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Preparation and characterization of magnetic carboxylated nanodiamonds for vortex-assisted magnetic solid-phase extraction of ziram in food and water samples

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ABSTRACT

A simple and rapid vortex-assisted magnetic solid phase extraction (VA-MSPE) method for the separation and preconcentration of ziram (zinc dimethyldithiocarbamate), subsequent detection of the zinc in complex structure of ziram by flame atomic absorption spectrometry (AAS) has been developed. The ziram content was calculated by using stoichiometric relationship between the zinc and ziram. Magnetic carboxylated nanodiamonds (MCNDs) as solid-phase extraction adsorbent was prepared and characterized by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD) spectrometry and scanning electron microscopy (SEM). These magnetic carboxylated nanodiamonds carrying the ziram could be easily separated from the aqueous solution by applying an external magnetic field; no filtration or centrifugation was necessary. Some important factors influencing the extraction efficiency of ziram such as pH of sample solution, amount of adsorbent, type and volume of eluent, extraction and desorption time and sample volume were studied and optimized. The total extraction and detection time was lower than 10 min. The preconcentration factor (PF), the precision (RSD, $n=7$), the limit of detection (LOD) and limit of quantification (LOQ) were 160, 7.0%, $5.3 \mu\text{g L}^{-1}$ and $17.5 \mu\text{g L}^{-1}$, respectively. The interference of various ions has been examined and the method has been applied for the determination of ziram in various waters, foodstuffs samples and synthetic mixtures.

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1. Introduction

Dithiocarbamates (DTCs) are widely used to control approximately 400 pathogens of more than 70 crops because of broad spectrum of antifungal activity and are registered in all the EU member states and many other countries [1,2]. They are also used as fungicide in fabrics, linen, paints, painted paper, leather, wood and plastic surfaces [3]. Direct effect of exposure to these fungicides can induce allergy to skin, asthmatic phenomena, and inflammation of eyes and respiratory tract in humans. Long-term exposure can also cause functional changes in the cardiovascular system [4–8]. Due to adverse effects of DTCs for human life and for environment, the rapid and accurate determination of DTCs environmental samples have become of increasing significance for chemists [9,10].

Flame atomic absorption spectrometry (FAAS) is an important technique for determination of trace zinc in environmental samples especially in natural waters due to its simplicity and its lower

price than other instruments for determinations [11,12]. In recent years, some organic compounds and analgesic-inflammatory drugs have been analyzed by using AAS indirectly [13–18]. Cassella et al. have analyzed zineb by flow injection atomic absorption spectrometry in commercial formulations of pesticide [18]. Türker and Sezer have used to flame atomic absorption spectrometry for indirect determination of maneb in some foods and drug formulations [19]. Agarwal et al. have used to visible spectrophotometry and by flame atomic absorption spectrometry for determination of ziram and zineb residues in fog-water samples [20]. Blas et al. have developed a new method for the indirect determination of organophosphorus pesticides by coupling flow injection analysis and atomic absorption spectrometry with hydride generation [17]. Jiang et al. have described an indirect flame atomic absorption spectrometric determination of ascorbic acid based on its reducing action to Fe(III) [14].

A number of preconcentration techniques such as solid phase extraction (SPE), liquid-liquid extraction (LLE), cloud point extraction (CPE) and coprecipitation have been developed for the trace determination of metal complexes from aqueous samples [21–31]. Among these procedures, the most commonly used

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method is solid phase extraction method, which has several advantages: high preconcentration factors, simplicity of phase separation and suitability for automation, minimized costs, organic solvent usage and exposure and extraction time for sample preparation [32,33].

Sorbents, such as active carbon [33], C_{18} or C_8 silica [34] different types of polymers [35], modified resin [36] and nano materials [37], have been used. Among these sorbents, nanomaterials have attracted great attention due to their special properties that result from the combination of their small size, chemical composition and surface structure. One of the most interesting properties is that the high surface area of nanomaterials provides high adsorption capacity for inorganic and organic compounds [38–40].

Nanodiamonds (NDs) have excellent mechanical properties, tunable surface structures and high surface areas. Nanodiamonds also non-toxic, which makes them well suited to chemical applications. For example, the theoretical surface area of nanodiamonds is about $450 \text{ m}^2/\text{g}$, which makes it potential superior adsorbents [40–42].

Magnetic nanoparticles, as a new kind of nanometer-sized material, are widely used in the fields of chemistry and medicine such as cell and DNA separation, drug delivery system, magnetic resonance imaging (MRI) and bio-separation. Moreover, these nanoparticles are known to be capable of sorption of some organic and inorganic compounds [43]. Uses of them have become increasingly popular for the development of magnetic extraction methods due to the advantages of easy control and simple separation. These particles can be collected by an external magnetic field. These suspended superparamagnetic particles adhered to the target can be removed very quickly from sample solution by using a magnetic field [44,45]. The magnetic extraction method is not only convenient, economical and highly efficient, but it also eliminates disadvantages of conventional solid phase extraction, (e.g., packing of sorbent into the column and time-consuming loading of large-volume samples) [5,46]. The best of my knowledge there is no work on the usage of magnetic carboxyl modified nanodiamonds for separation and preconcentration of the organic and inorganic analytes at trace levels.

