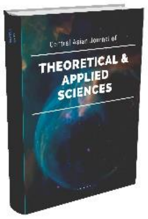

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Utilizing a Combination Of ICP-MS and Cloud Point Extraction, Zinc Oxide Nanoparticle Quant Detection in Aquatic Environment

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Abstract: *The rising utilization of zinc oxide nanoparticles (ZnONPs) undeniably prompts their conveyance into the environment. To fathom their predetermination and hurtfulness in water systems, a reliable method for the quantitative assessment of ZnONPs in normal waters is fundamentally expected to have been spread out. In this survey, a quantitative logical procedure for ZnONPs in normal waters was made by cloud point extraction (CPE) united inductively coupled plasma mass spectrometry (ICP-MS). To get high recoveries of ZnONPs, the CPE limits including pH, surfactant center, salt obsession, shower temperature, and time were smoothed out. The results showed that the development of β-mercaptoethylamine could on a very basic level reduce the impedance of Zn2+ on the extraction of ZnONPs, while the CPE approach was not influenced basically by the ordinary biological inorganic molecule and ENMs (like Au, TiO2, and Al2O3). The extraction system for ZnONPs with different widths was moreover reviewed, and great extraction capability was gained. The eventual outcomes of ZnONP center in assembled natural water were in the extent of - μg/L. Additionally, the recoveries of ZnONPs in different regular waters were - at low obsession spiked levels (12.57-54.68 μg/L), displaying that isolating follow ZnONPs from veritable natural waters is capable. This spread out method offered a strong procedure for the quantitative confirmation of ZnONPs in environmental waters, which could moreover propel the examination of the regular approach to acting, fate, and harmfulness of ZnONPs in a watery environment.*

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1. Introduction

Engineered nanomaterials (ENMs) will unavoidably be exposed to the environment due to their extensive use in a range of areas, which will then have a negative impact on the ecological environment and human health[1–3].The exceptional qualities of zinc oxide nanoparticles (ZnONPs) have led to their widespread application in a diverse range of industries, including cosmetics, catalysts, coatings, textiles, paints, sunscreens, polymers, and food additives. [4–6].ZnONPs would ultimately discharge into the environment due to their widespread manufacture and use[7]. According to Zanker and Schierz's research, the expected concentration of ZnONPs in the soil and water was 3194 g/kg and 76 g/L, respectively[8].Although the concentration of ZnONPs in the environment was modest, their negative consequences have caught the attention of researchers. Cell viability [9], DNA damage [10], fish [11], bacteria [12], and plants [13] have all been shown to be negatively impacted by ZnONPs.A reliable quantitative detection approach of ZnONPs in environmental water is vitally required in order to understand the action, destiny, and transportation of these chemicals in the aqueous environment[14].Traditional environmental ENM characterization and analysis approaches 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].However, when the SP-ICP-MS approach was employed to identify ZnONPs in ambient water, the signal of a high concentration of dissolved Zn ions may overlap the ZnONPs, resulting to a false identification between the ZnONPs and Zn2+.This time, it appears that analysing ZnONPs in ambient waters will not be possible with SP-ICP-MS without sample pretreatment [36]. Therefore, the need for a reliable and established approach for the quantitative detection of ZnONPs in environmental water matrices is important.

The target analyte can be concentrated using the CPE method, which is a very straightforward procedure [14, 37]. The CPE approach is also an inexpensive, low-toxic, and environmentally friendly technology [38].According to a recent study, the approach of CPE with a nonionic surfactant proved workable for removing silver nanoparticles (AgNPs) from ambient water, and positive separation outcomes were produced under optimal conditions [39].To extract ZnONPs from ambient waters, the CPE technique based on TX-114 appears to have some promise. Few studies have recently reported on the quantitative approach of ZnONPs in environmental water, and even fewer have looked at the influence of matrix ingredients in environmental water on ZnONP recoveries using the CPE technique.

In this study, we sought to develop an analytical technique for the quantitative detection of trace quantities of ZnONPs in the environment using the enhanced CPE method that was straightforward, affordable, and reliable.To achieve high ZnONP recovery, the CPE parameters, including solution pH, extracting concentration, salt concentration, bath temperature, and equilibration time in environmental water, were assessed. Additionally, the impact of matrix interference on ZnONP detection was covered. Finally, to assess the method's applicability, it was applied to the real environmental waters.

