Hindawi
Adsorption Science & Technology
Volume 2021, Article ID 9958422, 10 pages
https://doi.org/10.1155/2021/9958422

Research Article

Quantitative Detection of Zinc Oxide Nanoparticle in Environmental Water by Cloud Point Extraction Combined ICP-MS

Yuan Yang,[1,2] **Xin Liu**,[1] **Lin Luo**,[1] **Wenjing Wei**,[2] **Qiang Wang**,[2] **and Jiachao Zhang**[1]

[1]*International Joint Laboratory of Hunan Agricultural Typical Pollution Restoration and Water Resources Safety Utilization, College of Resources and Environment, Hunan Agricultural University, Changsha 410128, China*
[2]*Key Laboratory of Hunan Province for Water Environment and Agriculture Product Safety, College of Chemistry and Chemical Engineering, Central South University, No. 932 Lushan Nan Road, Yuelu District, Changsha 410083, China*

Correspondence should be addressed to Qiang Wang; qwangcsu@163.com and Jiachao Zhang; jiachao.zhang@163.com

Received 18 March 2021; Accepted 13 May 2021; Published 24 May 2021

Academic Editor: Haijian Bing

The increasing usage of zinc oxide nanoparticles (ZnONPs) inevitably leads to their release into the environment. To understand their fate and toxicity in water systems, a reliable method for the quantitative analysis of ZnONPs in environmental waters is urgently needed to be established. In this study, a quantitative analytical method of ZnONPs in environmental waters was developed by cloud point extraction (CPE) combined inductively coupled plasma mass spectrometry (ICP-MS). To obtain high recoveries of ZnONPs, the CPE parameters including pH, surfactant concentration, salt concentration, bath temperature, and time were optimized. The results demonstrated that the addition of β-mercaptoethylamine could significantly reduce the interference of Zn^{2+} on the extraction of ZnONPs, while the CPE approach was not affected significantly by the typical environmental inorganic ion and ENMs (such as Au, TiO_2, and Al_2O_3). The extraction method of ZnONPs with different diameters was also assessed, and satisfactory extraction efficiency was obtained. The results of ZnONP concentration in collected environmental water were in the range of 0.2 ± 0.009-8.2 ± 1.8 μg/L. And the recoveries of ZnONPs in different environmental waters were 62.2 ± 2.0-88.1 ± 9.6% at low concentration spiked levels (12.57-54.68 μg/L), demonstrating that it is efficient to extract trace ZnONPs from real environmental waters. This established method offered a reliable method for the quantitative determination of ZnONPs in environmental waters, which could further promote the study of the environmental behavior, fate, and toxicity of ZnONPs in an aqueous environment.

1. Introduction

Given their widespread application in a variety of fields, engineered nanomaterials (ENMs) will inevitably be exposed to the environment and then adversely affect the ecological environment and human health [1–3]. Zinc oxide nanoparticles (ZnONPs), as a nanomaterial with superior properties, have been widely used in various fields, including cosmetics, catalysts, coatings, textiles, paints, sunscreens, plastics, and food additives [4–6]. The production and wide usage of ZnONPs would inevitably make it release into the environment [7]. As Zanker and Schierz reported, the predicted concentration of ZnONPs that existed in water and soil was 76 μg/L and 3194 μg/kg, respectively [8]. Although the concentration of ZnONPs existing in the environment was low, the adverse effects of ZnONPs in the environment have aroused researcher's attention. It is reported that ZnONPs had negative effects on cell viability [9], DNA damage [10], fish [11], bacteria [12], and plant [13]. In order to understand the behavior, fate, and transportation of ZnONPs in the aqueous environment, a reliable quantitative detection method of ZnONPs in environmental water is urgently

Table 1: List of abbreviations.

Full name	Abbreviation
Zinc oxide nanoparticles	ZnONPs
Cloud point extraction	CPE
Inductively coupled plasma mass spectrometry	ICP-MS
Engineered nanomaterials	ENMs
Dynamic light scattering	DLS
Electron microscope	EM
Nanotracking analysis	NTA
Energy-dispersive X-ray spectroscopy	EDS
Ultraviolet-visible spectroscopy	UV-Vis
X-ray absorption near edge spectroscopy	XANES
Limits of detection	LOD
Hydrodynamic chromatography	HDC
Capillary electrophoresis	CE
Asymmetrical flow field-flow fractionation	AF4
Size exclusion chromatography	SEC
Single particle inductively coupled plasma mass spectrometry	SP-ICP-MS
Silver nanoparticles	AgNPs
Triton X-114	TX-114
Relative standard deviation	RSD
Standard deviation	SD

Table 2: Main operation parameters of ICP-MS.

Agilent 7700x ICP-MS	Value
RF power (w)	1550
Carrier gas (L/min)	1.05
Making up gas (L/min)	0.1
Cell gas flow (mL/min He mode)	4.2
Spray chamber temperature (d)	2
Nebulizer pump rate (rps)	0.1
Mass monitored	^{66}Zn
Internal element	^{74}Ge
Sample depth (mm)	8

needed [14]. Traditional characterization and analytical methods for ENMs in the environment include dynamic light scattering (DLS) [15], electron microscope (EM) [16], nanotracking analysis (NTA) [17], energy-dispersive X-ray spectroscopy (EDS) [14], ultraviolet-visible spectroscopy (UV-Vis) [18] and X-ray absorption near edge spectroscopy (XANES) [19]. However, the concentration of ZnONPs existing in the aqueous environment is usually below the limits of detection (LOD) of these commonly used characterization tools [20, 21]. Moreover, it is difficult to distinguish the ZnONPs and their corresponding ionic counterparts (Zn^{2+}) using these traditional characterization methods without the sample preconcentration sample method. Recently, a large number of new methods have been reported for the separation of ZnONPs from environmental matrices, including hydrodynamic chromatography (HDC) [22, 23], capillary electrophoresis (CE) [24–26], asymmetrical flow field-flow fractionation (AF4) [27, 28], size exclusion chromatography (SEC) [29, 30], and liquid chromatography coupled with ICP-MS [31, 32]. But most of the above methods are laborious, requiring complicated sample pretreatment, expensive equipment, time consuming, and suffering insufficient detection limits, which restricts the analysis of ZnONPs in real environmental water. As an emerging analytical method, the single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been widely used for the characterization and quantitative analysis of the mass concentration, number concentration, and size distribution of metallic nanoparticles in environmental matrices in recent years [33–35]. But the signal of high concentration of dissolved Zn ions may overlap the ZnONPs when the SP-ICP-MS method was used in the detection of ZnONPs in environmental water, leading to false identification between the ZnONPs and Zn^{2+}. In this case, the SP-ICP-MS without sample pretreatment also seems not to be suitable for characterizing ZnONPs in environmental waters [36]. Thus, an effective and validated method is urgently needed for selective species extraction and quantitative detection of ZnONPs in environmental water matrices.

