Ultrasound-assisted emulsification dispersive liquid-liquid microextraction for preconcentration and determination of cadmium in natural water samples by spectrophotometric technique

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Abstract

The aim of this work was to study ultrasound-assisted emulsification dispersive liquid-liquid microextraction for preconcentration cadmium in water samples using 4-(2-pyridylazo) resorcinol (PAR) as complexing agent. In the preconcentration step, the amount of 3 mL acetone (dispersive solvent) containing 150 µL of tetrachloroethylene (extraction solvent) was injected rapidly into the sample solution containing cadmium solution, 4.00 mL, 3.0 mmol L⁻¹ of 4-(2-pyridylazo) resorcinol (chelating agent) and 4.00 mL buffer solution pH 10 using a syringe. In this step, the cadmium/PAR complexes were extracted into the fine droplets of tetrachloroethylene. Then, the fine droplets of tetrachloroethylene were emulsified by ultrasonic bath before centrifugation (5 min at 3000 rpm). Finally, the organic phase containing enriched analytes was separated and determined by UV-Visible spectrophotometer. Under these optimum conditions, the limit of detection (LOD) was 0.14 mg/L and limit of quantitation (LOQ) was 0.47 mg L⁻¹ with sensitivity enhancement factor (EF) of 1.26. The proposed method showed the relative standard deviation (RSD) less than 5% and was successfully to apply for the recovery and determination of cadmium in different water samples. The results showed that the three collected samples have cadmium content in the range 0.00 – 0.60 mg L⁻¹ and the percentage recovery was in the range 90.3 – 105.30%.

Keywords: Cadmium, Preconcentration, Dispersive Liquid-Liquid Microextraction

Introduction

Cadmium is one of the toxic element, which could damage organs such as kidneys, liver and lungs, even in minute concentration (Wen, Yang et al., 2011; Sahin and Durukan, 2011). Cadmium is widely use metallurgical alloying, the manufacture of batteries and paints, ceramics, metal plating, photograph development, pigment works and textile printing industries (Sahin and Durukan, 2011). One of the pathways that the cadmium enters human body is through daily intake of water and food, thus the determination of cadmium concentrations in these samples is a great importance. The maximum tolerable level for cadmium(II) in drinking water has been strictly regulated. Recommended cadmium concentration in drinking water by the World Health Organization (WHO) is smaller than 0.005 mg L⁻¹ (Sahin and Durukan, 2011).

Due to low concentration of cadmium in environmental samples, a preconcentration step is generally required prior to determination. Several enrichment procedures have been reported in the
literature for cadmium determination involving different analytical techniques such as solid phase extraction (Tsogas, Giokas and Vlessidis, 2009), cloud point extraction (Silva et al., 2009), single drop extraction (Wen, Deng et al., 2011) and dispersive liquid–liquid extraction (Wen, Yang et al., 2011). In this work, dispersive liquid–liquid extraction (DLLME) was investigated due to its simplicity, easy to operate, rapidness, and high extraction efficiency (Zhou, Zhao and Xie, 2011). DLLME method depends on rapid injection of appropriate mixture of extractant and disperser solvent into the aqueous sample to form a cloudy solution. The cloudy state results from the formation of fine droplets of the extraction solvent which disperse in the sample solution (Wen, Yang et al., 2011; Wen et al., 2012). The cloudy solution is centrifuged and the fine droplets are settled at the bottom of the conical test tube. The analytes of interest are extracted from the initial solution and concentrated to a small volume of the settled phase (Tabrizi, 2010). The analyte in the settled phase can be determined by various analytical techniques such as ETAAS (López et al., 2013), AFS (Zhou, Zhao and Xie, 2011), ICP–OES (Sereshti, Khojeh and Samadi, 2011), FAAS (Rouhollah, Farzaneh and Behrooz, 2011), etc.. Recently, ultrasound–assisted DLLME has been reported (Molaakbari, Mostafavi and Afzali, 2011; Cortada, Vidal and Canals, 2011; Zhang et al., 2012; Berton et al., 2012) and most of them focused on advanced analytical instruments. Therefore, this work will carry out the ultrasound–assisted emulsification dispersive liquid–liquid microextraction (UAE–DLLME) coupled with UV–Visible spectrophotometer for cadmium determination. Because UV–Visible spectrophotometry is simple method and much more cost–efficient. The UAE–DLLME preconcentration technique can considerably improve the analytical performance of ordinary spectrophotometer (Wen, et al., 2012). The effect of various parameters affecting the extraction efficiency such as type and volume of extraction and disperser solvent, pH, extraction time and concentration of the chelating agent was studied and optimized to achieve high recovery.