In this study, magnetic carboxyl modified nanodiamonds (MCNDs) were synthesized, characterized and used as a magnetic solid phase extraction adsorbent for the separation and preconcentration of trace amounts of ziram (Zinc bis (dimethyldithiocarbamate), pesticide, from various water, foodstuff samples and synthetic mixtures prior to its indirect flame atomic absorption spectrometric detection.

2. Experimental

2.1. Instrumentation

The pH measurements were made with A Sartorius PT-10 model digital pH meter. Vortex mixer (VWR international model, Germany) was used for thorough mixing of solutions. An ultrasonic bath (Sonorex) was used in the synthesis step of magnetic carboxylated nanodiamonds. A Perkin-Elmer Analyst 300 atomic absorption spectrometer coupled with micro sampling system used for the determination of zinc in ziram. This system consists of a mini home-made Teflon funnel with an Eppendorf Pipette, which connected to the nebulizer of the FAAS. In this system, a $100\text{-}\mu\text{L}$ amount of the sample solutions were injected to the nebulizer of the FAAS by using the micro sampling system [47]. The FT-IR spectra of the pure carboxylated nanodiamonds and magnetic carboxylated nanodiamonds were recorded on a Perkin-Elmer Spectrum 400 Fourier Transform Infrared spectrometer (Waltham, MA, USA). X-ray diffraction (XRD) spectrum

measurements for carboxylated nanodiamonds and magnetic carboxylated nanodiamonds were performed using a Bruker AXS D8 advanced diffractometer. Scanning electron microscope (SEM) images were obtained on a LEO 440 SEM with an accelerating voltage of 20 kV.

2.2. Chemicals and reagents

Unless otherwise stated, all water is (18 $\text{M}\Omega$ cm, resistivity) pure water purified with a Milli-Q system (Millipore, USA) and all reagents used were of analytical grade. Nanodiamonds (Sigma-Aldrich No: 636,428-1G) were purchased from Sigma Aldrich, (St. Louis MO, USA). Nitric acid, acetone, acetonitrile were obtained from Merck (Darmstadt, Germany).

Ziram, Ferbam, diethyldithiocarbamate and dimethyldithiocarbamate were obtained from Sigma Aldrich Co. (St. Louis MO, USA). Stock solutions (200 mg L^{-1}) of these dithiocarbamates were prepared by dissolving 20 mg of each compound in convenient solvent and diluting to 100 mL with distilled water in a calibrated flask. Standard solutions were prepared by appropriate dilutions with water. The phosphate buffer solutions for pH 4.0–7.0 and ammonium/ammonia buffer solutions for pH 8.0–9.0 were prepared and used to adjust of pH of sample solutions.

2.3. Synthesis of magnetic carboxylated nanodiamonds

The synthesis of MCNDs consists of main two step: (a) Surface functionalization of nanodiamonds with carboxyl group and (b) Gaining magnetic feature of the carboxylated nanodiamonds.

- In this procedure [48], 0.5 g of as-received pristine nanodiamonds were treated with 60 mL of strong acid (98% H_2SO_4 and 70% HNO_3 at a ratio of 3:1) in a sonication bath (Model 2510, Branson). The mixture was poured into 90 °C hot water and stirred for 10 h. This oxidizing procedure generates carboxylated nanodiamond compounds, $\text{ND}-(\text{COOH})_n$. After filtration, the carboxylated nanodiamond particles were washed with distilled water and ethanol until the pH 7.0 and these particles were dried in an 80 °C oven for 4 h.
- The magnetic carboxylated nanodiamond particles have obtained by using Fe_3O_4 , which are attached to the carboxylated nanodiamonds only by physical adsorption or electrostatic interaction. The magnetic nanoparticles (MNPs) were prepared according to literature [37]. In this synthesis procedure: Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.745 g) and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (0.383 g) were dissolved in 50-mL deionized water under argon gas with vigorous stirring in a 100 mL round bottom flask at 85 °C. Carboxylated nanodiamond particles were added in the solution. Then, 20 mL of 30% ammonium hydroxide were slowly added to the solution. The color of bulk solution changed from orange to black immediately. At this stage, magnetic nanoparticles were obtained. The mixture was stirred for 30 min at 85 °C. The magnetic carboxylated nanodiamonds were collected by the magnet and thoroughly washed with distilled water and ethanol to remove excess amounts of ammonium hydroxide. It was dried in an oven at 80 °C for 24 h.

2.4. Vortex-assisted magnetic solid phase extraction method

A vortex-assisted magnetic solid phase extraction (VA-MSPE) method was performed for spiking the working standard or sample solution (10 mL) that contain 5 μg ziram and 2 mL of pH 6.0 phosphate buffer solution. 25 mg of the magnetic carboxylated nanodiamonds (MCNDs) were added to the solution and the solution was mixed for 2 min on vortex mixer to facilitate adsorption of the ziram onto the MCNDs. Then, the magnetic adsorbent was

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