The CPE method is a very simple technique that could concentrate target analyte in the surfactant phase [14, 37]. Moreover, the CPE method is an ecofriendly technology with low toxicity, low solvent consumption, and low cost [38]. Recently, our study suggested that the method of CPE with a nonionic surfactant was feasible for the separation of silver nanoparticles (AgNPs) from environmental water, and good separation results were obtained under the optimized conditions [39]. Thus, the method of CPE based on TX-114 seems

Table 3: Characterization of collecting water samples.

Components	Tap water (our own lab) (mg/L)	River water (Liuyang) (mg/L)	Lake water (Nan Lake) (mg/L)	Effluents (Changsha) (mg/L)
K^+	1.30	2.00	2.50	1.30
Na^+	1.10	2.60	1.50	2.10
Ca^{2+}	0.50	3.50	7.70	17.40
Mg^{2+}	0.80	5.20	2.40	3.30
Fe^{2+}	0.04	0.09	0.12	5.27
Mn^{2+}	0.058	0.010	0.082	0.90
Cl^-	3.70	2.70	5.30	41.50
NO_3^-	0.30	1.30	2.10	21.20
SO_4^{2-}	0.70	2.00	0.40	33.70
pH	7.20	7.70	6.40	6.30

to have the potential to be applied to extract ZnONPs from environmental waters. In recent studies, few researches have reported the quantitative method of ZnONPs in environmental water, and few studies were also performed on the impact of matrix constituents in environmental water on the recoveries of ZnONPs using the CPE method.

In this study, we aimed to establish a simple, cost effective, and credible analytical method for the quantitative detection of trace levels of ZnONPs in the environment with the optimized CPE method. The CPE parameters were evaluated to obtain high recovery of ZnONPs, such as solution pH, extracting concentration, salt concentration, bath temperature, and equilibration time in environmental water. Furthermore, the matrix interference on the detection of ZnONPs was also discussed. Finally, the optimized method was used for the actual environmental waters to evaluate its applicability. A list of abbreviations used in this article is found in Table 1.

2. Materials and Methods

2.1. Chemical Reagent. In zinc oxide nanoparticle suspensions (50% (*w*/*w*) in ultrapure water, mean diameter of ZnONPs is less than 35 nm (TEM result)) were obtained from Sigma Company (St. Louis, MO, USA). Nominal sizes of 30 ± 10 nm, 50 ± 10 nm, and 90 ± 10 nm ZnO nanopowder was provided by Aladdin (Shanghai, China). Dissolved Zn standard solution purchased from Shanghai Institute of Metrology (Shanghai, China, 100 mg/L) was used to establish the calibration curve of Zn. The AuNPs, TiO_2 nanopowder, Al_2O_3 nanopowder, reagent grade $Zn(NO_3)_2$, $Ca(NO_3)_2$, NaCl, $Mg(NO_3)_2$, Na_2SO_4, $AlCl_3$, $Cu(NO_3)_2$, $Co(NO_3)_2$, $Mn(NO_3)_2$, and $FeCl_3$ (Aladdin, Shanghai, China) were used to study the interference of different matrices on the extraction of ZnONPs. The surfactant of reagent grade Triton X-114 (TX-114) (Aladdin, Shanghai, China) was used as the extraction solvent in this study. Chromatographic grade methyl alcohol (Aladdin Shanghai, China) was used to dissolve surfactant phase in the extraction procedure of ZnONPs. Guarantee-reagent grade nitric acid (65%) and hydrogen peroxide (30%) provided by Aladdin (Shanghai, China) were used for the digestion of ZnONPs in the TX-114 phase. β-Mercaptoethylamine (95%, analytical reagent) obtained from Macklin (Shanghai, China) was used as a masking agent for zinc ion in an aqueous solution. Ultrapure water (UP water) (≥18.25 MΩ·cm) utilized for the preparation/dilution of all samples and standards was obtained by PERSEE company (Beijing, China). The pH meter (INESA Scientific Instrument, Shanghai, China) was used to detect the water pH value. All of the experimental vessels were soaked in 20%HNO_3 solution at least 12 h and washed with UP water before experiments.

2.2. Cloud Point Extraction of ZnONPs. Samples for the extraction experiments were performed in a 15 mL glass centrifuge tube. 10 mL water sample was transferred to the glass centrifuge tube, and the pH of water was adjusted to 10.5 using the diluted NaOH solution. Then, 250 μL of TX-114 surfactant (10% *w*/*w*, in UP water) and 100 μL of 1 M NaCl solution were added to water samples. Vortex mixer (Kylin-Bell, China) was used to mix water samples for 1 min, and then, the samples were kept in a water bath for incubation treatment (LiChen Instrument Company, Shanghai, China) at 40°C for 30 min. After the end of incubation, phase separation of the samples was conducted by centrifugation (MEK Instrument Company, Changsha, China) at 2800 rpm for 5 min. Subsequently, the pipette was used to remove the supernatant of samples, and 1 mL methyl alcohol was used to dissolve TX-114 phase, and the ZnONPs enriched in the surfactant phase was transferred to PTFE vessel using UP water for the next step of microwave digestion.

2.3. ICP-MS Analysis of ZnONPs after Microwave Digestion. To reduce the effect of sample solution's organic surfactant for the detection of ZnONPs, the microwave digestion of ZnONPs enriched in the surfactant phase with the modified EPA method 3050A was performed using a microwave system (Sineo microwave, Shanghai, China). The digestion procedure was as follows: samples were digested at 190°C for 30 min after the addition of 2 mL concentrated HNO_3 and 0.5 mL concentrated H_2O_2 into the PTFE vessels. Prior to the analysis of Zn concentration using ICP-MS (Agilent 7700x, USA), all of the samples were diluted to 10 mL using 1% HNO_3 and passed through 0.45 μm hydrophilic membranes (JINTENG, Tianjin, China) to avoid the blocking of ICP-MS MicroMist nebulizer. The internal element of ^{74}Ge was selected to reduce the drift and the physical interferences of the ICP-MS instrument. The calibration curve of Zn^{2+} solution was prepared by plotting signal intensity against 0, 5, 10, 20, 50, and 100 μg/L Zn^{2+} standard solution samples. Each standard sample solution was determined in triplicates, and the mean intensity of ^{66}Zn was converted to the concentration of ^{66}Zn using the established calibration curve. To avoid the potential polyatomic interference of $^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S^2$, and $^{48}Ca^{18}O$ for the detection of ^{66}Zn using ICP-MS, the collision/reaction cell (CRC) technique equipped by the 7700x ICP-MS was performed to reduce these interferences. The main operation parameters of ICP-MS were showed in Table 2.