Materials and Methods

1. Instrumentation and reagent

UV–Visible spectrophotometer model V–650 (Jasco, Japan) was used to analyze the enriched samples. A centrifuge model EBA 3S (HettichZentrifugen, USA) was used to assist phase separation. The ultrasound extraction process was carried out by ultrasonic cleaner model Transsonic 460/H (Elma, Germany). The pH values were measured by pH meter model Eutech instrument pH 700 (thermos Fisher Scientific, Singapore). Cadmium (BDH PROLABO, Belgium) working standard solutions were prepared by appropriate dilutions from standard stock solutions (1000 mg L⁻¹) in deionised water. The 4–(2–Pyridylazo) resorcinol monosodium salt hydrate (PAR) (Fluka, Switzerland) was used as a complexing agent for cadmium and was prepared daily by dissolving the required amount of PAR in deionised water. A potassium dihydrogen orthophosphate (Ajax Finchem,
Australia) and di-sodium hydrogen phosphate (Merck, Germany) buffer solutions were used in the pH range of 3.0–7.0 and the buffer solution in the range of 8.0–11.0 was prepared by using sodium tetraborate (Ajax Finchem, New Zealand) and sodium carbonate (Fluka, Switzerland). All the other reagents including extractants and disperser solvent were analytical reagent grade, as well as the reagents mentioned above.

2. Ultrasound-assisted emulsification dispersive liquid–liquid microextraction procedure

In this work, 10 mL of sample solution containing cadmium adjusted to pH 10 using carbonate buffer was placed in a glass test tube. Then, 4 mL of 3x10^{-3} mol L^{-1} 4-(2-pyridylazo) resorcinol (chelating agent, PAR) was added into the sample solution. In this step, the cadmium ions reacted with the chelating agent to form the related complexes. 3.00 mL of acetone (disperser solvent) containing 150 μL tetrachloroethylene (extraction solvent) was injected rapidly into the sample solution. After the injection, the extraction was accomplished under the effect of ultrasound in an ultrasonic bath for 5 min. A cloudy solution was formed and cadmium ions were extracted into the fine droplets of tetrachloroethylene. Then, the solutions were centrifuged at 3000 rpm for 5 min, and the dispersed fine droplets of tetrachloroethylene were sedimented at the bottom of centrifuge tube. The upper aqueous phase was removed with a syringe, and acetone was adapted to dilute the concentrated samples to 5 mL. Finally, the enriched analytes were determined by spectrophotometer.

3. Sample collection and preparation

All real water samples were collected from the pond, canal and reservoir around the Naresuan University in Phitsanulok province, Thailand, in cleaned polyethylene bottles. All samples were filtered through Whatman No. 42 paper filters after sampling. Then, the proposed method was applied to extraction of cadmium ions from the water samples.

Results and Discussion

1. The study of absorption spectra

The UV–Vis spectrophotometry was used in this work to determine the enriched samples after extraction. The maximum wavelength of the first derivative absorption was investigated in order to eliminate the absorption effect of chelating agent. The complex of Cd–PAR was determined in the range of wavelength between 490 and 600 nm. The absorption spectra are shown in Figure 1. The results showed that the maximum absorption wavelength was 532 nm.

2. Effect of UAE–DLLME parameters

Parameters of the proposed extraction procedure were optimized by univariate method. All analyses were carried out in triplicate and all the parameter results are shown in Table 1.
Figure 1 Absorption spectra of cadmium determination with/without UAE-DLLME.

