Talanta 161 (2016) 342–349

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Separation and determination of silver nanoparticle in environmental water and the UV-induced photochemical transformations study of AgNPs by cloud point extraction combined ICP-MS

Yuan Yang [a], Li Luo [a], Hai-Pu Li [a], Qiang Wang [a,*], Zhao-Guang Yang [a,b,**], Chen-Lu Long [a]

[a] Center for Environment and Water Resources, College of Chemistry and Chemical Engineering, Central South University, No. 392 Lushan Nan Road, Yuelu District, Changsha 410083, PR China

[b] Shenzhen Research Institute of Central South University, B406 Virtual University, Shenzhen High-tech Industrial Pk, Shenzhen, Guangdong 518057, PR China

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form
9 August 2016
Accepted 16 August 2016
Available online 18 August 2016

Keywords:
Silver nanoparticles
Cloud point extraction
Silver species
Environmental water
UV induced photochemical transformation

ABSTRACT

In this study, cloud point extraction (CPE) combined inductively coupled plasma mass spectrometry (ICP-MS) was used to determinate silver nanoparticles (AgNPs) in environmental water. AgNPs dispersed in water could be extracted into surfactant phase based on optimized CPE parameters which including pH, incubation temperature and equilibration time, the content of nonionic surfactants (Triton X-114, TX-114) and $Na_2S_3O_3$. Good separation results of AgNPs and ionic silver Ag(I) in aqueous environment was obtained with the addition of $Na_2S_3O_3$ when the concentration of Ag(I) was lower than ten times of AgNPs. High recoveries of different diameter AgNPs spiked into ultrapure water were obtained. The influence of environmentally relevant matrix on CPE of AgNPs was studied in detail. Our results showed that there were little interference of environmentally relevant ions and five representative engineering nanomaterials (ENMs) on CPE of AgNPs. Moreover high recoveries and good separation were obtained when natural organic matter (NOM) up to 30 mg/L mixed with AgNPs in ultrapure water. The detection limit of AgNPs in water using CPE combined ICPMS was 5 ng/L. The recoveries of the AgNPs spiked into natural and effluents water with this method were in the range of 79 ± 1–123 ± 13%. Furthermore CPE-ICPMS and Single particle-ICPMS were used to study the UV induced photochemical transformations of AgNPs suspension at environmental relevant concentrations.

1. Introduction

The application and production of engineering nanomatericals (ENMs) has been gradually increasing in the past two decades. According to the report of Emerging Nanotechnologies Programs, there are more than 1600 manufacturer nanotechnology commercial products on the markets and ca. 24% of the products are related to silver nanomaterial [1]. Since its antimicrobial activity, silver nanoparticles (AgNPs) are widely used in many fields of textile, water purification instruments, cosmetics, etc [2]. While the nanoscale dimensions give ENMs new characteristics, the potential for their release in the environment and subsequent effects on ecosystem health is becoming an increasing concern. Multiple studies have documented the toxicity of AgNPs to non-target bacteria, fish, cell lines and rodents [3–5]. Moreover, AgNPs can enter the human body by several routes, including air, water, food, or soil [6]. Thus reliable quantitative methodology methods should be established to analyze concentration, shape, and size distribution of AgNPs in environmental and biological matrixes. So far traditional characterization and analytical methods of ENMs such as electron microscope (EM), dynamic light scattering (DLS), nanotracking analysis (NTA) are mainly focus on synthetic ENMs and most of them are insufficient for ENMs in actual environmental sample due to their high detection limits [3,4]. On the other hand, many technologies have been applied for the separation of metallic ENMs, including field flow fractionation (FFF) [5–8], size exclusion chromatography (SEC) [9–11], capillary electrophoresis (CE) [12,13], hydrodynamic chromatography (HDC) [14] and reversed-phase liquid chromatography (RP-chromatography) combined with inductively coupled plasma mass spectrometry (ICP-MS) [15,16]. However expensive and complex instruments are needed for these methods and their recoveries are poor and detection limit (μg/L) are high. Single particle ICP-MS is a promising methodology to characterize and determine size distribution and particle number concentration of AgNPs in aquatic environment.

---

[*] Corresponding author.

[**] Corresponding author at: Center for Environment and Water Resources, College of Chemistry and Chemical Engineering, Central South University, No. 392 Lushan Nan Road, Yuelu District, Changsha 410083, PR China.

E-mail addresses: qwangcsu@163.com (Q. Wang), zgyang@csu.edu.cn (Z.-G. Yang).

http://dx.doi.org/10.1016/j.talanta.2016.08.052
0039-9140/

But this method is still at the development stage, the mass concentration information of AgNPs could not be provided directly and accurately with it and AgNPs of smaller than ~20 nm also can't be detected [17–21].

In consideration of AgNPs' environmental risk, an effective analytical method which can be used to separate and determine AgNPs is necessary. Cloud point extraction (CPE) is an emerging and promising approach for pre-concentration and separation of metal nano-materials. The hydrophobic analytes will be enriched into the surfactant-rich phase when nonionic surfactants in aqueous solutions are heated to the cloud point temperature. The CPE pretreatment is a green chemistry technique with little solvent consumption, low toxicity and inexpensive waste-disposal costs [22]. It has been applied successfully to separate and characterize the NPs from dissolved ion species. Nanoparticle size and morphology was preserved well in surfactant-rich phase and it can be characterized with transmission electron microscopy (TEM), scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS), and UV–visible spectroscopy [23,24]. The mass concentration of particles was determined using ICP-MS after microwave digestion or electrothermal atomic absorption spectrometry (ET AAS) [25,26].

