties such as negligible vapor pressure, good thermal stability and miscibility with water, ionic liquids (ILs) have been widely used in separation technology (Han and Row, 2010; Liu et al., 2005, 2009b; Tan et al., 2012). They have been applied for extraction of some nanoparticles. It was suggested that the extraction was achieved through anion exchange, and it was proved that the formation of a hydrophobic ion-pair between the stabilizer and ILs promoted the extraction (Zhao et al., 2006; Lee et al., 2010). Gold nanoparticles (López-Lorente et al., 2012), copper nanoparticles (Huang et al., 2006), Fe_3O_4 (Zhang et al., 2012), ZnO and ZnS nanoparticles (Huang et al., 2009) were successfully recycled from environmental water samples (López-Lorente et al., 2012; Huang et al., 2006; Zhang et al., 2012) and phosphor wastes (Huang et al., 2009) with ILs. Unlike these nanoparticles, AgNPs often coexisted with Ag^+, thus making it more difficult to separate and concentrate AgNPs from real samples than other nanoparticles (Yu et al., 2012).

Dispersive liquid–liquid microextraction (DLLME), first introduced by Rezaee et al. (2006), has been used for extraction of analytes from aqueous samples due to its advantages including high enrichment factor, simplicity of operation, and low cost (Zhang et al., 2013; Ojeda and Rojas, 2011). In addition, IL-based dispersive liquid–liquid microextraction (IL-DLLME) was also used in the extraction of not only organics like phenolic compounds (Jiang et al., 2011), phthalate (Chen et al., 2011) and fluoroquinolones (Vázquez et al., 2012), but also inorganic elements and species such as Au(III)/Ag(I) (Ashkenani and Taher, 2012), Tl(I) (Anthemidis and Ioannou, 2012), Cr(III) and Cr(VI) (López-García et al., 2012) from water samples.

The objective of this article is to develop a novel, convenient and efficient DLLME method to pre-concentrate trace AgNPs from water samples using 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF$_6$]) as the extraction solvent. The extracted AgNPs in the IL phase were characterized by ultraviolet–visible (UV–Vis) absorbance spectra and transmission electron microscopy (TEM), and quantified by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion.

1. Materials and methods

1.1. Chemicals and materials

A stock suspension of PVP (polyvinylpyrrolidone) capped AgNPs (AGS-WP001) was purchased from HZ NANO (HuZheng Nanotechnology Co., Ltd, Shanghai, China). [OMIM]PF$_6$ was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). Methanol and nitric acid (65%) were from Merck (Darmstadt, Germany). Certified reference material GBW 08610 (1000 μg/mL, National Institute of Metrology, Beijing, China) was used as the silver stock solution. Other chemicals were analytical-reagent grade or above and purchased from Sinopharm Chemical Reagent Beijing (Beijing, China). The water used throughout the study was from a Millipore Milli-Q deionized-water system (Billerica, MA, USA). The centrifugal filter units used for separating Ag^+ from AgNPs in the stock solution were cellulose membranes with 1–2 nm pore size from Amicon centrifugal ultrafilter units (Ultra-15, 3K, Millipore, Billerica, MA, USA).

1.2. Determination of AgNPs in stock dispersion

The free Ag^+ concentration in the AgNP stock dispersion was determined by ICP-MS (Agilent 7500ce, Palo Alto, USA) after ultrafiltration with Sigma 3–18 K (Sigma, Osterode am Harz, Germany) at 9600 r/min at 4°C for 25 min, while the total silver in the dispersion was determined by ICP-MS after microwave-assisted digestion (CEM Mars 5, Xpress, Matthews, NC, USA) as described in our previous study (Liu et al., 2009a). The content of AgNPs in the stock dispersion was obtained by subtracting the content of free Ag^+ from total silver. The AgNP stock dispersions were kept in the dark and used for one week, and the working dispersions were prepared and quantified by ICP-MS daily.