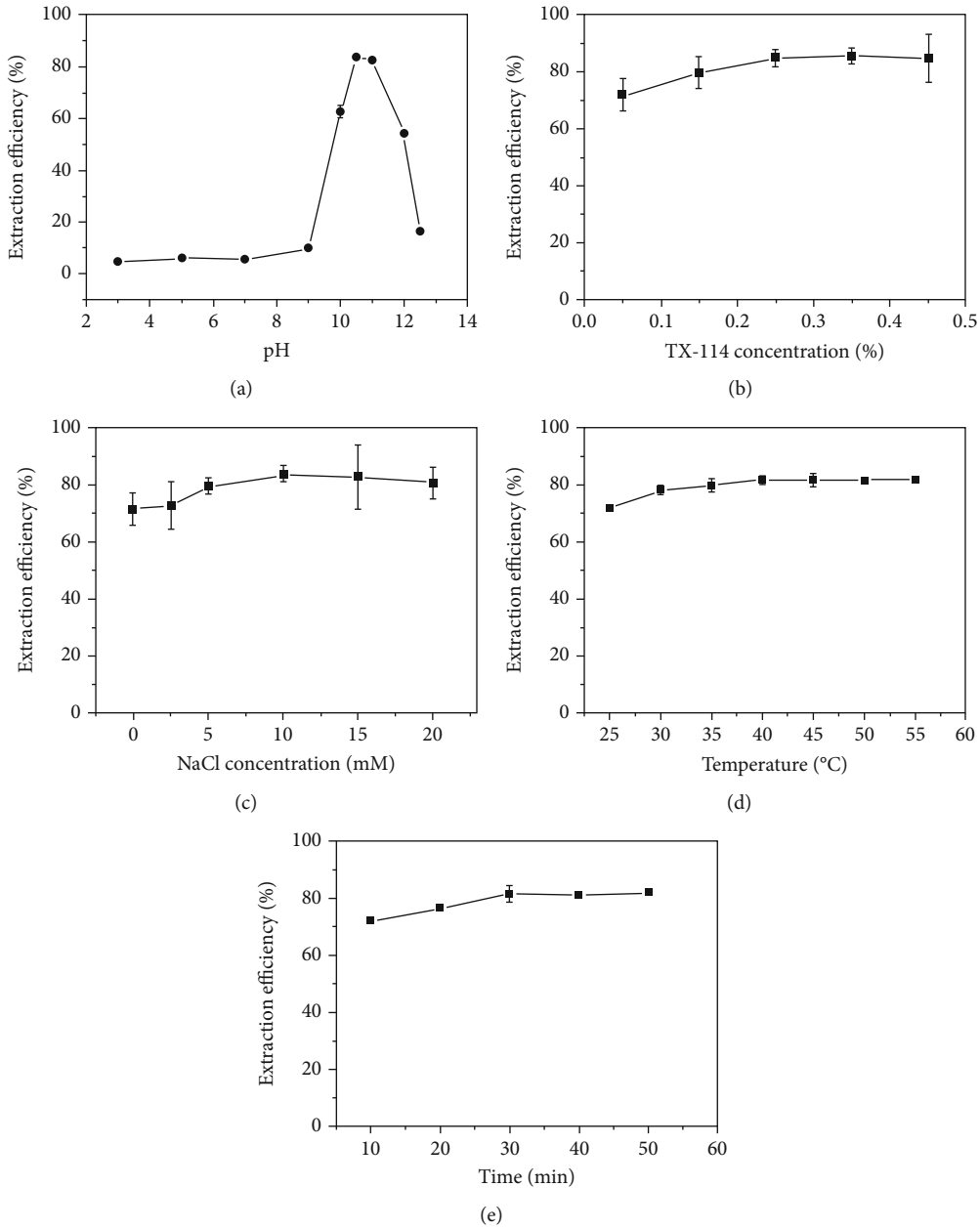

Figure 1: Optimization of CPE factors on the extraction of ZnONPs: (a) pH, (b) TX-114 concentration, (c) NaCl concentration, (d) bath temperature, and (e) equilibrium time ($n = 3$).

2.4. Water Sample Collection and Characterization. There are four types of water collected and then detected: wastewater treatment plant effluent water (N 28°15′56″ E113°04′47″), tap water (N 28°11′16″ E 113°4′52″), Liuyang River (N 28°10′13″ E 113°5′71″), and Nan Lake (N 29°20′52″ E 113°7′17″). All of the water samples were sent to the lab, and then, we started to analyze the concentration of ZnONPs immediately without filtration or adding a stabilization reagent. The concentration of K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+} in these collected samples was tested using ICP-OES (PerkinElmer optima 8000, USA), and anions was determined by ion chromatography (SHINE CIC-D160, Qingdao, China). Table 3 showed the characterization result of collecting water samples.

3. Results and Discussion

3.1. Optimization of the Extraction Procedure of ZnONPs. The main goal of this work was to separate and extract the ZnONPs into surfactant-rich phase from the environmental water. It is reported that the CPE method could concentrate the metallic nanoparticles from the aqueous solution [40]. The CPE parameters which may commonly affect the efficiency of ZnONPs, including the pH value, surfactant concentration, salt concentration, temperature

of the water bath, and incubation time, were optimized in detail in this study.