2. Materials and Methods

2.1. Chemical Reagent

Sigma Company provided zinc oxide nanoparticle suspensions with a mean diameter of ZnONPs that is smaller than 35 nm (in 50% of the cases, in ultrapure water) (St. Louis, MO, USA). Aladdin provided ZnO nanopowder in the nominal diameters of nm, nm, and nm (Shanghai, China).The calibration curve for Zn was created using a dispersed Zn standard solution that was acquired from the Shanghai Institute of Metrology (Shanghai, China), at a concentration of 100 mg/L. We investigated the impact of several matrices on the extraction of ZnONPs using AuNPs, TiO2 nanopowder, Al2O3 nanopowder, reagent grade Zn(NO3)2, Ca(NO3)2, NaCl, Mg(NO3)2, Na2SO4, AlCl3, Cu(NO3)2, Co(NO3)2, Mn(NO3)2, and FeCl3 (Aladdin, Shanghai, China).In this work, the extraction solvent used Triton X-114 (TX-114) (Aladdin, Shanghai, China), a reagent grade surfactant. The surfactant phase in the extraction process of ZnONPs was dissolved using chromatographic grade methyl alcohol (Aladdin Shanghai, China).ZnONPs were digested in the TX-114 phase using Aladdin's (Shanghai, China) guarantee-reagent grade nitric acid (65%) and hydrogen peroxide (30%). As a masking agent for zinc ion in an aqueous solution, -Mercaptoethylamine (95 percent, analytical reagent) was utilised, which was bought from Macklin (Shanghai, China).PERSEE firm acquired the 18.25 Mcm ultrapure water (UP water) used for the preparation and dilution of all tests and standards (Beijing, China). A pH metre (INESA Scientific Instrument, Shanghai, China) was used to measure the pH of the water. Prior to testing, all of the experimental vessels were cleaned with UP water and immersed in a 20%HNO3 solution for at least 12 hours.

2.2. Cloud Point Extraction of ZnONPs

The extraction tests used samples that were placed in a 15 mL glass centrifuge tube. The pH of the water was raised to 10.5 using the diluted NaOH solution after the 10 mL water sample was transferred to the glass centrifuge tube.Then, 250 L of TX-114 surfactant (10% w/w, in UP water) and 100 L of 1 M NaCl solution were added to the water samples. Water samples were mixed in a vortex mixer (made by Kylin-Bell, China) for one minute before being placed in a water bath (made by LiChen Instrument Company, Shanghai, China) for 30 minutes of incubation.Phase separation of the samples was carried out using centrifugation (MEK Instrument Company, Changsha, China) at 2800 rpm for 5 minutes after the incubation period had ended.Once the TX-114 phase had been dissolved with 1 mL of methyl alcohol and the ZnONPs enriched in the surfactant phase had been transferred to a PTFE jar using UP water for the subsequent microwave digestion stage, the supernatant of the samples had been removed using a pipette.

2.3. ICP-MS Analysis of ZnONPs after Microwave Digestion

Microwave digestion of ZnONPs enriched in the surfactant phase with the modified EPA method 3050A was carried out utilising a microwave system in order to lessen the impact of sample solution's organic surfactant for the detection of ZnONPs (Sineo microwave, Shanghai, China).Following the insertion of 2 mL concentrated HNO3 and 0.5 mL concentrated H2O2 into the PTFE tubes, samples were digested at 190°C for 30 min. All of the samples were diluted to 10 mL using 1% HNO3 and passed through 0.45 m hydrophilic membranes (JINTENG, Tianjin, China) prior to the detection of Zn concentration using ICP-MS (Agilent 7700x, USA). This was done to prevent the ICP-MS MicroMist nebulizer from becoming blocked. To lessen instrument drift and physical interferences, the internal element of 74Ge was chosen. By charting signal intensity against samples of 0, 5, 10, 20, 50, and 100 g/L Zn2+ standard solution, the calibration curve for Zn2+ solution was created. Each standard sample solution was assessed in triplicate, and the calibrated calibration curve was used to translate the mean intensity of 66Zn to the concentration of 66Zn. The collision/reaction cell (CRC) technique offered by the 7700x ICP-MS was used to decrease these interferences in order to avoid the potential polyatomic interference of 34S16O2, 32S34S, 33S2, and 48Ca18O for the detection of 66Zn utilising ICP-MS.

2.4. Water Sample Collection and Characterization

Water from wastewater treatment plants (N 28°1556 E 113°0447), tap water (N 28°1116 E 113°452), the Liuyang River (N 28°1013 E 113°571), and Nan Lake (N 29°2052 E 113°717) are the four types of water that were collected and identified.After sending all of the water samples to the lab, we immediately began analysing the ZnONP concentrations without filtering or adding stabilising agentsIon chromatography was used to measure anions, and ICP-OES (PerkinElmer optima 8000, USA) was used to analyse the concentrations of K+, Na+, Ca2+, Mg2+, Fe2+, and Mn2+ in these collected samples (SHINE CIC-D160, Qingdao, China).

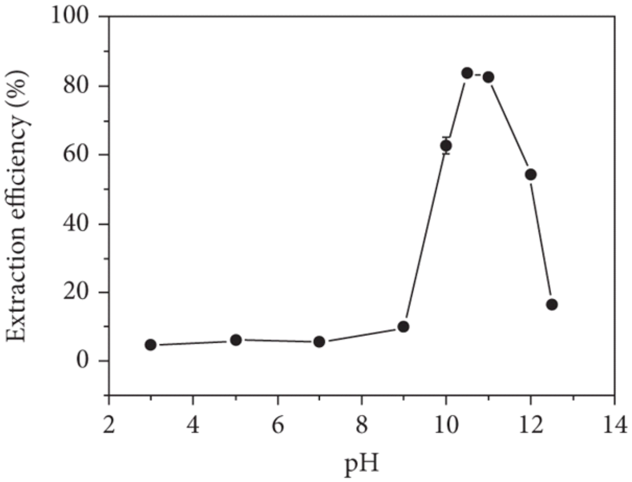
3. Results and Discussion

3.1. Optimization of the Extraction Procedure of ZnONPs

The major objective of this research was to separate and extract ZnONPs into a phase rich in surfactants from ambient water. The CPE approach is said to be able to concentrate metallic nanoparticles from the aqueous solution [40] The pH value, surfactant content, salt concentration, water bath temperature, and incubation period are some of the CPE parameters that may frequently affect the efficiency of ZnONPs. These parameters were carefully tuned in this work.

