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A novel *N*,*N*′-bis(acetylacetone)ethylenediimine functionalized silica-core shell magnetic nanosorbent for manetic dispersive solid phase extraction of copper in cereal and water samples

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ABSTRACT

Determination of heavy metals at trace levels has a great deal of importance due to their undesirable effects on human life. In this study, N,N′-bis (acetyl acetone) ethylenediimine (Fe_3O_4@SiO_2-EDN) was synthesized and applied for dispersive solid phase extraction of copper in water and cereal samples followed by FAAS. Sorbent characterization was investigated by SEM, FT-IR, EDX and VSM. The effective parameters were optimized using a central composite design. Under the optimal conditions, LOD (S/N = 3) and LOQ, preconcentration factor and RSD% were found to be 1.5 ng mL^{-1}, 4.0 ng mL^{-1}, 13 and 2.3%, respectively. The calibration curve was linear within the range of 4.0–175 ng mL^{-1} with $r^2 > 0.998$. Relative recoveries were achieved within the range of 90.0–95.0%. With thanks of the good resulting analytical performance in this work, the proposed method can be applied as a suitable alternative for trace analysis of copper.

1. Introduction

Pollution by heavy metals has attracted a considerable attention because they severely threat the human health and natural ecosystem (Bosch, O'Neill, Sigge, Kerwath, & Hoffman, 2016; Daşbaşı, Saçmacı, Çankaya, & Soykan, 2016; Gouda & Al Ghannam, 2016). However, some heavy metal ions like copper, cadmium and zinc are essential at trace levels (Asgharinezhad, Ebrahimzadeh, Rezvani, Shekari, & Loni, 2014; Mashhadizadeh, Amoli-Diva, Shapouri, & Afruzi, 2014). For example, copper is a basic element in nature and known as indispensable micronutrient at low doses due to its important role in biochemistry of every living organisms and normal biological growth (Ali, Ibrahim, Sulaiman, Kamboh, & Sanagi, 2016; Xiang, Ma, Jiang, & Mao, 2014). But the long-term exposure to low concentration of copper and gradual accumulation in living organism over their life can cause serious problems and negative impact on the human health such as bladder, brain, liver, kidney damage; various neurodegenerative disease like Alzheimer and Parkinson (Ali et al., 2016; Behbahani et al., 2014; Tobiasz & Walas, 2014; Wadhwa, Tuzen, Kazi, Soylak, & Hazer, 2014).

Assuming the risk of generalization, compared with the other quantification techniques, flame atomic absorption spectrometry (FAAS) is superior for determination of the heavy metals at trace levels due to several advantages such as simple application, accessibility, good precision and lower cost. However, the direct, sensitive, accurate and repeatable determination of heavy metal ions at trace levels in the most environmental and food samples is a difficult task due to their presence at low concentration and complexity of the matrices (Daşbaşı et al., 2016; Ibarra, Miranda, Rodriguez, Nebot, & Cepeda, 2014). Therefore, it needs to apply simple, inexpensive, eco-friendly, highly sensitive and selective sample preparation techniques before the final analysis (Bagheri, Afkhami, Saber-Tehrani, & Khoshsafar, 2012; Pourreza & Naghdi, 2014).

The popular choice to overcome this shortcoming is coupling of the FAAS technique with different preconcentration techniques like liquid-liquid extraction (El Hussaini & Rice, 2004), co-precipitation (Atanassova, Stefanova, & Russeva, 1998), cloud point extraction (Lemos, Santos, David, Maciel, & de Almeida Bezerra, 2008) and solid phase extraction (SPE) (Venkatesh & Singh, 2005). Among these techniques, SPE is the most preferred method because it benefits from important advantages including high recovery and enrichment factors, simplicity and high speed, low organic solvent consumption, being ecofriendly, time saving, low cost and low toxicity.