1.3. Extraction procedure

0.1 g [OMIM][PF$_6$] was added into a 15 mL long tapered Corning tube followed by 1 mL methanol, and the tube was hand shaken for a few seconds to mix with the IL. 9 mL of AgNP sample solution was added subsequently to obtain a milky turbid liquid. The mixture was mixed and incubated in a thermostatic water bath oscillator at 30°C for 30 min with a shaking velocity of 200 r/min. Then the tube was centrifuged at 4500 r/min for 5 min to facilitate the phase separation. Finally, the IL phase with concentrated AgNPs was collected for quantitative detection or characterization.

1.4. Characterization of AgNPs

The absorbance spectra of AgNPs before and after extraction were detected by a UV–Vis spectrophotometer (8453, Agilent Technology, Santa Clara, CA, USA), and TEM images were obtained for samples on carbon-coated grid sample holders with an H-7500 transmission electron microscope (Hitachi, Tokyo, Japan) at 80 kV. AgNPs enriched in the IL phase were dispersed and diluted by methanol or a mixture of water and methanol (1:1) for UV–Vis and TEM, respectively.
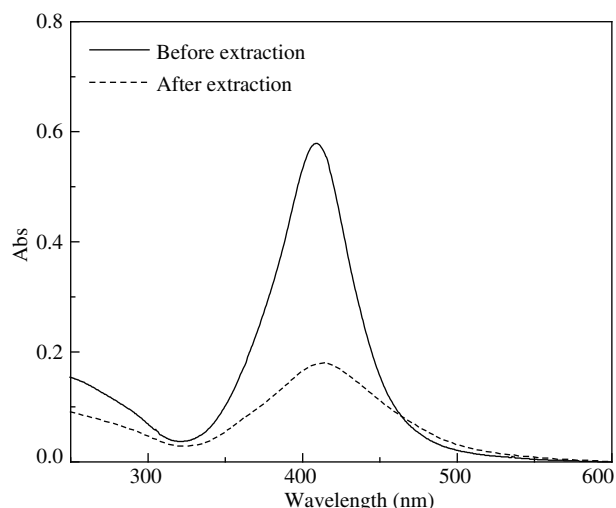
Fig. 1 – Ultraviolet–visible spectroscopy (UV–Vis) spectra of silver nanoparticles (AgNP) before and after extraction.

1.5. Determination of AgNPs with ICP-MS

In order to determine the concentration of the extracted AgNPs, the IL phase was digested with a microwave-assisted digestion procedure modified from the previous study (Liu et al., 2009a). Briefly, 4 mL of concentrated HNO_3 and 1 mL of 30% H_2O_2 were added into the IL phase and then the mixture was irradiated at 120°C (800 W) for 10 min, followed by 180°C (1600 W) for 30 min to guarantee complete digestion. After digestion, the sample was diluted with water to 50 mL and stored at room temperature until analysis. The Ag working standard solution was prepared by diluting a certified reference material (1000 μg/mL Ag, GBW 08610, National Institute of Metrology, Beijing, China) with 5% (V/V) HNO_3. [107]Ag was chosen as the determination isotope and [115]In was used as an internal standard.

1.6. Water sample preparation

Influent and effluent water samples were collected from a WWTP located in Xian County (Hebei, China). River water and lake water samples were collected from the Jingmi River, Yongding River, Olympic Green River, and Fuhai lake of the Summer Palace (Beijing, China). All samples were stored at 4°C for analysis after pH determination and filtered through a 0.22 μm membrane syringe filter.

2. Results and discussion

2.1. Confirmation of AgNPs after extraction

The UV–Vis and TEM results for AgNPs before and after extraction are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, the UV–Vis spectra of AgNPs in water and the IL phase exhibited a maximum absorbance of 411 nm, which demonstrated the presence of AgNPs (Liu et al., 2009a). Fig. 2b shows that the sizes and shapes of AgNPs in the IL phase agreed well with those in the original sample solution, with particle diameters around 20 nm as shown in Fig. 2a. The UV–Vis and TEM results revealed that the IL-DLLME method could preserve the sizes and shapes of AgNPs during the extraction.