3.1.1. Influence of pH on the Extraction Efficiency of ZnONPs

Solution pH played a significant role in the CPE procedure, as demonstrated by other research [39, 41, 42]. This research examined the effect of pH on the effectiveness of ZnONPs being extracted from water by optimising the solution pH from 3.0 to 12.5. In the following extraction studies, 200 g/L ZnONPs spiked into UP water was employed. As can be seen in Figure 1(a), In the pH range of 3.0-9.0, the extraction efficiency were quite low (10%). This might be explained by the decreased pH turning ZnONPs into Zn2+, which prevented the CPE process from transferring dispersive Zn2+ in aqueous solution into the surfactant phase. When the pH of a solution dropped below 6, it was claimed that ZnONPs were easily converted into Zn2+ and Zn(OH)+ [43]. When the pH level reached 10.5, the ZnONP extraction efficiency was at its highest. This could be as a result of ZnONPs' surface's propensity to produce a hydroxyl layer when exposed to alkaline environments, which stops the nanoparticles from further degrading. Additionally, during the CPE method, hydrophobic ZnONPs are more readily transported into the TX-114 phase [44]. This might be as a result of ZnONPs' surface tendency to generate a hydroxyl layer when exposed to alkaline environments, which prevents the nanoparticles from further deteriorating. Hydrophobic ZnONPs are additionally transferred into the TX-114 phase more easily when using the CPE technique [44].


Extraction efficiency (%)
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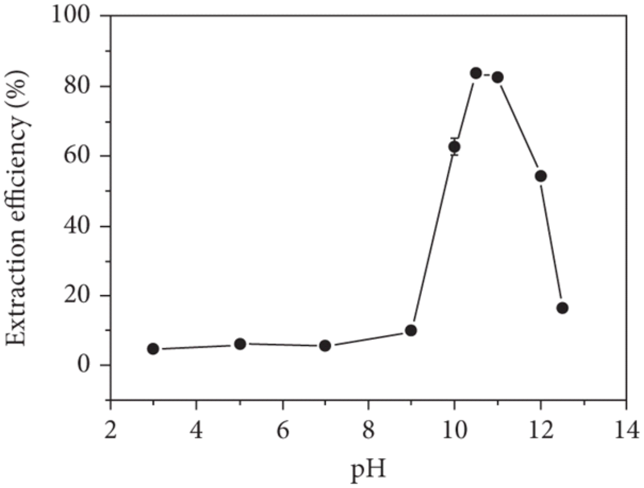
8
10
12
14
pH

(a)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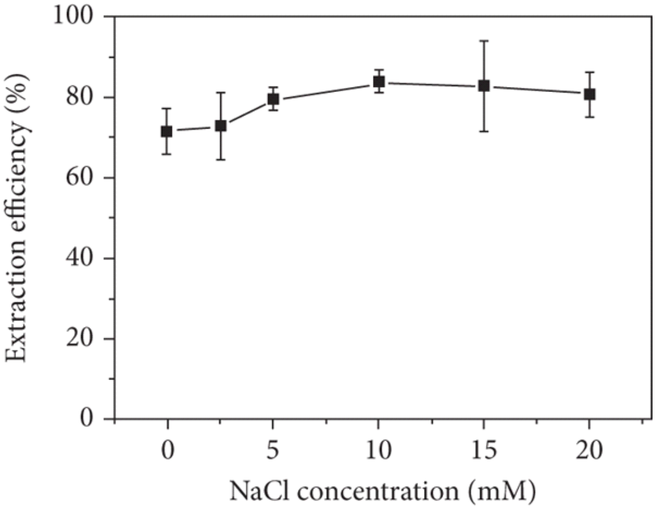
pH

(b)


Extraction efficiency (%)
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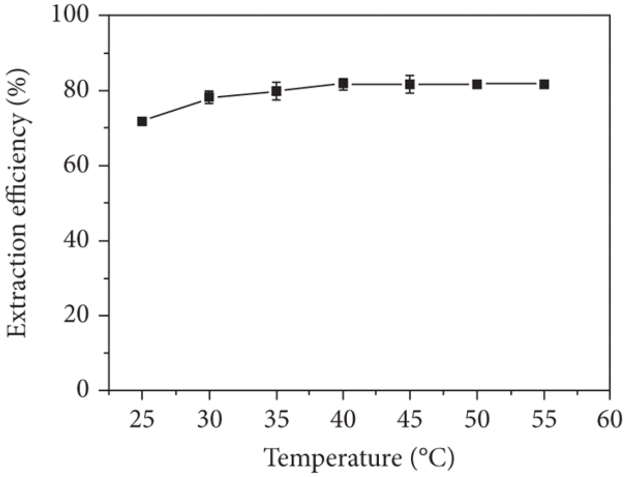
15
20
NaCl concentration (mM)

(c)


