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Novel ion imprinted magnetic mesoporous silica for selective magnetic solid phase extraction of trace Cd followed by graphite furnace atomic absorption spectrometry detection

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ABSTRACT

Determination of trace Cd in environmental, biological and food samples is of great significance to toxicological research and environmental pollution monitoring. While the direct determination of Cd in real-world samples is difficult due to its low concentration and the complex matrix. Herein, a novel Cd(II)-ion imprinted magnetic mesoporous silica (Cd(II)-II-MMS) was prepared and was employed as a selective magnetic solid-phase extraction (MSPE) material for extraction of trace Cd in real-world samples followed by graphite furnace atomic absorption spectrometry (GFAAS) detection. Under the optimized conditions, the detection limit of the proposed method was 6.1 ng L^{-1} for Cd with the relative standard deviation (RSD) of 4.0% (c = 50 ng L^{-1}, n = 7), and the enrichment factor was 50-fold. To validate the proposed method, Certified Reference Materials of GSBZ 50009–88 environmental water, ZK018-1 lyophilized human urine and NIES10-b rice flour were analyzed and the determined values were in a good agreement with the certified values. The proposed method exhibited a robust anti-interference ability due to the good selectivity of Cd(II)-II-MMS toward Cd(II). It was successfully employed for the determination of trace Cd(II) in environmental water, human urine and rice samples with recoveries of 89.3–116%, demonstrating that the proposed method has good application potential in real world samples with complex matrix.

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1. Introduction

Cd has been used in many fields[1], including the manufacture of steel, pigment, electric batteries and electronic components, however, it is listed as the sixth most poisonous substance jeopardizing human's health[2]. Even at low dose Cd may cause gastrointestinal irritation, vomiting, abdominal pain and diarrohea[3]. Moreover, Cd has an extremely long biological half-life[4]. Consequently, developing accurate and reliable methods for the determination of trace Cd(II) in environmental, biological and food samples is of particular significance to toxicological research and environmental pollution monitoring.

Several analytical techniques including graphite furnace atomic absorption spectrometry[5] (GFAAS), flame atomic absorption spectrometry[6] (FAAS), inductively coupled plasma optical emission spectrometry[7] (ICP-OES) and inductively coupled plasma mass spectrometry[8] (ICP-MS) have been used for the determination of Cd in different matrixes. Among them, GFAAS has the advantages of high sensitivity, low cost, and small sample consumption, and suits to single elemental analysis at trace level[9]. However, the measured signals of GFAAS are inherently very susceptible to the composition of the sample matrix [10]. The accurate determination of cadmium is frequently very difficult due to the interference of the sample matrix (spectroscopic and non-spectroscopic interferences)[11]. Moreover, in some cases, the concentration of Cd in real-word samples might be too low to be analyzed directly. Therefore, an appropriate extraction or preconcentration protocol[12] is usually required prior to GFAAS determination to concentrate Cd and eliminate or decrease the matrix interference in real-world sample analysis, especially for samples with complicated matrix. Several technologies including solid-phase extraction(SPE), liquid-liquid extraction(LLE), coprecipitation and chemical vapor generation[10] have been employed for the preconcentration/separation of cadmium[11]. Among then, SPE has been proven to be the most attractive way due to its high efficiency, good sensitive and simplicity, and has been widely applied for the separation and preconcentration of metal ions [13, 14] in the real-world samples.

Magnetic solid phase extraction (MSPE) is an favourable SPE method with functionalized magnetic nanoparticles (MNPs) as the sorbents[15]. Due to the superparamagnetism, MNPs can be separated from large-volume aqueous samples rapidly by using a magnet instead of high-speed centrifugation or filtration. Surface coating on MNPs not only can provide active sites for adsorption, but also can prevent the oxidation of pure inorganic magnetic cores. MNPs are easy to be coated with inorganic materials (e.g., silica or alumina) or organic polymers

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(e.g., polyethylene), and then further modified with functional groups[16]. Ion imprinted polymer (IIP), similar to molecular imprinted polymer (MIP), has a predetermined selectivity for a given target ion. Coating IIP on MNPs, resulting in magnetic ion-imprinted material (MIIM), would inherit both superparamagnetism and high selectivity for the target ion[17], which have been reported for selective separation and preconcentration of metal ions such as Pb(II)[18], Au(III)[19], Cd(II)[20] and Cu(II)[21].