2.2. Optimization of the extraction parameters

As mentioned above, the AgNPs could preserve their characteristics during the IL-DLLME procedure. Using [OMIM][PF$_6$] as the extractant and methanol as the dispersion agent, a series of parameters that commonly influence the extraction efficiency were optimized. Considering that insufficient IL results in inefficient extraction while excessive amount of IL may increase the average particle diameters of the transferred metal nanoparticles, due to the formation of hydrophobic ion-pairs on the nanoparticle surface (Lee et al., 2010), the IL concentration was optimized in the range of 0.5%–1.5% (W/V), and results are shown in Fig. 3a. It could be seen that the extraction efficiency increased with IL concentration up to 1% (W/V), whereas with further increase of IL concentration, the extraction efficiency declined slightly, which might be attributed to incomplete dispersion of ILs in methanol, and resulted in insufficient extraction. Therefore, 1% (W/V) [OMIM][PF$_6$] was adopted in the subsequent studies.

Temperature and extraction time are two key factors impacting the extraction efficiency. Lower temperature and shorter incubation time resulted in incomplete dispersion of the
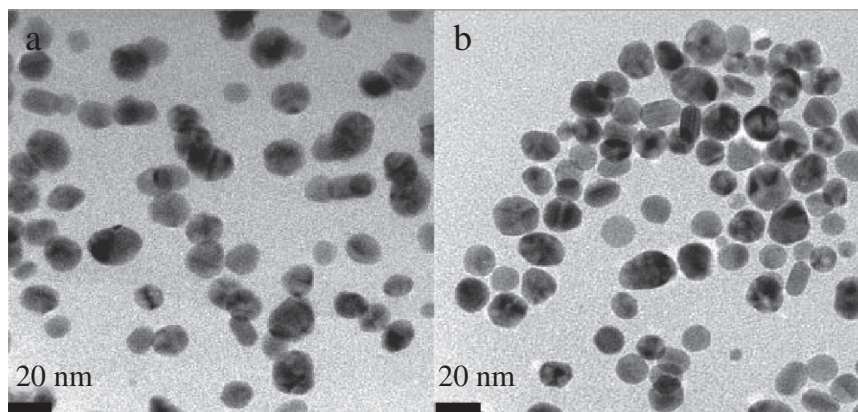

Fig. 2 – Transmission electron microscopy (TEM) images of AgNPs before (a) and after (b) extraction.

AgNPs in the mixture. However, excessively incubation time might give rise to the aggregation of [OMIM][PF$_6$], while higher temperature could enhance the dissolution of [OMIM][PF$_6$] in solutions. As shown in Fig. 3b and c, the highest extraction recoveries were obtained at the temperature of 30°C and incubation time of 30 min, which were adopted in the following studies.

In order to completely and rapidly separate the IL phase and aqueous phase, the centrifugation rate and time were optimized. It was demonstrated that by centrifugation at 4500 r/min for 5 min, the aqueous phase became clear and transparent, which indicated that the two phases were completely separated. After all parameters were optimized, the results showed that the extraction efficiency of AgNPs could be up to 91.4% ± 0.6%.

The effect of pH on the extraction efficiency of AgNPs was determined by quantification of the Ag content in the IL phase by ICP-MS. Results shown in Fig. 3d indicated that the extraction efficiency of AgNPs decreased with the increase of pH up to 8.1, and then increased with the further increase of pH. The enhanced extraction efficiency of AgNPs after pH 10.3 could be attributed to the co-extraction of the Ag$_2$O formed by the reaction between Ag$^+$ and OH$^-$ (Liu et al., 2009a). To verify this speculation, the extraction efficiency of Ag$^+$ was tested at different pH values. Results showed that 88.2% ± 3.8% Ag$^+$ could be extracted into the IL phase at pH 11, but only 0.51% ± 0.06% at pH 6.2, while at pH 3, the extraction efficiency of Ag$^+$ was 18.5% ± 1.9%. Given that low pH may enhance the release of Ag$^+$ from AgNPs with weak capping agents, pH 6.2 was chosen in the following experiments.

Fig. 4 – Effects of Ag$^+$ on the extraction efficiency of AgNPs. A 10 mL mixture of 0.931 mg/L AgNPs and 1% (W/V) [OMIM][PF$_6$] with different Ag$^+$ content was adopted for studying the effect of Ag$^+$, and the mixture was incubated at 30°C for 30 min.