Extraction efficiency (%)
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30
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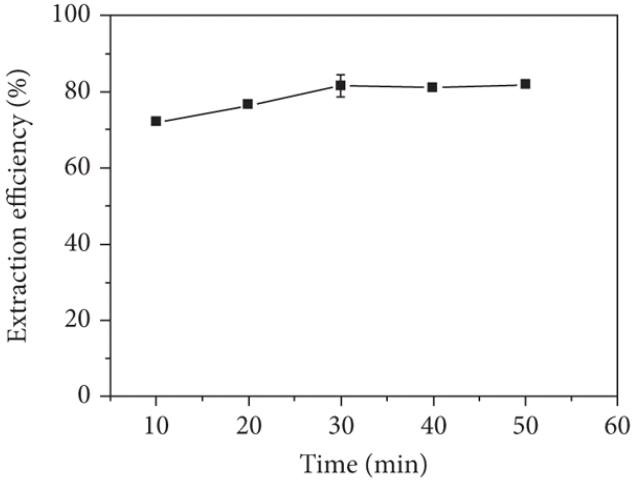
55
60
Temperature (°C)

(d)


Extraction efficiency (%)
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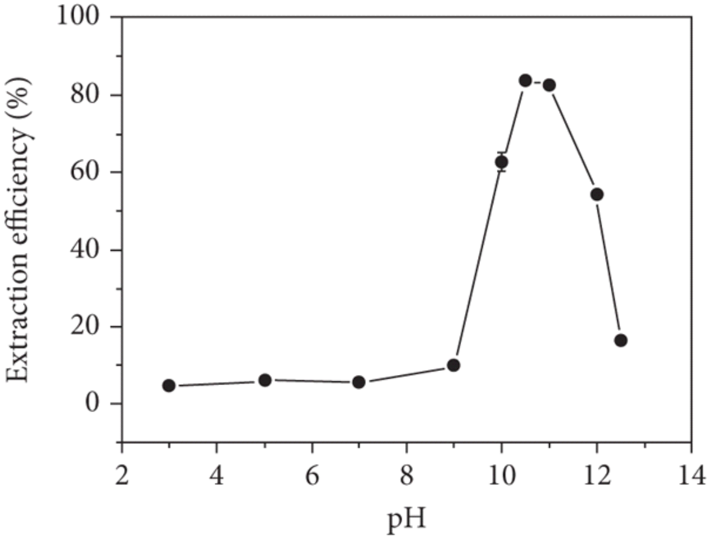
Time (min)

(e)


Extraction efficiency (%)
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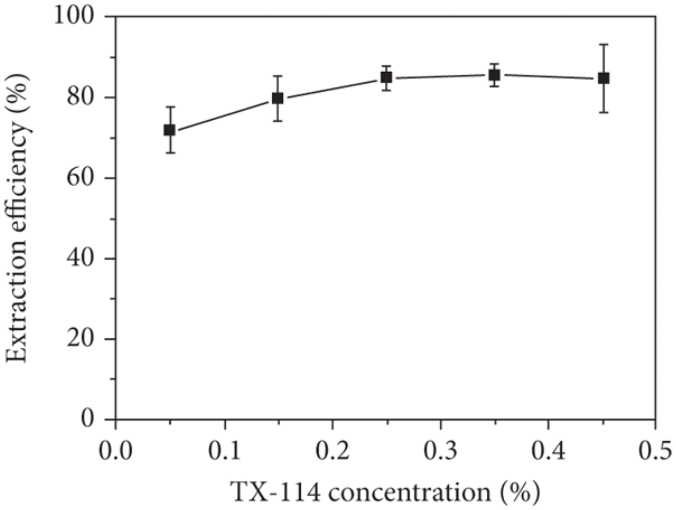
pH

(a)


Extraction efficiency (%)
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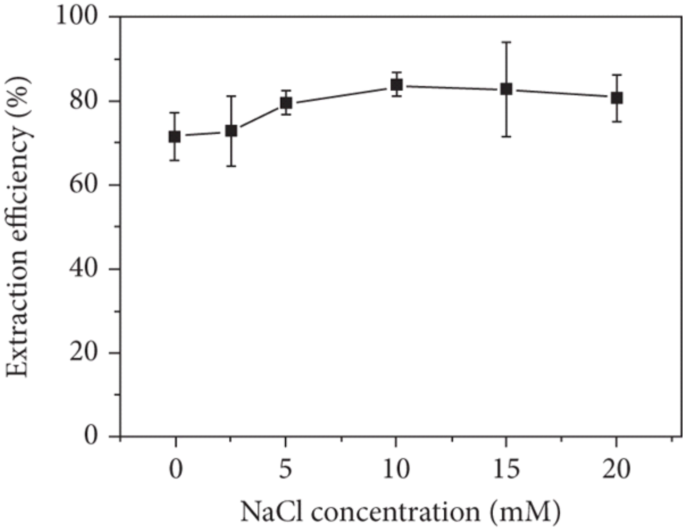
0.4
0.5
TX-114 concentration (%)

(b)


