Research Article

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

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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 Zn²⁺ on the extraction of ZnONPs, while the CPE approach was not affected significantly by the typical environmental inorganic ion and ENMs (such as Au, TiO₂, and Al₂O₃). 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
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

| 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 1: List of abbreviations.**

**Table 2: Main operation parameters of ICP-MS.**

| Parameter                                   | Value   |
|---------------------------------------------|---------|
| Agilent 7700x ICP-MS                        |         |
| 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       |
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$_2$O$_3$ nanopowder, reagent grade Zn(NO$_3$)$_2$, Ca(NO$_3$)$_2$, NaCl, Mg(NO$_3$)$_2$, Na$_2$SO$_4$, AlCl$_3$, Cu(NO$_3$)$_2$, Co(NO$_3$)$_2$, Mn(NO$_3$)$_2$, and FeCl$_3$ (Aladdin, Shanghai, China) were used for the microwave digestion of ZnONPs in the TX-114 phase. β-Mercaptoethyamine (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$_2$O$_2$ 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 $^{32}$S$^{16}$O$_2$, $^{34}$S$^{16}$O$_2$, $^{33}$S$^{16}$O, 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.

### 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$^{3+}$      | 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                        |

#### Table 2: Components in water samples.

| Components | lab (mg/L) | env (mg/L) |
|------------|------------|------------|
| Na$^+$     | 0.5 ± 0.1  | 2.0 ± 0.2  |
| K$^+$      | 1.0 ± 0.1  | 2.5 ± 0.2  |
| Cl$^-$     | 3.0 ± 0.2  | 5.0 ± 0.3  |

#### Table 1: Materials and Methods.

| Component        | Description                                                                 |
|------------------|------------------------------------------------------------------------------|
| K$^+$            | Potassium chloride.                                                          |
| Na$^+$           | Sodium chloride.                                                            |
| Ca$^{2+}$        | Calcium chloride.                                                            |
| Mg$^{2+}$        | Magnesium chloride.                                                          |
| Fe$^{3+}$        | Iron (III) chloride.                                                         |
| Mn$^{2+}$        | Manganese (II) chloride.                                                     |
| NO$_3^-$         | Nitrate ion.                                                                 |
| SO$_4^{2-}$      | Sulfate ion.                                                                 |
| pH               | pH of the water samples.                                                     |

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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" E 113°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⁺, Ca²⁺, Mg²⁺, Fe²⁺, and Mn²⁺ 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 anions and cations during the CPE procedure [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 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,
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\textsuperscript{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\textsuperscript{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\textsuperscript{2+} (200-1600 μg/L) were premixed and then the separation of ZnONPs and Zn\textsuperscript{2+} was carried out with the optimized CPE conditions. As can be seen from Figure 2, when the mass concentration ratio of Zn\textsuperscript{2+} and ZnONPs (C\textsubscript{Zn} : C\textsubscript{ZnONPs}) was below 4, the extraction efficiencies of ZnONPs in the mixture of ZnONPs and Zn\textsuperscript{2+} were in the range of 86-100%, indicating that the ZnONPs could be effectively separated from Zn\textsuperscript{2+} in water solution and extracted into surfactant-rich phase. When the C\textsubscript{Zn} : C\textsubscript{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\textsuperscript{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-Mercaptotri ethanolamine, as a masking reagent, could combine with Zn\textsuperscript{2+} to form a stable and well-dispersed complex in the aqueous phase. Compared with EDTA, the addition of small amount of β-mercaptoethanolamine 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\textsubscript{Zn} : C\textsubscript{ZnONPs} range from 4 to 8) when 0.1 mM β-mercaptoethanolamine was added to the solution. And the recovery of ZnONPs was 99.4% at the C\textsubscript{Zn} : C\textsubscript{ZnONPs} of 8, which indicated that β-mercaptoethanolamine could effectively complex with Zn\textsuperscript{2+} and remain in the aqueous phase. Therefore, we can conclude that it will be an effective way for separate ZnONPs from Zn\textsuperscript{2+} by adding 0.1 mM β-mercaptoethanolamine to the solution with a high Zn\textsuperscript{2+} concentration.

3.3. Analytical Performance. In this work, the concentration of ZnONPs were quantified using the ICP-MS detection of Zn\textsuperscript{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\textsuperscript{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 effectively separated from Zn\textsuperscript{2+} in water solution which may decrease the corresponding ion extracted into the TX-114 phase [55]. β-Mercaptotri ethanolamine 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\textsubscript{Zn} : C\textsubscript{ZnONPs} range from 4 to 8) when 0.1 mM β-mercaptoethanolamine was added to the solution. And the recovery of ZnONPs was 99.4% at the C\textsubscript{Zn} : C\textsubscript{ZnONPs} of 8, which indicated that β-mercaptoethanolamine could effectively complex with Zn\textsuperscript{2+} and remain in the aqueous phase. Therefore, we can conclude that it will be an effective way for separate ZnONPs from Zn\textsuperscript{2+} by adding 0.1 mM β-mercaptoethanolamine to the solution with a high Zn\textsuperscript{2+} concentration.

Figure 3: Recoveries of ZnONPs with different particle diameters in water samples (n = 3).
and Fe\textsuperscript{3+}) and typical engineered nanoparticles (Au, TiO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3}) 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\textsuperscript{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. 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\textsuperscript{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.

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