2.3. Effects of interferences

The coexisting Ag$^+$ might be adsorbed on the surface of AgNPs and coextracted into the extracted phase, which would result in positive errors (Liu et al., 2009a). Therefore, complexing
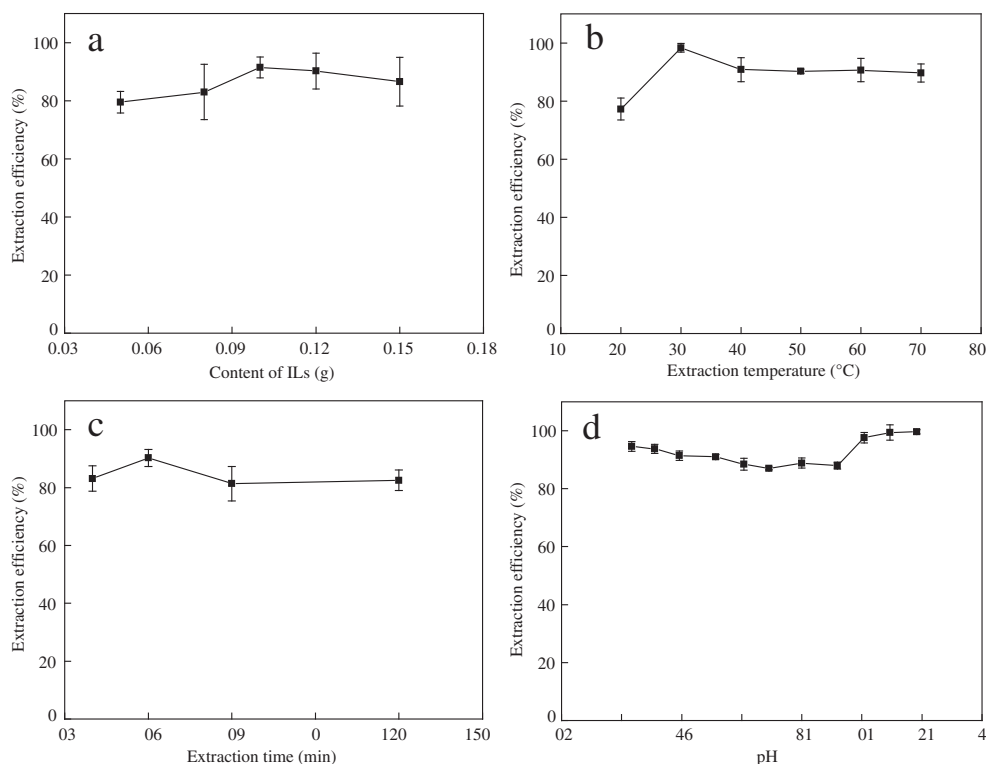

Fig. 3 – Effect of extraction conditions: effects of IL content (a); effect of extraction temperature (b); effect of extraction time (c); effect of pH (d).
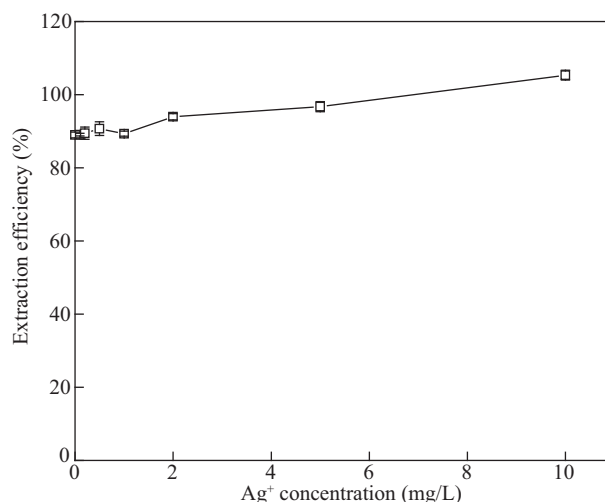
agents were always used during the extraction procedure to prevent the interference of Ag^+ (Liu et al., 2009a; Chao et al., 2011; Li et al., 2013). In this study, in order to test the interference of Ag^+, dispersions with constant AgNP (0.931 mg/L) and varied Ag^+ (0, 0.1, 0.2, 0.5, 1, 2, 5, 10 mg/L) concentrations were mixed, and the extraction was performed at optimized conditions. Results (Fig. 4) indicated that the interference of Ag^+ without complexing agents could be considered negligible when the concentration of Ag^+ was lower than 2 mg/L. It could be seen that IL-DLLME showed higher selection for AgNPs than Ag^+.