Extraction efficiency (%)
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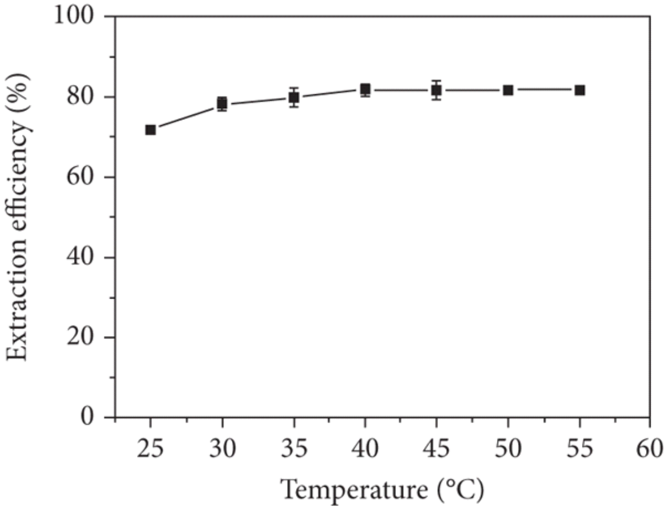
NaCl concentration (mM)

(c)


Extraction efficiency (%)
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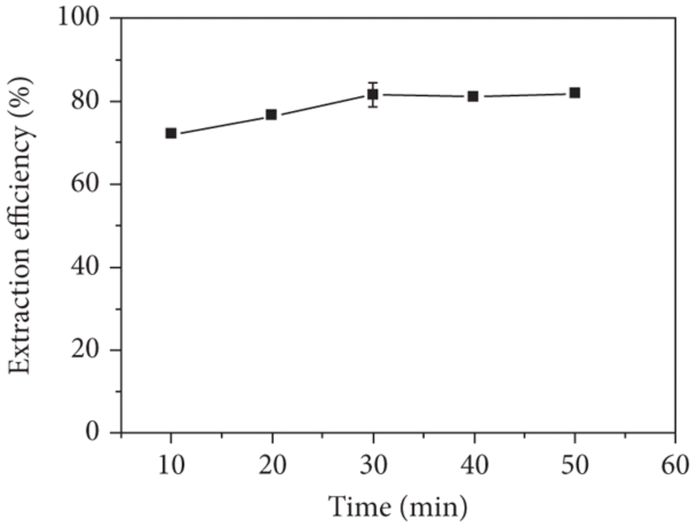
Temperature (°C)

(d)


Extraction efficiency (%)
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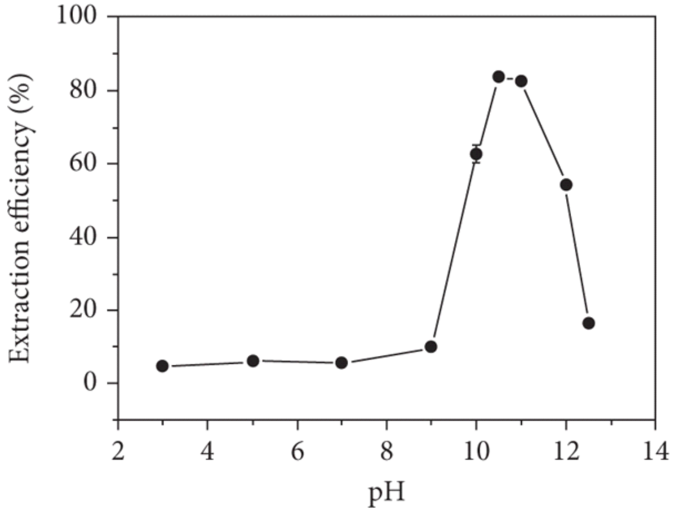
60
Time (min)

(e)


Extraction efficiency (%)
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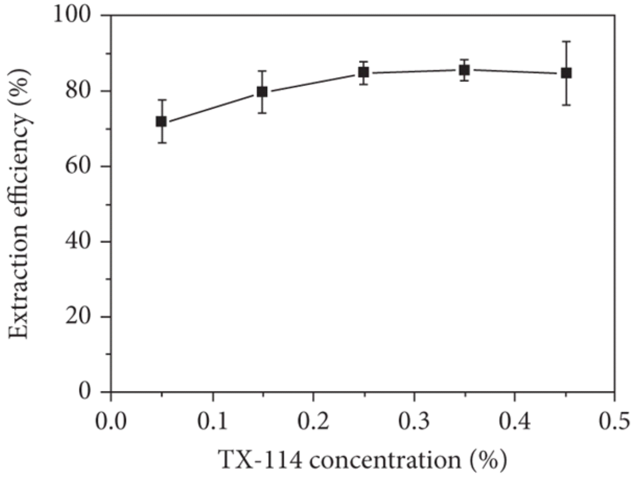
pH

(a)


Extraction efficiency (%)
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80
60
40
20
0
0.0
0.1
0.2
0.3
0.4
0.5
TX-114 concentration (%)

(b)