3.1.1. Influence of pH on the Extraction Efficiency of ZnONPs. As previous studies show, solution pH was a very important factor in the CPE procedure [39, 41, 42]. In this work, the solution pH from 3.0 to 12.5 was optimized to investigate the impact of pH on the extraction efficiency of ZnONPs in water. 200 μg/L ZnONPs spiked into UP water was used to the next extraction experiments. As can be seen in Figure 1(a), the extraction efficiencies were very low (<10%) in the range of pH 3.0-9.0. This could be attributed to the lower pH resulting in the transformation of ZnONPs to Zn^{2+}; then, dispersive Zn^{2+} in aqueous solution could not be transferred into the surfactant phase by CPE process. It was reported that the ZnONPs were easy to transform into Zn^{2+} and $Zn(OH)^{+}$ when the solution of pH was below 6 [43]. The best extraction efficiency of ZnONPs (83.73% ± 1.03%) was acquired when the pH value was 10.5. This may be because the surface of ZnONPs is prone to form a hydroxyl layer under alkaline conditions, thereby preventing further degradation of the nanoparticles. Furthermore, hydrophobic ZnONPs are more easily transferred into the TX-114 phase during CPE procedure [44]. Meanwhile, the extraction efficiency of ZnONPs was decreased significantly when the pH value was up to 12.5. This might be attributed to the water-soluble $Zn(OH)^{3-}$ or $Zn(OH)_4^{2-}$ formed by the reaction between ZnONPs and OH^- under strongly alkaline conditions [45].

3.1.2. Influence of Concentration of TX-114 on the Extraction Efficiency of ZnONPs. As a nonionic surfactant, TX-114 could not be affected by the anions and cations during the CPE procedure, and the stability of TX-114 is affected little by the solution pH. Moreover, the cloud point temperature of TX-114 is relatively low in the 23-26°C range, and good phase separation could be achieved due to the high density of TX-114 [39]. Considering the critical micellar concentration (CMC) of TX-114 is 0.01% (*w*/*v*), the surfactant of TX-114 concentration from 0.05 to 0.45% (*w*/*v*) was optimized to obtain high recoveries of ZnONPs by the determination of 200 μg/L ZnONPs in water using the CPE-ICP-MS method. Furthermore, the impact results of different concentrations of TX-114 on the recoveries of ZnONPs were displayed in Figure 1(b). Results showed that the recoveries of ZnONPs were slow growth when the concentration of surfactant was from 0.05 to 0.35% (*w*/*v*), then held steady when the concentration of surfactant was 0.45% (*w*/*v*). However, the difficulty of the sample digestion procedure would be enhanced when the TX-114 phase volume was high. Thus, 0.35% (*w*/*v*) TX-114 was employed as the surfactant for the CPE process for ZnONPs.

3.1.3. Influence of Ionic Strength on the Extraction Efficiency of ZnONPs. It is reported that the ionic strength of the aqueous solution could influence the phase-separation process of the surfactant and aqueous solution phase [46]. With the increment of ionic strength, the surfactant size and the aggregation number are increased; however, the concentration of

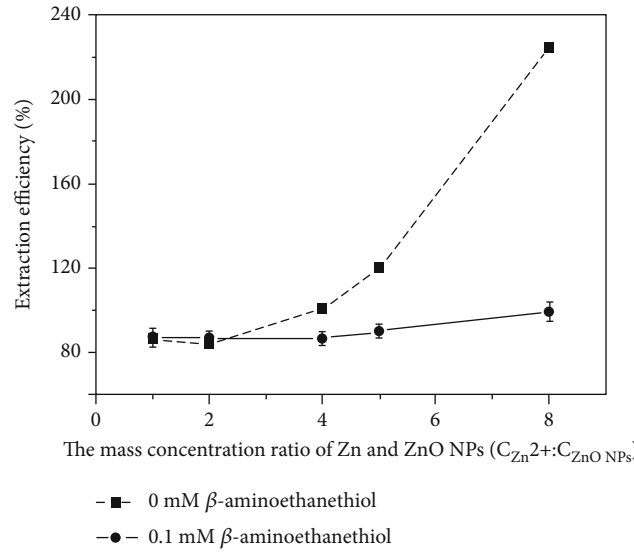

FIGURE 2: Effect of β-mercaptoethylamine on the separation of Zn^{2+} and ZnONPs using the optimal CPE conditions ($n = 3$).

critical micellar still keeps stable [47]. Moreover, the ionic strength was an essential factor using the CPE method for the extraction of metallic nanomaterials in an aqueous environment since the Coulomb repulsion of the charged metallic nanomaterials could be reduced in the high ionic strength in TX-114 micelles; then, the phase separation could be enhanced [48]. So, NaCl as common salt was chosen for the present study to evaluate the impact of ion strength on the extraction of ZnONPs. The NaCl concentration was optimized in the range from 0 to 20 mM. Figure 1(c) showed that the recoveries of ZnONPs were increased when the NaCl concentration was from 0 to 10 mM; it suggested that the ion strength had a positive effect on the extraction of metallic NPs using the CPE method. And then, the recoveries of ZnONPs were kept relatively constant when the concentration of NaCl was from 10 to 20 mM. Therefore, 10 mM NaCl was selected for the CPE procedure for the extraction of ZnONPs in the subsequent studies.

3.1.4. Influence of Temperature and Time on the Extraction Efficiency of ZnONPs. The temperature and time may be a vital role in the CPE method for the extraction of the analyte [38, 49, 50]. Due to the low cloud point temperature of the surfactant (TX-114, 23-26°C), an investigation of incubation temperature (25-55°C) was performed in this study. Figure 1(d) revealed that the recoveries of ZnONPs were increased when the incubation temperature was from 25 to 40°C, and the best recoveries of ZnONPs were obtained from 40 to 55°C. To avoid higher temperature causing the decrement of association between ZnONPs and TX-114 micelles [51], 40°C was selected as the optimal temperature for the CPE of ZnONPs in waters. Then, the impact of time was also discussed within the time from 10 to 50 min at 40°C. It was showed that the recoveries of ZnONPs were increased with the time up to 30 min and remained stable from 30 to 50 min (see Figure 1(e)). To reduce the experimental time,

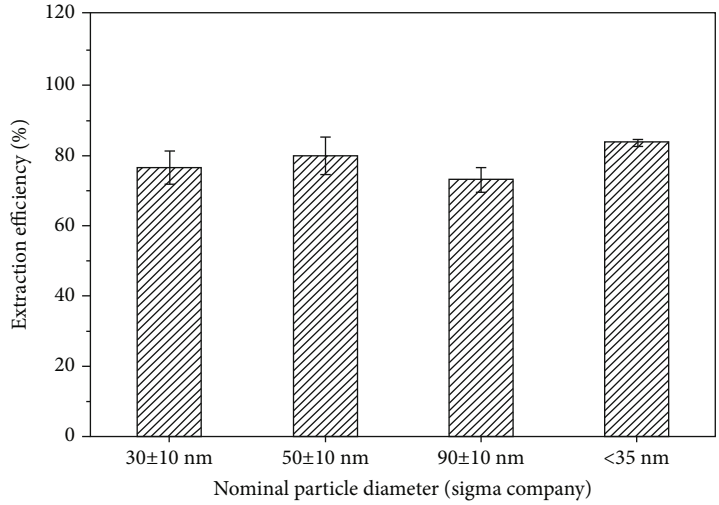

Figure 3: Recoveries of ZnONPs with different particle diameters in water samples ($n = 3$).

the equilibrium time of 30 min was considered an appropriate factor for the extraction of ZnONPs in the next study.