Besides Ag^+, other cations commonly found in environmental and biological samples such as K^+, Na^+, Ca^{2+} and Mg^{2+} could affect the extraction of AgNPs. Therefore mixtures of AgNPs (0.46 μg/mL) with different concentrations of KNO_3, $NaNO_3$, $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$ were extracted and determined under the optimized extraction conditions, respectively. Other relevant ions such as Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+} were also tested for the investigation of environmental samples. As shown in Fig. 5, all these ions had little influence on the extraction efficiency of AgNPs.

2.4. Analytical performance

The method performance, such as linearity of calibration curve, reproducibility and detection limit under the optimized conditions, was evaluated. Eleven solutions containing 0, 1.0, 2.0, 5.0, 10, 20, 50, 100, 300, 500 and 1000 μg/L of AgNPs were determined,

and the obtained linearity was very satisfactory with correlation coefficients (r^2) of 0.9992 over the entire range of 0–1000 μg/L, with 0.9926 in the range of 0–300 μg/L, and 0.9861 in the range of 0–50 μg/L AgNPs, respectively. The spiked recovery of AgNPs was 84.4% with a relative standard deviation (RSD) of 3.8% ($n = 6$) at a spiking level of 5 μg/L, and 89.7% with a RSD of 2.2% ($n = 6$) at a spiking level of 300 μg/L, respectively. The detection limit, defined as 3 times the baseline noise (S/N = 3), was 0.01 μg/L. This detection limit meets the requirement for detection of AgNPs in environmental samples, as the model estimated that the concentration of AgNPs in environmental water samples was about 0.03 μg/L (Mueller and Nowack, 2008).

2.5. Sample analysis

To further evaluate the applicability of the developed method, the influent and effluent of a WWTP, river water and lake water samples were analyzed. The pH values of these water samples were in the range of 6–8, which had little influence on the extraction efficiency as shown in Fig. 3d, so these samples could be used directly after filtration without pH adjustment. As seen from results shown in Table 1, the total Ag contents in the non-spiked samples were in the range of 0.018–0.05 μg/L, while AgNPs were not found, as their concentration was below the limit of quantification. The recoveries at spiked levels of 0.11–4.7 μg/L of AgNPs were in the range of 71.0%–90.9%, which was satisfactory considering the low spiking levels.
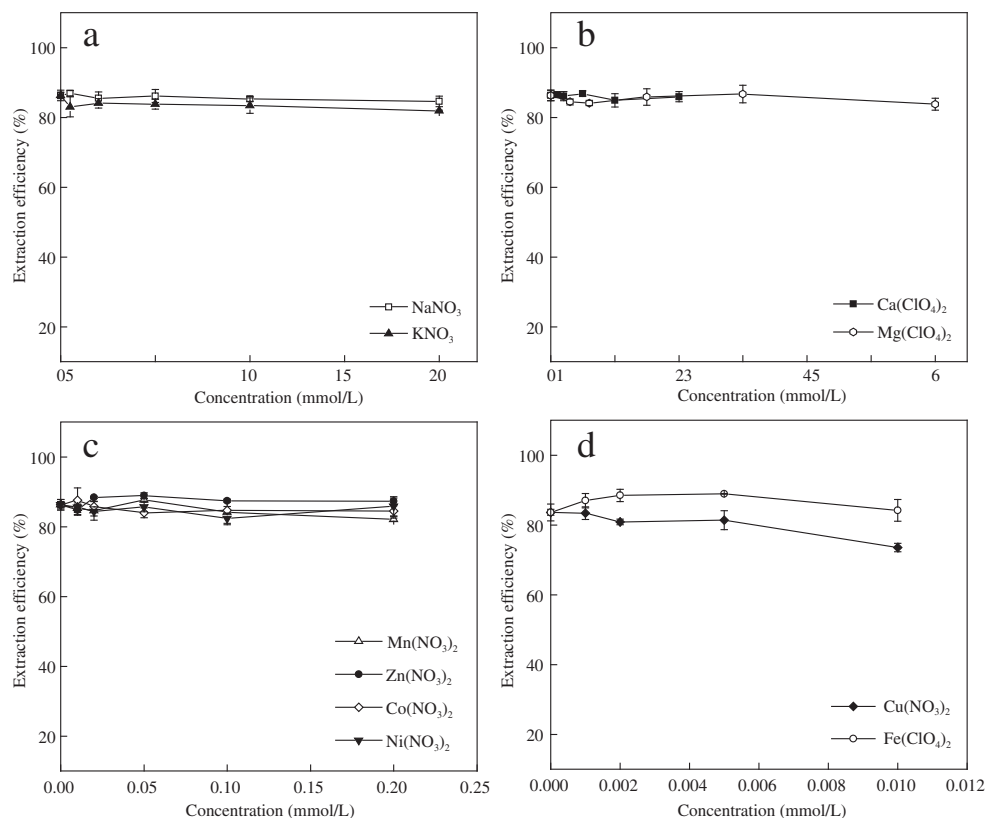