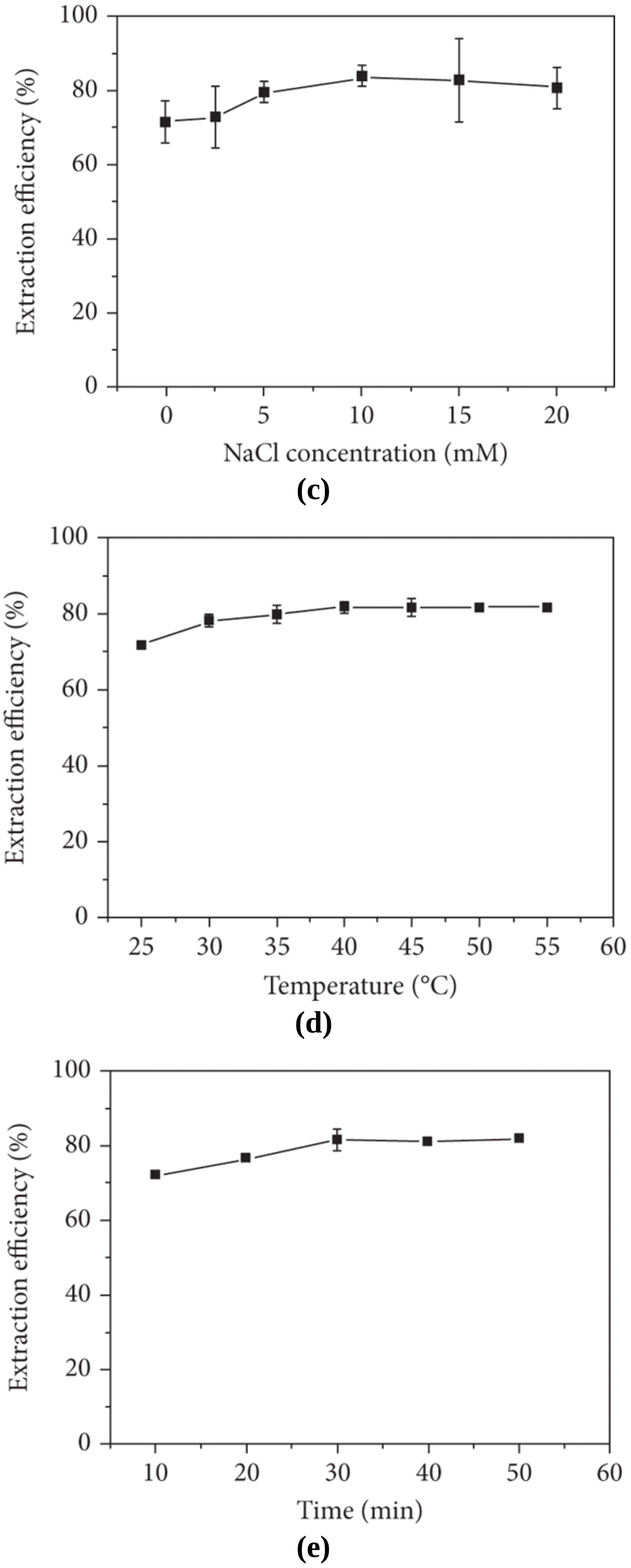

Figure 1. Optimization of CPE factors on the extraction of ZnONPs: (a) pH, (b) TX-114 concentration, (c) NaCl concentration, (d) bath temperature, and (e) equilibrium time ().

3.1.2. Influence of Concentration of TX-114 on the Extraction Efficiency of ZnONPs

Being a nonionic surfactant, TX-114 was unaffected by the anions and cations produced during the CPE process, and the pH of the solution has little impact on TX-114's stability. Additionally, TX-114 has a high density and a relatively low cloud point temperature in the 23–26°C range, which could result in good phase separation[39].Given that TX-114's critical micellar concentration (CMC) is 0.01% (), the surfactant concentration of TX-114 was tuned from 0.05 to 0.45% () to achieve high ZnONP recoveries by the measurement of 200 g/L ZnONPs in water using the CPE-ICP-MS method. Additionally, Figure 1 showed the effects of various TX-114 concentrations on the recoveries of ZnONPs (b). Results indicated that ZnONP recoveries grew slowly when surfactant concentrations ranged from 0.05 to 0.35 percent, then remained stable at 0.45 percent. However, a large TX-114 phase volume would make the sample digestion process more challenging. TX-114 was therefore used as the surfactant in the CPE process for ZnONPs at a concentration of 0.35 percent.

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].Although the surfactant size and aggregation number rise with an increase in ionic strength, the concentration of crucial micellar remains consistent[47].Furthermore, as the high ionic strength of TX-114 micelles could minimise the Coulomb repulsion of the charged metallic nanomaterials, the phase separation could be improved when utilising the CPE approach to extract metallic nanomaterials in an aqueous environment[48].In order to assess the effect of ion strength on the extraction of ZnONPs, NaCl, a common salt, was used in the current investigation. The range of 0 to 20 mM was chosen as the optimal NaCl concentration. Figure 1(c) The current investigation used NaCl, a common salt, to assess the effect of ion strength on the extraction of ZnONPs. As the ideal NaCl concentration, a range of 0 to 20 mM was selected.

3.1.4. Influence of Temperature and Time on the Extraction Efficiency of ZnONPs

The CPE method for the extraction of the analyte may be extremely dependent on temperature and duration [38, 49, 50]. This study investigated incubation temperature (25–55°C) due to the low cloud point temperature of the surfactant (TX–114, 23–26°C).Figure 1(d)demonstrated that the incubation temperature range of 25 to 40°C boosted ZnONP recoveries, and the best ZnONP recoveries were obtained between 40 and 55°C.40°C was chosen as the ideal temperature for the CPE of ZnONPs in waters because higher temperatures have been shown to reduce the connection between ZnONPs and TX-114 micelles [51]. The effects of time between 10 and 50 minutes at 40°C were then discussed. It was demonstrated that ZnONP recoveries increased with time up to 30 min, but then stabilised between 30 and 50 min (see Figure 1(e)).The equilibrium time of 30 min was deemed an adequate factor for the extraction of ZnONPs in the next study in order to shorten the experimental time.