It is great challenge to extract trace NMs selectively from complex environmental matrixes. To overcome this problem, Triton X-114 ((1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol, TX-114) was used extensively in CPE, and this methodology was proposed as an effective separation way for the discrimination of AgNPs and Ag(I) species recently [24,25,27].

AgNPs usually mixed with Ag(I) in environmental water due to the release of Ag(I) from AgNPs. A more detailed study was performed to evaluate the separation ability of CPE method for AgNPs and Ag(I) in aqueous matrix. AgNPs suspended in surface waters are subjected to sunlight exposure. Little is known about the influence of irradiation from wide spectrum sunlight (including the ultraviolet range) on the stability of AgNPs at environmental concentrations and their subsequent toxicity to human. Now the UV–visible spectroscopy, atomic force microscopy and dynamic light scattering were commonly applied on the study of UV-induced AgNPs transformation [28]. The detection limit of these methodologies was in ~mg/L level. Compared to these methods, the CPE method is a more promising technology which could be applied on the AgNPs transformation study at environmental related concentrations for its high sensitivity and species selectivity.

In this study, the aim of this work is (1) to develop a CPE combined ICP-MS method to extract and detect the AgNPs in environmental water, (2) to study the UV induced photochemical transformations of AgNPs suspension at environmental concentration with the CPE-ICP-MS method.

2. Materials and methods

2.1. Materials

Silver nanoparticles suspensions were obtained from nanoComposix (San Diego, CA, USA) (nominal sizes of 10 (9.3 ± 1.9) nm, 30 (32.3) nm, 50 (53.4 ± 4.4) nm, 80 (79.0 ± 8.7) nm, 100 (99.4) nm). Results of TEM provided by manufacturer have proved that the nanoparticles are near-spherical shape and highly monodisperse. AgNPs suspensions were stabilized with 2 mM sodium citrate. Mass concentration of each AgNPs suspension was 0.02 mg/mL. Silver nanoparticle suspension (2 nm) and silver nanowire (60 nm) was purchased from the JCNANO (NanJing, China). Gold nanoparticle suspensions were from the nanoComposix (San Diego, CA, USA). TiO_2, Al_2O_3, ZnO and C_{60} nanopowder was purchased from the Aladdin (Shanghai, China). The dissolved Ag standard solution was obtained from China Iron & Steel Research institute (Beijing, China, 1000 mg/L). Triton X-114 (TX-114, reagent grade), nitric acid (65%, guarantee-reagent grade), humic acid dry power (fulvic acid $FA \geq 90\%$), methyl alcohol (chromatographic grade) and silver nitrate (99.999% metals basis) were purchased from Aladdin (Shanghai, China). Guarantee-reagent grade sodium thiosulfate, sodium nitrate, sodium thiocyanate, ethylenediaminetetraacetic acid (EDTA, tetrasodium salt), sodium acetate and hydrogen peroxide ($30-35\%$ *w/v*) were obtained from Sinopharm Chemical Reagent (Shanghai, China). Ultrapure water (PERSEE, resistance = 18.2 MΩ, China) was used in all the experiments. The pH meter was purchased from the Shanghai INESA Scientific Instrument (Shanghai, China). The study of the UV induced photochemical transformations of AgNP suspensions was performed by the photochemical reacting apparatus (BL-GHX-V, Shanghai). All vessels were soaked in 20% (*v/v*) HNO_3 solution at least 24 h and washed with ultrapure water.

2.2. Procedure for CPE of AgNPs from water samples

10 mL of aqueous sample solution adjusted to pH 3.5 using diluted HNO_3 was placed in a 15 mL glass centrifuge tube. 50 μL of 1 M $Na_2S_3O_3$ and 200 μL of 10% (*w/w* in ultrapure water) TX-114 were added into sample. Samples was stirred using vortex mixer for 1 min and incubated at 40 °C in water bath for 20 min, then it was centrifuged at 2800 rpm at room temperature for 5 min to accelerate the phase separation. Afterwards, the aqueous phase was removed with a dropper, and the concentrated AgNPs contained in the TX-114-rich phase (ca.100 μL) was transferred into microwave digestion vessel with ultrapure water.

2.3. Sample preparation and analysis of AgNPs

The TX-114 phase were digested with microwave system (Sineo microwave, Shanghai, China) followed the EPA method 3050b and 3052. An Agilent 7700x quadrupole ICP-MS with MicroMist nebulizer (Agilent, USA) was used for the determination of silver concentration. To obtain maximum sensitivity and minimum double oxide level ($<2\%$), the instrument was tuned daily using tune solution (1 μg/L Li, Co, Y, Tl, Ce and Ba, Agilent, USA in 2% *v/v* HNO_3 solution) before analysis. The initial calibration verification (ICV) standard solution was prepared after the calibration curve was established to verify the accuracy of initial calibration. After every 10 samples, the continuing calibration verification (CCV) standard solution and continuing calibration blank (CCB) was used to verify the ICP-MS drift. ^{103}Rh was chose as internal standard to minimize the instrument drift and the physical interferences.

2.4. Interference study for the determination of AgNPs

The interference of different elements in environmental matrix on the extraction of AgNPs by CPE was studied, including the inorganic ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-}, Zn^{2+}, Al^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}), engineering nanoparticles (Au, TiO_2, Al_2O_3, ZnO, C_{60}) and natural organic matter (NOM). The concentrations of interference elements were close to the expectant concentration in real environment water. Spiked AgNPs solutions with different interference elements were extracted by CPE and detected by ICP-MS after microwave digestion.

2.5. Water samples collection

Samples of wastewater treatment plant (WWTP) effluent were collected from the JingJiang Road treatment plant in ChangSha, Hunan province (N 28°10′52″E 112°56′21″), China. The natural water sampling locations include Xiangjiang River (N 28°10′28″E