Fig. 5 – Effects of different cations on the extraction efficiency of AgNPs. A 10 mL mixture of 0.46 mg/L AgNPs with 1% (W/V) [OMIM][PF$_6$] was adopted for studying the effect of varied contents of K$^+$, Na$^+$ (a), Ca^{2+} and Mg^{2+} (b), Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} (c) and Cu^{2+}, Fe^{2+} (d). The mixture was incubated at 30°C for 30 min.

Table 1 – Determination of AgNPs in environmental waters.

Sample	pH	Detected total Ag (μg/L)	Spiked AgNPs (μg/L)	Detected AgNPs after spiking (μg/L)	Recovery of AgNPs (%)
Influents of WWTP	7.70	0.050 ± 0.000	0.93	0.66 ± 0.03	71.0 ± 2.8
			4.72	3.99 ± 0.05	84.5 ± 1.1
Effluents of WWTP	7.67	0.026 ± 0.001	0.93	0.70 ± 0.05	75.3 ± 4.9
			4.72	4.15 ± 0.18	87.9 ± 3.8
Jingmi River	7.95	0.031 ± 0.005	0.11	0.08 ± 0.001	72.7 ± 1.3
			0.53	0.46 ± 0.002	86.8 ± 0.3
			0.96	0.78 ± 0.005	81.3 ± 0.5
Yongding River	8.05	0.033 ± 0.005	0.11	0.10 ± 0.005	90.9 ± 5.1
			0.53	0.47 ± 0.004	88.7 ± 0.7
			0.96	0.72 ± 0.01	75.0 ± 1.4
Summer Palace Fuhai	8.05	0.019 ± 0.001	0.89	0.74 ± 0.01	83.1 ± 1.2
Olympic Green River	8.12	0.018 ± 0.001	0.89	0.73 ± 0.03	82.0 ± 2.9

WWTP: wastewater treatment plant. Data are presented as Mean ± SD, $n = 3$.

3. Conclusions

For the first time, an IL-based dispersive liquid–liquid microextraction method (IL-DLLME) was developed for the selective extraction of AgNPs in water samples. This method provided extraction efficiencies up to 90%, enrichment factor of over 90, and detection limit of 0.01 μg/L by coupling with ICP-MS detection. The UV–Vis and TEM detection demonstrated that this extraction procedure preserved the sizes and shapes of AgNPs. The method satisfied the requirement for 'real' water samples, and results showed that common coexisting ions such as K^+, Na^+, Ca^{2+} and Mg^{2+} and other environmentally relevant ions such as Cu^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} had very limited influence on the extraction efficiency, which meant that IL-DLLME provided a novel approach for tracing AgNPs in environmental waters. This proposed method is easy to conduct, sensitive and low cost, and has considerable potential in studying the behavior and fate of AgNPs in the environment.

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