3.2. Species Selectivity of ZnONPs and Zn^{2+} Using CPE Method in Aqueous Solution

According to reports, the presence of their corresponding dissolved component will have an impact on both the qualitative and quantitative characterization of nanoparticles during the ICP-MS determination process [52, 53]. As a result, the separation of ZnONPs and Zn2+ coexisting in environmental water is the main challenge for the detection using the CPE procedure.

In this investigation, dispersions with fixed ZnONP concentrations (200 g/L) and variable Zn2+ concentrations (200–1600 g/L) were premixed, and the separation of ZnONPs and Zn2+ was subsequently carried out under optimal CPE conditions. As shown in Figure 2, the extraction efficiencies of ZnONPs in the mixture of ZnONPs and Zn2+ were in the range of 86-100%, showing that the ZnONPs could be successfully separated from Zn2+ in aqueous solution and extracted into surfactant-rich phase. ZnONP extraction efficiencies ranged from 100 to 224% when the CZn2+ : CZnONPs ratio was between 4 and 8. The high concentration of Zn2+ that was adsorbed on the ZnONPs and then transported into the surfactant phase may be the cause of the ZnONPs' exceptional extraction efficiency [54].

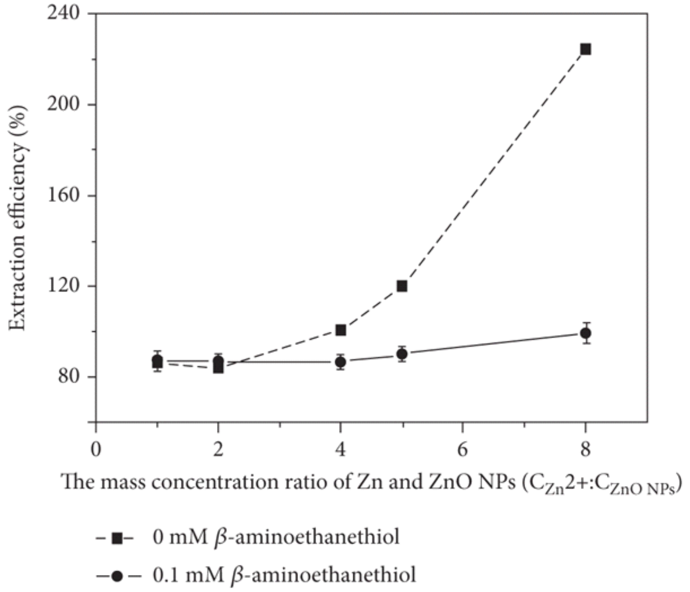

Figure 2 Effect of β-mercaptoethylamine on the separation of Zn^{2+} and ZnONPs using the optimal CPE conditions ().

The complexation reaction between the respective ionic counterparts and the masking reagent would occur during the CPE procedure when the masking reagent was added to the water solution. The complex molecule would still be present in the aqueous solution, potentially reducing the amount of the corresponding ion extracted into the TX-114 phase[55].A stable and evenly disseminated combination of Zn2+ and -Mercaptoethylamine could be formed in the aqueous phase as a masking reagent. The pH of the ZnONP solution, which is necessary for the extraction of ZnONPs by the CPE method, barely changes when a modest amount of -mercaptoethylamine is added compared to EDTA (the pH value of samples was determined using a pH metre). As shown in Figure 2, the addition of 0.1 mM -mercaptoethylamine greatly reduced the recovery of ZnONPs (at the CZn2+ : CZnONPs range of 4 to 8). Furthermore, 99.4% of ZnONPs were recovered at a CZn2+ : CZnONPs ratio of 8, proving that -mercaptoethylamine could successfully interact with Zn2+ while still remaining in the aqueous phase. This leads us to the conclusion that adding 0.1 mM -mercaptoethylamine to the solution containing a high Zn2+ concentration will be a successful method for separating ZnONPs from Zn2+.

3.3. Analytical Performance

This study used ICP-MS to measure the content of Zn2+ following microwave digestion of ZnONPs enhanced in the surfactant phase by the optimised CPE stages. By removing ZnONPs from water, the LOD and accuracy of this proposed strategy were investigated. The LOD of ZnONPs using this CPE-ICP-MS method was 0.06 g/L, which could be computed as three times of SD divided by, where SD was standard deviation determined from the concentration of eleven independent blank samples, and was the slope of the element of Zn2+ calibration curve.For six separate solutions containing 200 and 10 g/L ZnONPs, respectively, the relative standard deviation (RSD) was 1.0% and 4.6%, while the sample recoveries were 81.3% () and 77.2% (), respectively. The requirements for determining ZnONPs in water samples could be met by this low detection limit and good precision.