3.2. Species Selectivity of ZnONPs and Zn^{2+} Using CPE Method in Aqueous Solution. It is reported that the presence of their corresponding dissolved component will affect the qualitative and quantitative characterization of nanoparticles during the ICP-MS determination process [52, 53]; thus, the separation of ZnONPs and Zn^{2+} coexisting in environmental water is the main challenge for the detection using the CPE procedure.

In this study, dispersions with constant ZnONPs (200 μg/L) and varied Zn^{2+} (200-1600 μg/L) were premixed and then the separation of ZnONPs and Zn^{2+} was carried out with the optimized CPE conditions. As can be seen from Figure 2, when the mass concentration ratio of Zn^{2+} and ZnONPs ($C_{Zn}{}^{2+} : C_{ZnONPs}$) was below 4, the extraction efficiencies of ZnONPs in the mixture of ZnONPs and Zn^{2+} were in the range of 86-100%, indicating that the ZnONPs could be effectively separated from Zn^{2+} in water solution and extracted into surfactant-rich phase. When the $C_{Zn}{}^{2+} : C_{ZnONPs}$ was in the range from 4 to 8, the extraction efficiencies of ZnONPs were from 100 to 224%. The reason for the high extraction efficiency of ZnONPs could be attributed to the high concentration of Zn^{2+} being adsorbed on the ZnONPs and then transferred into the surfactant phase [54].

In the CPE procedure, the complexation reaction of corresponding ionic counterparts and masking reagent would happen with the addition of the masking reagent into the water solution. The complex compound would still remain in the aqueous solution which may decrease the corresponding ion extracted into the TX-114 phase [55]. β-Mercaptoethylamine, as a masking reagent, could combine with Zn^{2+} to form a stable and well-dispersed complex in the aqueous phase. Compared with EDTA, the addition of small amount of β-mercaptoethylamine hardly changes the pH of the ZnONP solution (the pH value of samples were detected using the pH meter), which is essential for the extraction of ZnONPs by the CPE process. As can be seen in Figure 2, the recovery of ZnONPs was significantly decreased (at the $C_{Zn}{}^{2+} : C_{ZnONPs}$ range from 4 to 8) when 0.1 mM β-mercaptoethylamine was added to the solution. And the recovery of ZnONPs was 99.4% at the $C_{Zn}{}^{2+} : C_{ZnONPs}$ of 8, which indicated that β-mercaptoethylamine could effectively complex with Zn^{2+} and remain in the aqueous phase. Therefore, we can conclude that it will be an effective way for separate ZnONPs from Zn^{2+} by adding 0.1 mM β-mercaptoethylamine to the solution with a high Zn^{2+}concentration.

3.3. Analytical Performance. In this work, the concentration of ZnONPs were quantified using the ICP-MS detection of Zn^{2+} concentration after the microwave digestion of ZnONPs enriched in surfactant phase by the optimized CPE steps. The LOD and precision of this proposed method were evaluated by extracting ZnONPs from water. The LOD of ZnONPs with this CPE-ICP-MS method was 0.06 μg/L which could be calculated as three times of SD divided by m, where SD was standard deviation obtained from the concentration of eleven independent blank samples, and m was the curve slope of element of Zn^{2+} calibration. The relative standard deviation (RSD) was 1.0% and 4.6% for six independent solutions containing 200 and 10 μg/L ZnONPs, respectively, and the recoveries of samples were 81.3% ($n = 6$) and 77.2% ($n = 6$), respectively. This low detection limit and good precision could be satisfied with the demands for determination of ZnONPs in water samples.

3.4. Extraction of ZnONPs with Different Sizes Using CPE Method. The extraction efficiencies of ZnONPs with different particle sizes (30 nm, 50 nm, 90 nm, and<35 nm) in water samples were tested with the above optimized CPE parameters. It could be observed in Figure 3 that the recovered ZnONPs with four particle sizes in water samples were obtained; the extraction efficiencies were 73.1 ± 3.7 -83.8 ± 0.9%. It demonstrated that the optimized CPE procedure could effectively extract the ZnONPs with different sizes into the surfactant phase. So, this optimized CPE-ICP-MS

Table 4: Potential interfering ions and ENMs on the recoveries of ZnONPs ($n = 3$).

Components	Added as	Concentration (μg/mL)	Detected Zn (μg/L)	Recoveries (%)
Ions				
Ca^{2+}	$Ca(NO_3)_2$	100	149.9 ± 7.1	74.9 ± 3.6
Mg^{2+}	$Mg(NO_3)_2$	1000	143.9 ± 4.4	71.9 ± 2.2
SO_4^{2-}	Na_2SO_4	1000	147.3 ± 8.4	73.7 ± 4.2
Al^{3+}	$AlCl_3$	10	142.8 ± 0.9	71.4 ± 0.4
Cu^{2+}	$Cu(NO_3)_2$	10	146.7 ± 7.8	73.4 ± 3.9
Co^{2+}	$Co(NO_3)_2$	10	161.0 ± 3.7	80.5 ± 1.9
Mn^{2+}	$Mn(NO_3)_2$	1	154.3 ± 4.7	77.1 ± 2.4
Fe^{3+}	$FeCl_3$	1	155.5 ± 2.5	77.7 ± 1.3
ENMs				
Au	—	0.1	143.5 ± 9.4	71.8 ± 4.7
TiO_2	—	20.0	146.0 ± 4.0	73.0 ± 2.0
Al_2O_3	—	20.0	150.5 ± 3.5	75.3 ± 1.7

Table 5: Recoveries of ZnONP in environmental waters by the CPE-ICP-MS method ($n = 3$).