At present, nanoparticles (NPs) have been extensively developed and used in different research fields such as separation sciences (Henglein, 1989) and chromatographic separations due to their special characteristics including extremely small size and high surface-area-to-volume ratio. Also, NPs contain highly active surface sites that provide a tremendous driving force for diffusion and consequently, high mass

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transfer and short separation time (Ozmen et al., 2010). Among various types of NPs, magnetic NPs (MNPs) with the general formula of MFe_2O_4 (where M = Fe, Co, Cu, Mn, *etc.*), mainly magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), have been widely utilized in SPE procedure due to benefits of easy preparation and high-efficiency production, simple separation and lower prices (Aguilar-Arteaga, Rodriguez, & Barrado, 2010; Bagheri et al., 2012). Fe_3O_4 nanoparticles with paramagnetic properties tagged with target species, can be easily separated from the aqueous medium or complex matrices with the aid of an external magnet and do not require any filtration or centrifugation.

However, the magnetic property and dispersibility of the MNPs could be affected by the surrounding environment as well as aggregation possibility. Thus, a suitable protective coating on a magnetic core is often used *via* specific modification of chemical functional group on their surface (Chen & Zhu, 2016). For this purpose, different strategies can be used such as surfactant steric stabilization, shifting the isoelectric point with citric acid, utilization of chitosan, silica, carbon *etc.* (Aguilar-Arteaga et al., 2010; Ali et al., 2016; Sun et al., 2005). Among these, silica is an excellent coating material for MNPs because it has several advantages such as stability in acidic mediums, biocompatibility, high thermal resistance, low cost and easy surface modification due to abundance of surface hydroxyl groups (Xie, Jiang, Zhu, Liu, & Ouyang, 2014; Zhao, Shi, Wang, Cai, & Jiang, 2008).

In this work, a novel magnetic nanosorbent based on N,N′-bis (acetylacetone)ethylenediimine (EDN) functionalized silica-core shell Fe_3O_4 was synthesized for dispersive solid phase extraction (DSPE). The sorbent was used for rapid separation, preconcentration and determination of Cu^{2+} at trace levels in food (cereals) and water samples followed by FAAS determination. Experimental design and response surface methodology were applied to optimize different parameters affecting the extraction efficiency.

2. Experimental

2.1. Apparatus

Copper measurement was carried out by a flame atomic absorption spectrometer (GBC Scientific Equipment, Australia) equipped with a hollow cathode lamp for copper as a radiation source, a deuterium background corrector and an air-acetylene flame. The flame composition was operated according to optimum operation conditions recommended by the manufacturer (wavelength 324.7 nm, spectrum bandwidth 0.5 nm, lamp current 3 mA, the flow rate of acetylene 1600 mL min^{-1}). The pH values were controlled with a Metrohm model 827 pH meter (Herisau, Switzerland) with a combined pH glass electrode. A magnet (Nd–Fe–B, 60 mm × 3 mm × 10 mm) was used for the magnetic separation.

Infrared spectra (4000–400 cm^{-1}) in KBr were recorded by a ABB Bomem MB102 IR spectrophotometer (Québec, Canada). The size, morphology and structure of the nanoparticles were observed by a EM3200 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX) analyzer from KYKY Zhongguancun (Beijing, China). The magnetic characteristics of Fe_3O_4 and Fe_3O_4@SiO_2-EDN were evaluated by a vibrating sample magnetometer (VSM), model AGFM/VSM 3886 (Kashan, Iran), at room temperature in a magnetic field strength of 1 T. An ultrasonic water bath (Bandelin sonorex, 80 Hz, 250 V) was used to disperse the magnetic sorbent in solution. A Uniscope muffle furnace (model SM 9080, Surgifriend Medicals, England) was used for dry ashing of the cereal samples .Whatman filter paper (Whatman Inc., Clifton, NJ, USA) was used for sample filtering.

2.2. Standard solutions and reagents

Analytical grade chemicals and ultrapure water were used throughout this work. A 1000 mg L^{-1} stock solutions of Cu(II) was prepared by dissolving an appropriate amount of $Cu(NO_3)_2$ in 1% HNO_3. The other working solutions were freshly prepared by diluting of the stock solution with ultrapure water. All used glasswares were cleaned by soaking in dilute HNO_3 (1:5) for 24 h and later washed with ultrapure water. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$), tetraethyl orthosilicate (TEOS), acetylacetone, sodium hydride, toluene, tetrahydrofuran (THF), 3-chloropropyltrimethoxysilane (CPTMS), ethylenediimine, sodium hydroxide, sulfuric acid, nitric acid, hydrochloric acid, ethanol and hydrogen peroxide were purchased from Merck (Darmstadt, Germany).