3.4. Extraction of ZnONPs with Different Sizes Using CPE Method

The effectiveness of extracting ZnONPs with various particle sizes (30 nm, 50 nm, 90 nm, and 35 nm) from water samples was evaluated using the aforementioned optimised CPE settings. Figure 3 showed the recovered ZnONPs in water samples with four different particle sizes; the extraction efficiencies were.It proved that the CPE technique could successfully extract ZnONPs of various sizes into the surfactant phase by optimising it. Therefore, this improved CPE-ICP-MS approach holds promise for locating polydisperse ZnONPs in an aqueous environment.

3.5. Effects of Different Matrices on the Extraction of ZnONPs

Given that the presence of inorganic ions and other engineered nanoparticles widely distributed in environmental waters may 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 primary ions (Ca2+, Mg2+, SO42-, Al3+, Cu2+, Co2+, Mn2+, and Fe3+) and typical engineered nanop.

Potential interference ingredients were present at concentrations that were close to or greater than real water. Table 2 shows that the primary matrix ingredients had a minor impact on the extraction of ZnONPs utilising the CPE-ICP-MS technique. The recoveries of ZnONPs were good in the 1 mg/L of Fe3+ and Mn2+ aqueous solutions, but the extraction efficiency of ZnONPs will drop when significant concentrations of transition metal ions existed in ambient water (data not shown).According to the report of the probable MNP concentration in natural water, 0.10 g/mL, 20 g/mL, and 20 g/mL, respectively, were chosen for this study's AuNP, TiO2NP, and Al2O3NP concentrations.[8]. As shown in Table 4,These three typical engineering nanoparticles showed no effect from the proposed strategy on ZnONP recoveries. In conclusion, the CPE-ICP-MS approach offers an efficient means of detecting ZnONPs quantitatively in the ambient aquatic environment.

3.6. Analysis of Environmental Water Samples

The recovery experiments of ZnONPs with the concentration from 12.57 to 54.68 g/L spiked into the relevant samples of environmental water were investigated to evaluate the real matrices using this proposed technology of CPE-ICP-MSThe detected ZnONP concentration in environmental water samples was in the range of - g/L (Table 5), and the corresponding ZnONP recoveries were in the range of -%, showing that the majority of the ZnONPs spiked into the water samples could be converted into the surfactant phase with this suggested CPE procedure; the recoveries of ZnONPs using the CPE-ICP-MS method were slightly affected by the complex matrix constituents in environmental waters. For removing ZnONPs from environmental water samples, this improved extraction technique works well.

4. Conclusions

In this study, a method for the quantitative detection of ZnONPs in environmental water was developed using cloud point extraction and ICP-MS. In order to test the method's applicability, we systematically improved the extraction conditions for ZnONPs. When used as a masking agent, -mercaptoethylamine might greatly lessen Zn2interference +'s with the extraction of ZnONPs. The usual ambient inorganic ions and ENMs did not have a substantial impact on the CPE strategy. This method's viability for the detection of ZnONPs in environmental water samples was validated by the low detection limit (0.06 g/L) and high recoveries of ZnONPs in environmental water samples (-%) under the improved CPE technique. In conclusion, this well-established approach provided a precise and trustworthy analytical method that might support ZnONP risk assessment in the aquatic environment.

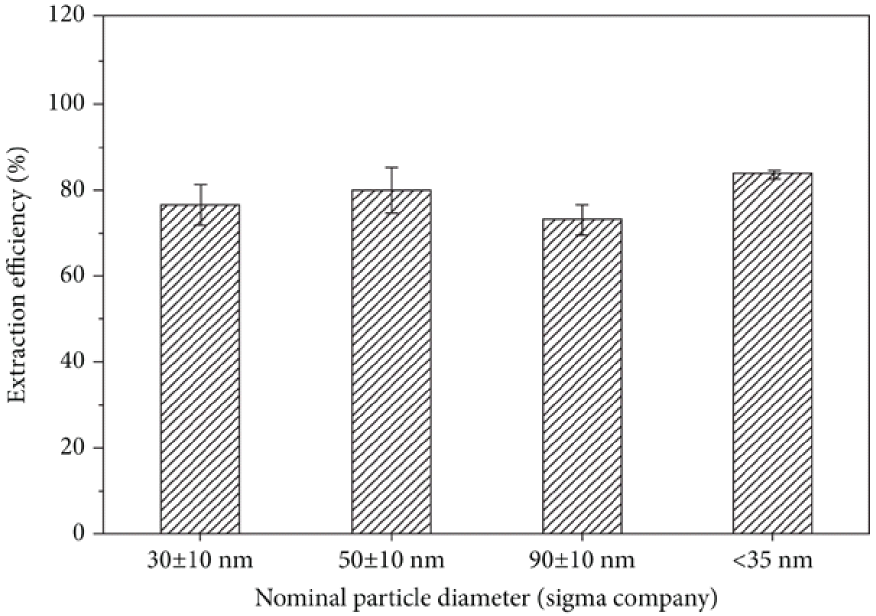

Figure 3 Recoveries of ZnONPs with different particle diameters in water samples ().

3.5. Effects of Different Matrices on the Extraction of ZnONPs

Given that the presence of inorganic ions and other engineered nanoparticles dispersed widely in environmental waters may affect the determination of ZnONPs using the CPE-ICP-MS method, the effectiveness of the extraction of ZnONPs with the CPE-ICP-MS method on the interference of main ions (Ca2+, Mg2+, SO42-, Al3+, Cu2+, Co2+, Mn2+, and Fe3+) .

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