Water samples	Spiked ZnONPs (μg/L as Zn)	Detected Zn (μg/L)	Recoveries (%)
Tap water (our lab)	0	5.9 ± 0.6	—
	13.67	16.2 ± 1.5	75.6 ± 10.6
	54.68	53.9 ± 0.7	87.8 ± 1.2
River water (Xiangjiang)	0	0.2 ± 0.009	—
	12.57	10.1 ± 0.7	78.6 ± 5.3
	50.28	38.3 ± 0.9	75.8 ± 1.7
Lake water (Taozi Lake)	0	0	—
	12.57	9.7 ± 0.2	76.8 ± 1.6
	50.28	31.3 ± 1.0	62.2 ± 2.0
Effluent water (WWTP)	0	8.2 ± 1.8	—
	13.67	20.3 ± 1.3	88.1 ± 9.6
	54.68	49.7 ± 0.8	75.9 ± 1.4

method is promising for the determination of the polydisperse ZnONPs in the aqueous environment.

3.5. Effects of Different Matrices on the Extraction of ZnONPs. Considering the fact that the presence of inorganic ions and other engineered nanoparticles distributed widely in environmental waters might affect the determination of ZnONPs using the CPE-ICP-MS method, the extraction efficiency of ZnONPs with the CPE-ICP-MS method on the interference of main ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Al^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, and Fe^{3+}) and typical engineered nanoparticles (Au, TiO_2, and Al_2O_3) existed in environmental water was studied.

The setting concentration of potential interference constituents was approached or exceeded real environment water. It could be observed from Table 2 that the extraction of ZnONPs using the CPE-ICP-MS method was affected slightly by the main matrix constituents. However, the extraction efficiency of ZnONPs will decrease when high concentration of transition metal ions (data not shown) existed in environmental water, although the recoveries of ZnONPs were good in the 1 mg/L of Fe^{3+} and Mn^{2+} aqueous solution, respectively. In this study, the concentrations of AuNPs, TiO_2NPs, and Al_2O_3NPs were set as 0.10 μg/mL, 20 μg/mL, and 20 μg/mL, respectively, according to the report of the potential MNP concentration in natural water [8]. As shown in Table 4, little impact on the recoveries of ZnONPs was obtained by these three representative engineering nanoparticles with the proposed method. In conclusion, this CPE-ICP-MS method is an effective way for the quantitative detection of ZnONPs in the natural aqueous environment.

3.6. Analysis of Environmental Water Samples. To assess the real matrices on this proposed methodology of CPE-ICP-MS, the recovery experiments of ZnONPs with the concentration from 12.57 to 54.68 μg/L spiked into the corresponding environmental water samples were analyzed. The detected ZnONP concentration in environmental water samples were in the range of 0.2 ± 0.009-8.2 ± 1.8 μg/L (Table 5), and the corresponding recoveries of ZnONPs were in the range of 62.2 ± 2.0-88.1 ± 9.6%, demonstrating that most of the ZnONPs spiked into the water samples could be transferred into the surfactant phase with this proposed CPE procedure; the recoveries of ZnONPs using the CPE-ICP-MS method were impacted slightly by the complex matrix constituents in environmental waters. This optimized extraction method is effective for extracting ZnONPs in environmental water samples.

4. Conclusions

In this work, a method for the quantitative detection of ZnONPs in environmental water was established based on cloud point extraction combined ICP-MS. We systematically optimized the extraction conditions for ZnONPs and then applied the optimized method to several types of environmental water to evaluate its applicability. As a masking agent, β-mercaptoethylamine could significantly reduce the interference of Zn^{2+} on the extraction of ZnONPs. The CPE approach was not significantly affected by the typical environmental inorganic ion and ENMs. The low detection limit (0.06 μg/L) and high recoveries of ZnONPs in environmental water samples (62.2 ± 2.0-88.1 ± 9.6%) under the optimized CPE procedure confirmed the feasibility of this method for the detection of ZnONPs in environmental water samples. In conclusion, this established technique offered an accurate and reliable analytical method that could further promote the risk assessment of ZnONPs in the aqueous environment.

Data Availability

All data generated or analyzed during this study are included in this article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This study was financially supported by the China Postdoctoral Science Foundation (Grant No. 2019M652768), National Natural Science Foundation of China (Grant No. 42077380), National Natural Science Foundation of Hunan province (Grant No. 2020JJ5227 and 2020JJ5259), Hunan Provincial Key R&D (Grant No. 2019WK2031), and Research Foundation of Education Bureau of Hunan Province (Grant No. 20A239).

References

[1] V. D. Rajput, T. M. Minkina, A. Behal et al., "Effects of zinc-oxide nanoparticles on soil, plants, animals and soil organisms: a review," *Environmental Nanotechnology, Monitoring and Management*, vol. 9, pp. 76–84, 2018.

[2] T. Cai, X. L. Liu, J. C. Zhang et al., "Silicate-modified oiltea camellia shell-derived biochar: A novel and cost- effective sorbent for cadmium removal," *Journal of Cleaner Production*, vol. 281, article 125390, 2021.

[3] Y. Y. Wang, K. X. Zheng, W. H. Zhan et al., "Highly effective stabilization of Cd and Cu in two different soils and improvement of soil properties by multiple-modified biochar," *Ecotoxicology and Environmental Safety*, vol. 207, article 111294, 2021.

[4] D. Zhou and A. A. Keller, "Role of morphology in the aggregation kinetics of ZnO nanoparticles," *Water Research*, vol. 44, no. 9, pp. 2948–2956, 2010.

[5] Y. Xie, Y. He, P. L. Irwin, T. Jin, and X. Shi, "Antibacterial activity and mechanism of action of zinc oxide nanoparticles against Campylobacter jejuni," *Environmental Microbiology*, vol. 77, no. 7, pp. 2325–2331, 2011.

[6] L. He, Y. Liu, A. Mustapha, and M. Lin, "Antifungal activity of zinc oxide nanoparticles against _Botrytis cinerea_ and _Penicillium expansum_," *Microbiological Research*, vol. 166, no. 3, pp. 207–215, 2011.

[7] M. Ghosh, S. Sinha, M. Jothiramajayam, A. Jana, A. Nag, and A. Mukherjee, "Cyto-genotoxicity and oxidative stress induced by zinc oxide nanoparticle in human lymphocyte cells _in vitro_ and Swiss albino male mice _in vivo_," *Food and Chemical Toxicology*, vol. 97, pp. 286–296, 2016.

