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A green and efficient in-syringe ionic liquid-based single step microextraction procedure for preconcentration and determination of cadmium in water samples

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ABSTRACT

An in-syringe ionic liquid-based single step microextraction has been analytically presented. 1-butyl-3-methylimidazolium hexafluorophosphate as extractant and Triton X-100 as dispersing medium were used. Cd-Dithizone was extracted within a syringe. The effects of some variables such as $[C_4mim][PF_6]$ volume, pH, TX-100 volume, dithizone concentration, incubation time, diluents nature and matrix effect were investigated. The limit of detection and preconcentration factor were found as 0.35 $\mu g\ L^{-1}$ and 50, respectively. The validity was checked by using certified reference materials. The relative standard deviation (RSD) was 4.2%. The method was satisfactorily applied to preconcentration of cadmium in natural water samples.

Introduction

Nowadays a great concern to Cadmium because it contaminated different environmental sources including natural waters. In many parts of the world, cadmium induced water pollution is causing serious ecological problems [1–3]. The cadmium toxicology has been associated with lots of disease like kidney and heart problems [4–9]. Consequently its determination in trace level in aqueous media have become a matter of importance, but because of complex template and generally low concentration of cadmium it is not easy in water samples and thus a separation-enrichment step is required [10].

Despite the valuable advances developed in separation science, a number of techniques that differ in extraction performance have been derived from traditional liquid–liquid microextraction (LLME) [11,12] are still widely used for sample treatment. LLME is based on the dispersion of extractant into the sample to increase the contact area between the extractant and the solution, thus the equilibrium state can be achieved earlier [13,14]. The use of liquid–liquid microextraction (LLME) coupled with other techniques i.e. mass spectrometry, liquid chromatograhy etc. for organic molecules at trace levels were also very popular [15–19].

The search for new solvents is a new trend in LLME evolution. Ionic liquids (ILs) [20,21] have attracted much attention taking into account their special features like: low-vapour pressure, high viscosity, dual natural polarity and a wide range of miscibility with water and other organic solvents [20–25].

A novel extraction procedure alternative which avoids usage of lethal organic solvents, thermal dispersion and especially centrifugation step for cadmium at trace levels in real samples has been established in this work. The proposed procedure was termed as in-syringe ionic liquid based single step microextraction.

Materials and methods

Reagents and solutions

All solutions were made through reverse osmosis purified water. All reagents used were analytical grade. Concentrated nitric acid (HNO_3, purity 65%) and ethanol were obtained from Merck (Germany) and Sigma Aldrich (St. Louis, USA), respectively.

Standard solution of Cd^{2+} was prepared by the dilution of stock solution (1000 mg/L) (Merck, Darmstadt, Germany). Dithizone was obtained from Riedel de-Heden (Sleeze, Germany) and its 0.1% (w/V) solution was prepared by dissolving 0.1 g in 100 mL of methanol.

1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), nonionic surfactant Triton X-100 and methanol were

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purchased Merck, Darmstadt, Germany. Triton X-100 is obtained from Riedel de-Heden (Sleeze, Germany). Triton X-100 solutions are prepared in methanol. The buffer solutions given in the literature [26] were used in the presented work.

Instrumentation

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) was used for metal analysis. All measurements were carried out in an air/acetylene flame. The operating parameters were set as recommended by the manufacturer. The final solutions contain of cadmium were injected to the nebulizer of the flame atomic absorption spectrometer by using the micro injection method. In the micro injection method, 100 μL of the samples were injected to a mini home-made Teflon funnel that was connected to the nebulizer with capillary tubing with an Eppendorf pipette. The peak height signals were recorded.

A pH meter, Nel pH-900 (Ankara-Turkey) Model glass-electrode was employed for measuring pH values in the aqueous phase. The pure water used in all experiments was purified in a Human model RO 180 (HUMAN Corp., Seoul, Korea), resulting water with a conductivity of 1 μS/cm.

Sample collection

Water samples were collected from Lake Camlik, Yozgat, from industrial effluent sites of Kayseri and from our research laboratory. The samples were taken by using plastic bottles (1.5 L capacity) which were soaked in 10% nitric acid for 24 h and before use rinsed with ultra pure water. The samples were filtered through a 0.45 μm pore size membrane filter (Millipore Corporation, Bedford, MA, USA) and were stored at 4 °C.