2.3. Synthesis of Fe_3O_4@SiO_2-EDN sorbent

2.3.1. Preparation of Fe_3O_4 magnetic nanoparticles

For preparation of Fe_3O_4 nanoparticles (Sadeghi, Seidi, & Ghasemi, 2017), briefly, 9.4 g of $FeCl_3{\cdot}6H_2O$ and 3.5 g of $FeCl_2{\cdot}4H_2O$ (molar ratio 2:1 of Fe^{3+}/Fe^{2+}) were dissolved in 400 mL of distilled water under purging of nitrogen gas to prevent the penetration of oxygen at 80 °C. Then, 30 mL of concentrated ammonia was added into the mixture and solution was stirred with a overhead stirrer for 30 min leading to the formation of smaller and more homogenized MNPs. The precipitated particles were separated by a strong magnet, washed with ultrapure water and dried at 60 °C in an oven.

2.3.2. Synthesis of silica coated Fe_3O_4 core-shell

The surface of the Fe_3O_4 NPs was coated with a layer of silica using a sol–gel with minor modifications (Lu, Yin, Mayers, & Xia, 2002). In a typical procedure, 6.0 g of the synthesized Fe_3O_4 NPs was mixed with 400 mL of ultrapure water and 48 mL of 2-propyl alcohol in a beaker and sonicated for 15 min. Then, 40 mL of concentrated ammonia solution was added to the reaction mixture under constantly stirring at 40 °C. After 30 min, 20 mL of TEOS was added to the precursor solution and mixture was stirred for 12 h at 40 °C. The resultant product was collected using an external magnet and rinsed for three times with water, ethanol and finally dried at 60 °C for 24 h in an oven.

2.3.3. Surface modification of Fe_3O_4@SiO_2 by N,N′-bis(acetylacetone) ethylenediimine

In this step, 72 mg of sodium hydride (3 mmol) was used to activate 0.3 mL of acetylacetone (3 mmol) in 10 mL of toluene:THF (1:1) solution for 30 min and then, 0.55 mL of CPTMS (3 mmol) was added. The reaction mixture was purged with nitrogen and stirred at solvent reflux temperature for a period of 5 h. Then, Fe_3O_4@SiO_2 (6.0 g) was added to this solution and the mixture was allowed to stand for another 12 h at reflux conditions. Finally, the resulting modified NPs (Fe_3O_4@SiO_2-acacsil) were isolated using a magnet, washed with distilled water and ethanol several times, respectively and then, dried at 60 °C in an oven.

Then, 1.0 g of Fe_3O_4@SiO_2-acacsil NPs was dispersed in 10 mL of DMF and treated with 0.75 mL of ethylenediimine. The reaction mixture was refluxed for 4 h. The obtained product (Fe_3O_4@SiO_2-EDN) was collected using a magnet, washed with ultrapure water and methanol, sequentially and then, dried in an oven. Fig. 1 illustrates the schematic diagram of the synthesis procedure of Fe_3O_4@SiO_2-EDN.

2.4. Extraction procedure

Fig. 1S shows the batch experiments for solid phase extraction (SPE) of Cu^{2+} ions. The following steps were applied for extraction, preconcentration and determination of Cu^{2+}; fifty mililiters of sample solution (pH 7) containing appropriate amount of Cu^{2+} was transferred to a glass beaker and 447 mg of Fe_3O_4@SiO_2-EDN was added to the solution. The mixture was mechanically stirred at 200 rpm for 20 min. Afterward, the magnetic sorbent was quickly collected from the suspension with the magnet and the supernatant was decanted. Then, the adsorbed ions were eluted with 1.8 mL of 2.5 mol L^{-1} HNO_3 under fierce vortex for 4 min. Finally, the sorbent was collected with a magnet