



A polyethyleneimine-modified attapulgite as a novel solid support in matrix solid-phase dispersion for the extraction of cadmium traces in seafood products

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ABSTRACT

In current study, a new polyethyleneimine (PEI)-modified attapulgite material was prepared serving as a solid support in matrix solid-phase dispersion for the extraction and determination (by atomic absorption spectrometry) of cadmium in seafood products. The major factors affecting PEI grafting were optimized using various PEI amounts and molecular weights. Parameters pivotal to MSPD extraction efficiency, like: pH, volume of eluting solvent, and the sorbent mass-to-sample ratio were investigated. Quantitative recoveries were achieved with 0.21 g of fish sample, 0.13 g of PEI-modified attapulgite dispersing agent, and 50% HNO₃ eluting solution. The limit of detection and the limit of quantification were found to be 2.5 and 8.3 μg kg⁻¹ for cadmium in surimi samples, respectively. The recoveries were in the range of 89.2–100.1%, with RSDs ranged from 3.0% to 7.9% (n = 5). When compared to the method stipulated by the Chinese National Standard GB 5009.15-2014, the newly developed MSPD provides comparable accuracy and even better repeatability for the analysis of the cadmium in real seafood samples.

1. Introduction

Cadmium, a highly toxic and persistent pollutant, may lead to bioaccumulate in hearts, lungs, bones and especially kidneys for a relatively long time [1]. Prolonged exposure to cadmium results in severe kidney dysfunctions [2]. Therefore, accurate and rapid determination of trace amount of cadmium, for example in seafood samples, is urgently needed for routine food safety monitoring.

To perform accurate quantification of target analytes, sample pretreatment is crucial due to common concentrations of compounds at trace level and the matrix effect. Extractive methods like liquid-liquid extraction (LLE) and later introduced solid-phase extraction (SPE) have been used as effective sample pretreatment techniques for decades [3,4]. Although frequently applied, LLE suffers from serious drawbacks as tediousness, long extraction time or consumption of bulky solvents of mostly hazardous properties. More abundant approach to wit: SPE, has demonstrated certain pluses over LLE, like easiness and sometimes almost solventless performances. The ongoing seeking for the greener

analytical techniques (i.e., Green analytical chemistry -GAC), has brought their miniaturization by the developing liquid-phase microextraction [5,6] and solid-phase microextraction, among others. Lately, these setups were successfully automated [7–15] contributing to GAC development, even though, this field of research has been still in its "cradle" as there is remaining lack of such methods compared to manual ones [16,17]. Electrochemistry [18], chromatography (e.g., immuno-chromatography [19] and ion exchange resin [20]), and spectrometry (e.g., atomic absorption spectrometry [21–24], atomic fluorescence spectrometry [25] and plasma mass spectrometry [26]), have been used for the quantification of cadmium in food samples. The noteworthy to say is that most of sample preparation procedures for cadmium were based on acid digestion [21–26], with the assistance of microwave [21], ultrasound [22] or conventional heating [22–26]. However, multistep processes of acid digestions are tedious requiring longer digestion time without necessity of assistance of alternative energy (e.g., ultrasound, microwave, or conventional heating). Matrix solid-phase dispersion (MSPD), firstly introduced by Barker et al. [27],

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is most of promising solid-based extraction methods for cleanup of organic compounds from viscous, solid and semi-solid samples [28]. The MSPD method has advantages over the methods with the use of alternative energy since it is performed at room temperature and atmospheric pressure. In addition, MSPD acid digestion procedure is not needed for, which not only minimizes processes of sample preparation but also reduces low waste production. However, few studies on the extraction of heavy metals by MSPD have been reported [29–32], especially for cadmium analysis [29]. Although selection of an appropriate sorbent is crucial to MSPD method development, only several sorbents, such as sea sand [29], multiwall carbon nanotubes [30], silica [31] and diatomaceous earth [32] were served as dispersing agents for cadmium [29], mercury [30,31] and arsenic [32] extraction. Thus the development of new types of sorbent with high adsorption capacity and high selectivity would facilitate the analysis of cadmium in complex matrices.

Owing to its large specific surface area, reactive-OH groups and appropriate cation exchange capacity, attapulgite has been exploited as an efficient sorbent for adsorption of heavy metals [33]. In order to improve the adsorption capacity and the selectivity of heavy metals, attapulgite grafted with various functional groups, such as polyacrylamide [34], N-methylimidazole [35], ammonium citrate tribasic [36] and hyperbranched aliphatic polyester [37], were developed. Polyethyleneimine (PEI), a cationic polymer which contains numerous amine groups that can donate electrons and chelate metal ions, have been successfully developed as sorbents for the adsorption of heavy metals [38,39], with the affinity order of adsorption $\text{Cd(II)} > \text{Cu(II)} > \text{Pb(II)}$ [39]. However, little has been focused on the desorption of metal ions from these materials for sample preparation, especially in a MSPD format.

In this study, the PEI-modified attapulgite-based MSPD was proposed for the first time, as a novel sample preparation technique for cadmium analysis from seafood products. The PEI-modified attapulgite was characterized by fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy/energy dispersive analysis of X-ray (SEM/EDAX), and X-ray diffraction (XRD). We thoroughly optimized the different parameters affecting the extraction efficiency of MSPD and compared the performance with that obtained from the Chinese National Standard GB 5009.15-2014.