[8] H. Zanker and A. Schierz, "Engineered nanoparticles and their identification among natural nanoparticles," *Reviews in Analytical Chemistry*, vol. 5, no. 1, pp. 107–132, 2012.

[9] V. Sharma, R. K. Shukla, N. Saxena, D. Parmar, M. Das, and A. Dhawan, "DNA damaging potential of zinc oxide nanoparticles in human epidermal cells," *Toxicology Letters*, vol. 185, no. 3, pp. 211–218, 2009.

[10] H. L. Karlsson, C. Pontus, G. Johanna, and M. L. Lennart, "Copper oxide nanoparticles are highly toxic: a comparison between metal oxide nanoparticles and carbon nanotubes," *Rresearch in Toxicology*, vol. 21, no. 9, pp. 1726–1732, 2008.

[11] H. Ma, P. L. Williams, and S. A. Diamond, "Ecotoxicity of manufactured ZnO nanoparticles - A review," *Environmental Pollution*, vol. 172, pp. 76–85, 2013.

[12] W. Jiang, H. Mashayekhi, and B. Xing, "Bacterial toxicity comparison between nano- and micro-scaled oxide particles," *Environmental Pollution*, vol. 157, no. 5, pp. 1619–1625, 2009.

[13] X. Ma, J. Geiser-Lee, Y. Deng, and A. Kolmakov, "Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation," *Science of the Total Environment*, vol. 408, no. 16, pp. 3053–3061, 2010.

[14] J.-f. Liu, J.-b. Chao, R. Liu et al., "Cloud point extraction as an advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters," *Analytical Chemistry*, vol. 81, no. 15, pp. 6496–6502, 2009.

[15] G. Cornelis, L. Pang, C. Doolette, J. K. Kirby, and M. J. McLaughlin, "Transport of silver nanoparticles in saturated columns of natural soils," *Science of the Total Environment*, vol. 463-464, pp. 120–130, 2013.

[16] B. Kim, M. Murayama, B. P. Colman, and M. F. Hochella, "Characterization and environmental implications of nano- and larger TiO2 particles in sewage sludge, and soils amended with sewage sludge," *Journal of Environmental Monitoring*, vol. 14, pp. 1128–1136, 2012.

[17] P. Steppert, D. Burgstaller, M. Klausberger, A. Tover, E. Berger, and A. Jungbauer, "Quantification and characterization of virus-like particles by size-exclusion chromatography and nanoparticle tracking analysis," *Journal of Chromatography*, vol. 1487, pp. 89–99, 2017.

[18] G. C. Waissi-Leinonen, I. Nybom, K. Pakarinen, J. Akkanen, M. T. Leppänen, and J. V. Kukkonen, "Fullerenes(nC_{60}) affect the growth and development of the sediment-dwelling invertebrate _Chironomus riparius_ larvae," *Environmental Pollution*, vol. 206, pp. 17–23, 2015.

[19] Y. Ma, X. He, P. Zhang et al., "Xylem and phloem based transport of CeO2 nanoparticles in hydroponic cucumber plants," *Science and Technology*, vol. 51, no. 9, pp. 5215–5221, 2017.

[20] J. A. Gallego-Urrea, J. Tuoriniemi, and M. Hassellöv, "Applications of particle-tracking analysis to the determination of size distributions and concentrations of nanoparticles in environmental, biological and food samples," *Trends in Analytical Chemistry*, vol. 30, no. 3, pp. 473–483, 2011.

[21] V. D. K. Frank, P. L. Ferguson, P. A. Holden et al., "Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies," *Environmental Toxicology and Chemistry*, vol. 31, pp. 32–49, 2011.

[22] K. Tiede, A. B. A. Boxall, X. Wang et al., "Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge," *Analytical Atomic Spectrometry*, vol. 25, no. 7, pp. 1149–1154, 2010.

[23] M. Roman, C. Rigo, H. Castillo-Michel et al., "Hydrodynamic chromatography coupled to single-particle ICP-MS for the simultaneous characterization of AgNPs and determination of dissolved Ag in plasma and blood of burn patients," *Analytical and Bioanalytical Chemistry*, vol. 408, pp. 5109–5124, 2015.

[24] H. Qu, T. K. Mudalige, and S. W. Linder, "Capillary electrophoresis/inductively-coupled plasma-mass spectrometry: development and optimization of a high resolution analytical tool for the size-based characterization of nanomaterials in dietary supplements," *Analytical Chemistry*, vol. 86, no. 23, pp. 11620–11627, 2014.

[25] H. Qu, T. K. Mudalige, and S. W. Linder, "Capillary electrophoresis coupled with inductively coupled mass spectrometry as an alternative to cloud point extraction based methods for

rapid quantification of silver ions and surface coated silver nanoparticles," *Journal of Chromatography. A*, vol. 1429, pp. 348–353, 2016.

[26] L. Liu, B. He, Q. Liu et al., "Identification and accurate size characterization of nanoparticles in complex media," *Chem. Int. Ed. Engl.*, vol. 53, no. 52, pp. 14476–14479, 2014.

[27] A. R. Jochem, G. N. Ankah, L. A. Meyer, S. Elsenberg, C. Johann, and T. Kraus, "Colloidal mechanisms of gold nanoparticle loss in asymmetric flow field-flow fractionation," *Analytical Chemistry*, vol. 88, no. 20, pp. 10065–10073, 2016.

[28] B. Meisterjahn, E. Neubauer, F. Von der Kammer, D. Hennecke, and T. Hofmann, "Asymmetrical flow-field-flow fractionation coupled with inductively coupled plasma mass spectrometry for the analysis of gold nanoparticles in the presence of natural nanoparticles," *Journal of Chromatography. A*, vol. 1372C, pp. 204–211, 2014.

[29] F. K. Liu, "SEC characterization of Au nanoparticles prepared through seed-assisted synthesis," *Chromatographia*, vol. 66, no. 9-10, pp. 791–796, 2007.

[30] X. X. Zhou, J. F. Liu, and F. L. Geng, "Determination of metal oxide nanoparticles and their ionic counterparts in environmental waters by size exclusion chromatography coupled to ICP-MS," *Nano*, vol. 1, pp. 13–20, 2016.

[31] Y. Yang, L. Luo, H. P. Li et al., "Analysis of metallic nanoparticles and their ionic counterparts in complex matrix by reversed-phase liquid chromatography coupled to ICP-MS," *Talanta*, vol. 182, pp. 156–163, 2018.