In-syringe ionic liquid based single step microextraction procedure

In proposed simple and rapid extraction system uses a 10 mL plastic syringe as extraction unit, a 1 mL plastic for the injection of the extractant/disperser mixture and for recovery of extractant. For Cd^{2+} preconcentration, 10 mL aliquots of model solution containing 10 μg of Cd^{2+} whose pH was adjusted with appropriate volume of desired buffer is sucked in the 10 mL syringe by means of its needle and 1 mL of chelating agent was added. After spraying 500 μL of 0.05% (v/v) TX-100 by using the 1 mL plastic syringe, a cloudy solution was immediately formed. At this stage 100 μL of extractant [C_4mim][PF_6] is added and slightly shook to disperse the IL. Afterward, the piston of the 10 mL syringe was slowly moved to the initial point, which allowed the recovery of IL from syringe wall and its lower part whereas the aqueous phase is removed. At last, the IL phase with analyte was easily recovered from the tip of syringe. Added 0.2 mL of acidic diluent in order to decrease the viscosity ionic liquid phase, and 100 μL sample solution was aspirated into FAAS nebulizer using microinjection system. A blank also submitted to the same procedure.

Results and discussion

Effect of pH

The pH plays an idiosyncratic role on metal-chelate formation and subsequent extraction [27–32]. In the presented work, dithizone was selected as chelating agent for the complexation of Cd^{2+} (Fig. 1.) The effect of pH on microextraction procedure of Cd^{2+} was investigated at the pH range of 4.0–10.0. The results illustrated in Fig. 2. The quantitative recovery of Cd^{2+} was obtained at pH 9.0. Phosphate buffer of pH 9.0 was chosen for all further works.

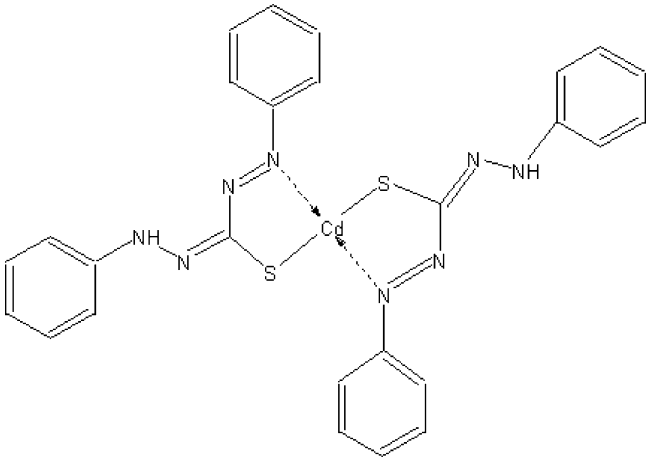

Fig. 1. The structure of Cd^{2+}–Dithizone complex.

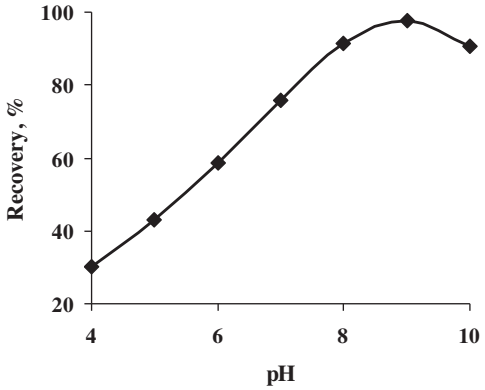

Fig. 2. Effect of pH on the % recovery of Cd^{2+} (μg/L).

Effect of IL volume

[C_4mim][PF_6] was chosen as the extraction solvent due to its good thermal stability, hydrophobicity and negligible vapour pressure. The influences of volume of ionic liquid were investigated in the range of 60–250 μL (Fig. 3). The recovery value of the analyte was affected by ionic liquid volume. The quantitative recoveries of analyte were obtained with 100 μL of ionic liquid. 200 μL of IL was found to be optimum.

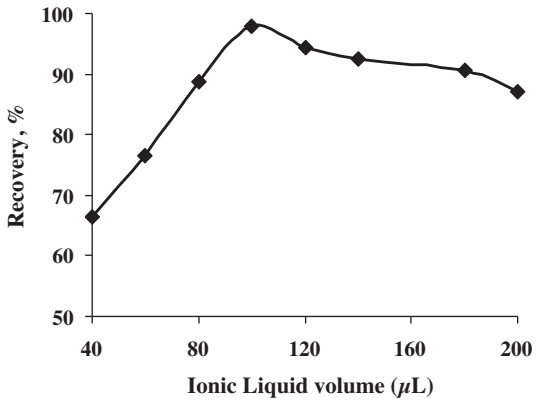

Fig. 3. Effect of IL on the % recovery of Cd^{2+} (μg/L).