2. Materials and methods

2.1. Reagents and materials

Polyethyleneimine (MW. 600, 1,800, 10,000, 99%) was purchased from Aladdin (Shanghai, China). The attapulgite was purchased from Jiangsu Xuyi Anhalt Nonmetallic Mining Ltd. (Jiangsu, China). 3-aminopropyltriethoxysilane (APTES, 98%) and glutaraldehyde (50%) were obtained from J&K Scientific Ltd (Shanghai, China). The standards of metal ions (e. g., cadmium, lead, mercury, arsenic, zinc, nickel, copper and antimony) were purchased from Central Iron & Steel Research Institute (Beijing, China). The ultra-pure water was supplied by a Milli-Q system (Millipore, Molsheim, France). All inorganic reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The empty cartridges (6 mL) and frits (5 μm and 20 μm porosity) were purchased from Shenzhen Biocomma Biotech Co. (Shenzhen, China).

2.2. Instrumentation

FT-IR analysis was performed using a Bruker MPA FT-IR spectrometer (Bremen, Germany). The SEM/EDAX analysis was carried out on a Hitachi S-4800 scanning electron microscope (Tokyo, Japan). XRD pattern of the sample structure was acquired with a Bruker AXS D8 advance diffractometer using $\text{Cu K}\alpha$ radiation. A Visiprep™ DL SPE vacuum manifold used for MSPD procedure was purchased from Supelco (Bellefonte, PA, USA). The quantitative analysis of cadmium

after MSPD was performed on Varian SpectraAA 220Z Atomic Absorption Spectrophotometer (Manasquan, New Jersey, USA) equipped with a Zeeman-effect background correction system, a 220Z auto sampler and GTA 110Z Furnace. Hollow cathode lamp for cadmium was used as the radiation source at a wavelength of 228.8 nm. All instrumental parameters were used under the conditions recommended by the manufacturer.

2.3. Preparation of the polyethyleneimine-modified attapulgite

Natural attapulgite was acidified by hydrochloric acid according to our previous work [40]. The 6.0 g acidified attapulgite (dried at 110 °C) was dispersed in 100 mL dried toluene. APTES of 6.0 mL was added to the mixture with stirring. The acidified attapulgite was uniform dispersion in the mixture solution, and then refluxed for 10 h at temperature of 110 °C. The resulting APTES-modified attapulgite was washed with ethanol and dried for PEI modification. Before PEI modification, the APTES-modified attapulgite was rinsed with 100 mmol L^{-1} phosphate buffer (pH 8.0). A solution of 40.0 mL 10% (v/v) glutaraldehyde in 100 mmol L^{-1} phosphate buffer (pH 8.0) was added to 2.0 g APTES-modified attapulgite and incubated for 0.5 h at 90 °C followed by washing with 100 mmol L^{-1} phosphate buffer (pH 8.0) for 3 times. After that, PEI was grafted onto the support by incubating with a solution of 5.0 mL PEI (1.5 g) containing 5 mg mL^{-1} NaCNBH_3 in 100 mmol L^{-1} phosphate buffer (pH 8.0) for 0.5 h at 90 °C. Finally, the PEI-modified attapulgite was rinsed with water and ethanol for 2–3 times, respectively, and then dried at 85 °C for 7 h.

2.4. Detection of amine group content

The content of amine group on the surface of attapulgite was detected by nonaqueous acid-base titration according to previous work with slightly modification [39]. The APTES-modified or PEI-modified attapulgite (about 0.4 g) was dispersed in 25 mL ethanol. The solution was titrated with HCl by using thymol blue as indicator. The HCl solution was previously standardized with NaOH solution. The NaOH solution also standardized with potassium hydrogen phthalate.

2.5. Sample preparation

Samples of squid and surimi (hairtail) were purchased in a local supermarket. The surimi and soft tissues of squid were homogenized by mechanical blending, and semi-dried 4 h at 110 °C. Then, the samples were blended again and completely dried over 4 h at 110 °C. The samples were then ground in a mortar with a pestle. The surimi sample which did not contain cadmium was used to optimize the MSPD procedure. The metal ions-containing samples were prepared by spiking different amounts of standard stock solutions into surimi samples. The squid, containing cadmium itself, was used to evaluate the accuracy of the method.

2.6. MSPD procedure

Around 0.21 g of the previously milled sample and 0.13 g of PEI-modified attapulgite were blended together in an agate mortar using an agate pestle to obtain a homogeneous mixture. The mixture was quantitatively transferred into a 6 mL cartridge containing a 5 μm pore size polyethylene frit at the bottom. Then another 20 μm pore size polyethylene frit was placed on the top of the mixture by slight compression with a syringe plunger. The mixture was rinsed with 6.0 mL of water at 1 mL min^{-1} (total time 6 min). Due to strong adsorption cadmium on the sorbent by chelation, 8 mL of 50% $\text{HNO}_3/\text{H}_2\text{O}$ (v/v) was adopted to release cadmium by destroying crystalline structure of attapulgite. The eluted product was collected and heated to drive acid at 95 °C, and then diluted by water to 25 mL. This resulting solution was used as the working solution.

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