[32] J. Soto-Alvaredo, M. Montes-Bayón, and J. Bettmer, "Speciation of silver nanoparticles and silver(I) by reversed-phase liquid chromatography coupled to ICPMS," *Analytical Chemistry*, vol. 85, no. 3, pp. 1316–1321, 2013.

[33] Y. Yang, C. L. Long, H. P. Li, Q. Wang, and Z. G. Yang, "Analysis of silver and gold nanoparticles in environmental water using single particle-inductively coupled plasma-mass spectrometry," *Science of the Total Environment*, vol. 563-564, pp. 996–1007, 2016.

[34] A. R. Donovan, C. D. Adams, Y. Ma, C. Stephan, T. Eichholz, and H. Shi, "Single particle ICP-MS characterization of titanium dioxide, silver, and gold nanoparticles during drinking water treatment," *Chemosphere*, vol. 144, pp. 148–153, 2016.

[35] K. Kińska, J. Jiménez-Lamana, J. Kowalska, B. Krasnodębska-Ostręga, and J. Szpunar, "Study of the uptake and bioaccumulation of palladium nanoparticles by Sinapis alba using single particle ICP-MS," *Total Environment*, vol. 615, pp. 1078–1085, 2018.

[36] M. Hadioui, V. Merdzan, and K. J. Wilkinson, "Detection and characterization of ZnO nanoparticles in surface and waste waters using single particle ICPMS," *Science and Technology*, vol. 49, no. 10, pp. 6141–6148, 2015.

[37] S. M. Majedi, H. K. Lee, and B. C. Kelly, "Chemometric analytical approach for the cloud point extraction and inductively coupled plasma mass spectrometric determination of zinc oxide nanoparticles in water samples," *Analytical Chemistry*, vol. 84, no. 15, pp. 6546–6552, 2012.

[38] P. Samaddar and K. Sen, "Cloud point extraction: a sustainable method of elemental preconcentration and speciation," *Industrial and Engineering Chemistry*, vol. 20, no. 4, pp. 1209–1219, 2014.

[39] G. Hartmann, T. Baumgartner, and H. Schuster, "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," *Analytical Chemistry*, vol. 86, no. 1, pp. 790–796, 2014.

[40] J. F. Liu, R. Liu, Y. G. Yin, and G. B. Jiang, "Triton X-114 based cloud point extraction: a thermoreversible approach for separation/concentration and dispersion of nanomaterials in the aqueous phase," *Chemical Communications*, pp. 1514–1516, 2009.

[41] G. Hartmann, C. Hutterer, and M. Schuster, "Ultra-trace determination of silver nanoparticles in water samples using cloud point extraction and ETAAS," *Analytical Atomic Spectrometry*, vol. 28, no. 4, pp. 567–572, 2013.

[42] G. Hartmann and M. Schuster, "Species selective preconcentration and quantification of gold nanoparticles using cloud point extraction and electrothermal atomic absorption spectrometry," *Chimica Acta*, vol. 761, pp. 27–33, 2013.

[43] S. Yamabi and H. Imai, "Growth conditions for wurtzite zinc oxide films in aqueous solutions," *Materials Chemistry*, vol. 12, no. 12, pp. 3773–3778, 2002.

[44] S. M. Majedi and H. K. Lee, "Recent advances in the separation and quantification of metallic nanoparticles and ions in the environment," *TrAC Trends in Analytical Chemistry*, vol. 75, pp. 183–196, 2016.

[45] S.-W. Bian, I. A. Mudunkotuwa, T. Rupasinghe, and V. H. Grassian, "Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid," *Langmuir*, vol. 27, no. 10, pp. 6059–6068, 2011.

[46] A. R. Fontana, M. F. Silva, L. D. Martinez, R. G. Wuilloud, and J. C. Altamirano, "Determination of polybrominated diphenyl ethers in water and soil samples by cloud point extraction-ultrasound-assisted back-extraction-gas chromatography-mass spectrometry," *The Journal of Chromatography A*, vol. 1216, no. 20, pp. 4339–4346, 2009.

[47] Z. Sosa Ferrera, C. Padrón Sanz, C. Mahugo Santana, and J. J. Santana Rodríguez, "The use of micellar systems in the extraction and pre-concentration of organic pollutants in environmental samples," *Trends in Analytical Chemistry*, vol. 23, no. 7, pp. 469–479, 2004.

[48] S. M. Majedi, B. C. Kelly, and H. K. Lee, "Evaluation of a cloud point extraction approach for the preconcentration and quantification of trace CuO nanoparticles in environmental waters," *Analytica Chimica Acta*, vol. 814, pp. 39–48, 2014.

[49] E. L. Silva, P. S. Roldan, and M. F. Giné, "Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optic emission spectrometry," *Hazardous Materials*, vol. 171, no. 1-3, pp. 1133–1138, 2009.

[50] L. Zhao, S. Zhong, K. Fang, Z. Qian, and J. Chen, "Determination of cadmium(II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry," *Hazardous Materials*, vol. 239-240, pp. 206–212, 2012.

[51] D. Segets, R. Marczak, S. Schafer et al., "Experimental and theoretical studies of the colloidal stability of nanoparticles - a general interpretation based on stability maps," *ACS Nano*, vol. 5, no. 6, pp. 4658–4669, 2011.

[52] D. M. Schwertfeger, J. R. Velicogna, A. H. Jesmer, R. P. Scroggins, and J. I. Princz, "Single particle-inductively coupled plasma mass spectroscopy analysis of metallic nanoparticles in environmental samples with large dissolved analyte

fractions," *Analytical Chemistry*, vol. 88, no. 20, pp. 9908–9914, 2016.

[53] L. Luo, Y. Yang, H. Li, R. Ding, Q. Wang, and Z. Yang, "Size characterization of silver nanoparticles after separation from silver ions in environmental water using magnetic reduced graphene oxide," *Total Environment*, vol. 612, pp. 1215–1222, 2018.

[54] T. Sheela, Y. A. Nayaka, R. Viswanatha, S. Basavanna, and T. G. Venkatesha, "Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles," *Powder Technology*, vol. 217, pp. 163–170, 2012.

[55] S. J. Yu, J. B. Chao, J. Sun, Y. G. Yin, J. F. Liu, and G. B. Jiang, "Quantification of the uptake of silver nanoparticles and ions to HepG2 cells," *Environmental Science & Technology*, vol. 47, no. 7, pp. 3268–3274, 2013.