UAE-DLLME condition: 1.20 mg L\(^{-1}\) Cd, 3.0\(\times\)10\(^{-3}\) mol L\(^{-1}\) PAR, pH 10, ultrasound extraction time 5 min., dilution solvent – acetone. Without UAE-DLLME condition: 1.20 mg L\(^{-1}\) Cd, 3.0\(\times\)10\(^{-3}\) mol L\(^{-1}\) PAR, pH 10.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>studied</th>
<th>optimum</th>
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<tbody>
<tr>
<td>pH</td>
<td>6.5–11.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Extraction solvent</td>
<td>Dichloromethane, Trichloromethane, Tetrachloroethylene</td>
<td>Tetrachloroethylene</td>
</tr>
<tr>
<td>Volume of Extraction solvent (µL)</td>
<td>50–200</td>
<td>150</td>
</tr>
<tr>
<td>Disperser solvent</td>
<td>Methanol, Ethanol, Acetone</td>
<td>Acetone</td>
</tr>
<tr>
<td>Volume of disperser solvent (mL)</td>
<td>1.0–5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>PAR concentration (mol L(^{-1}))</td>
<td>0.10(\times)10(^{-3})–5.00(\times)10(^{-3})</td>
<td>3.00(\times)10(^{-3})</td>
</tr>
<tr>
<td>ultrasound extraction time (min)</td>
<td>0–10</td>
<td>5</td>
</tr>
<tr>
<td>centrifugation time at 3000 rpm (min)</td>
<td>1–15</td>
<td>5</td>
</tr>
<tr>
<td>Dilution solvent</td>
<td>Methanol, Ethanol, Acetone, Pure water</td>
<td>Acetone</td>
</tr>
</tbody>
</table>

3. Interferences

Many metal ions existing in natural waters would form stable chelating complexes with PAR within the wide range and may be co-extracted along with analytes. This could decrease the extraction efficiency. Therefore, the experiments have been designed using standard solution of 1 mg L\(^{-1}\) Cd(II) under the above optimized conditions. The effect of each species was considered to be interference when the signal in the presence of the species resulted in an absorbance deviation of more than \(\pm\) 5%. The results showed that less than 100 \(\mu\)g L\(^{-1}\) of Mg(II) and Zn(II) and up to 500 \(\mu\)g L\(^{-1}\) of Ca(II) and Pb(II) did not cause interference in the determination of Cd(II). Thus, the pH for the determination of Cd(II) must be strictly controlled to enhance its specificity, coupled with using a solution containing phosphate and citrate to mask several interferences [Klamtet, Suprom and Wanwat, 2008].
4. Analytical Performance

The analytical performance of UAE–DLLME couple with UV–Visible spectrophotometry for preconcentration and determination of Cd in natural waters was investigated under the optimal conditions. The results indicated that linear calibration graph was in the range 0.20–1.40 mg L⁻¹ (A = 0.0091C Cd + 0.0039 r² = 0.9902). The precision of this method was 4.50% (RSD, n=7) at the spiked concentration of 0.80 mg L⁻¹. The limit of detection (LOD), which is defined as the concentration corresponding to three times the standard deviation of the blank samples, was 0.14 mg L⁻¹ and the limit of quantitation (LOQ) was 0.46 mg L⁻¹. The enrichment factor, obtained from the slope ratio of the calibration graph after and before the extraction, was 1.26 for 10 mL of the sample solution.

5. Analysis of real water samples

In order to demonstrate the applicability and reliability of the proposed method for real samples, three natural water samples were collected. The analytical results are given in Table 2. These results showed that the recovery of spiked samples were in the acceptable range (90.3–105.3%).

Conclusion

The ultrasound-assisted emulsification dispersive liquid–liquid microextraction method was developed for preconcentration and determination of cadmium in water samples coupled with spectrophotometry. The results demonstrated that the proposed method is simple, rapid, sensitive, cost effective and low consumption of organic solvents. The proposed method showed good limit of detection with the enhancement factor of 1.26. The developed method was applied to the determination of real samples with a satisfactory analytical results.

Table 2 Analytical results for cadmium determination in real samples (Avg. ± SD, n=3)

<table>
<thead>
<tr>
<th>Real sample</th>
<th>Added (mg L⁻¹)</th>
<th>Found (mg L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0</td>
<td>0.36 ± 0.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.57 ± 0.16</td>
<td>105.3 ± 9.0</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0</td>
<td>0.11 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.31 ± 0.04</td>
<td>100.1 ± 0.5</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0</td>
<td>0.19 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.37 ± 0.03</td>
<td>90.3 ± 10.1</td>
</tr>
</tbody>
</table>

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References