For the preparation of metal ion imprinted materials, traditional IIP prepared by conventional methods (bulk polymerization[22], suspension polymerization[23] and precipitation polymerization[24], etc.) exhibit some disadvantages such as limited site accessibility to the target ion[25], low rebinding capacity, slow mass-transfer rate and incomplete removal of templates[21]. In order to increase site accessibility, surface imprinting technique attracted extensive research interest. Using surface imprinting technique, IIP shows good accessibility to the target species, low mass-transfer resistance, easy removal of templates, fast adsorption kinetics and ease of preparation.[21] Up to now, surface imprinting technique combined with a sol–gel process has been successfully used for the preparation of the imprinted coating on silica gel[26–28], and magnetic particles[18,21,29]. It is worth noting that the surface imprinting on magnetic cores results in high extraction selectivity and efficiency.[30] Nevertheless, in the surface imprinting process, the specific recognition sites are limited on the surface of magnetic particles, which restricted the amount of binding sites. To resolve this problem, synthesis of mesoporous MIIM is a promising method. Aboufazeli et al.[31] successfully prepared a high surface area MIIM by coating mesoporous silica on Fe_3O_4 particles and then grafting a selective Pb(II)-IIP on it. By the introduction of mesoporous silica structure in the magnetic material, polymerization reaction can not only happened on the surface of the magnetic particles but also proceed on the pore wall of mesoporous silica. Those ion imprinted magnetic mesoporous silica nanoparticles have a high adsorption capacity of 68.1 mg · g^{-1} for Pb(II) and could be applied in food samples analysis. However, the preparation of Pb(II)-MIIM is complicated. Meng et al.[32] prepared a Ce(III)-IIP based on the supporting material of ordered mesoporous silica SBA-15 by surface imprinting technique via reversible addition fragmentation chain transfer polymerization. The
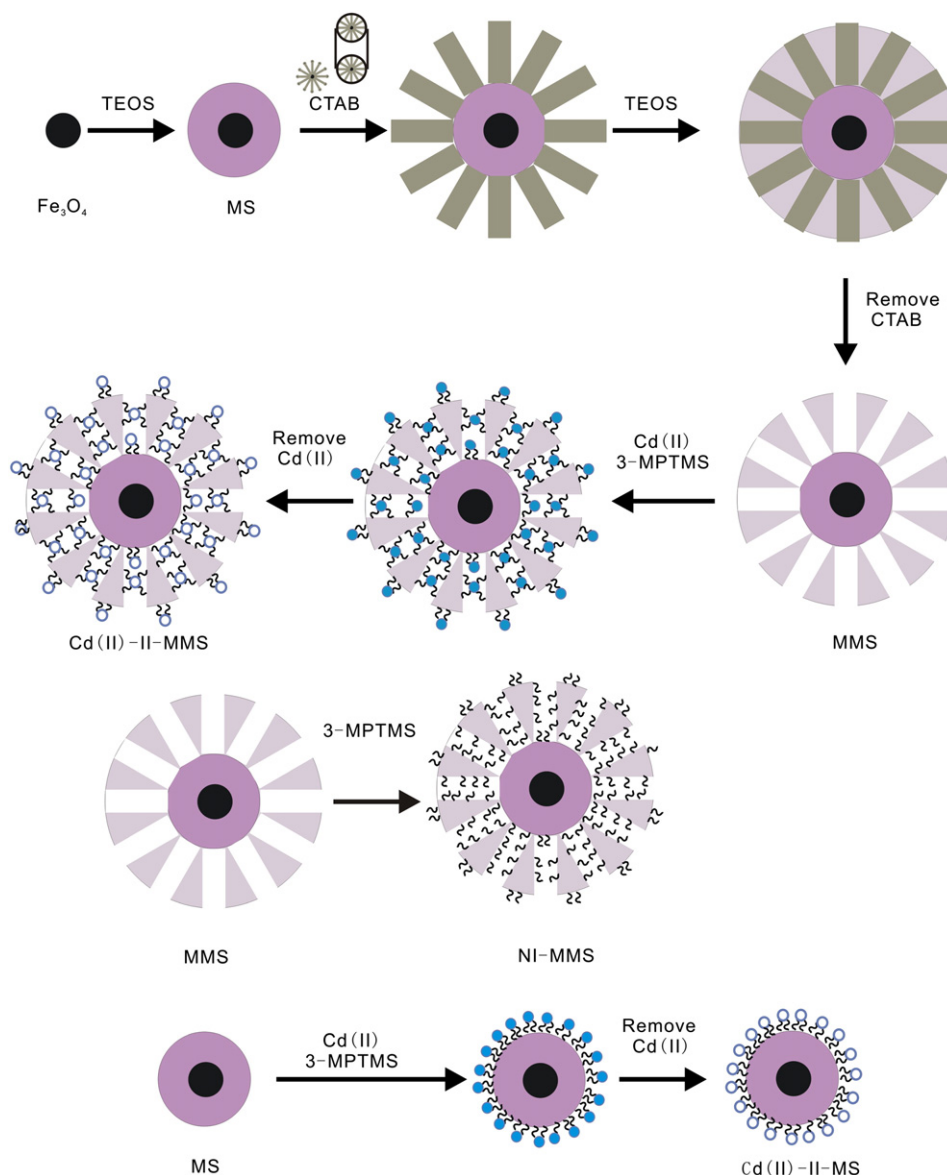
Scheme 1. Schematic diagram of the preparation of Cd(II)-II-MMS, NI-MMS and Cd(II)-II-MS.