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Synthesis and application of novel ion-imprinted polymer coated magnetic multi-walled carbon nanotubes for selective solid phase extraction of lead(II) ions

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ABSTRACT

In this study, novel magnetic ion-imprinted polymer (MIIP) nanoparticles were utilized for the sensitive and selective detection of Pb(II) ions by graphite furnace atomic absorption spectrometry (GFAAS). The Pb(II)-imprinted polymer was synthesized by using 4-vinylpyridine (4VP) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linker, 2,3,5,6-tetra(2-pyridyl) pyrazine (TPPZ) as the chelating agent and magnetic multi-walled carbon nanotubes (MMWCNTs) as the carrier. The synthesized MIIP materials were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and vibrating sample magnetometer (VSM). Various analytical parameters such as extraction and desorption time, eluent type and concentration, pH and sample volume were systematically examined. The selectivity of MIIP sorbent for Pb(II) ions in the presence of some cations was also evaluated. The limit of detection (LOD, $3S_b$) and the relative standard deviation (RSD, $n = 8$, $c = 25$ ng L^{-1}) were found to be 2.4 ng L^{-1} and 5.6%, respectively. The maximum sorption capacity of the MIIP for Pb(II) was found to be 48.1 mg g^{-1}. Finally, the proposed analytical procedure was successfully applied to monitoring lead in human hair and water samples with satisfactory results for the spiked samples.

1. Introduction

Lead is one of the most significant trace elements due to high toxicity even at very low concentrations. Because of the rather slow rate of excretion, lead can accumulate in body tissues by long-term exposure at low dose. Consequently, it can lead to serious nervous system problems (especially in young children) and cause blood and brain disorders [1]. The U.S. Environmental Protection Agency (USEPA) has set the action level for Pb in drinking water at 15 μg L^{-1} [2]. Therefore, the development of sensitive and reliable methods for the determination of Pb(II) ions in food, biological and water samples is very important. Numerous instrumental technologies have been proposed for the determination of lead in trace levels, including flame atomic absorption spectrometry (FAAS) [3], inductively coupled plasma-optical emission spectrometry (ICP-OES) [4], graphite furnace atomic absorption spectrometry (GFAAS) [5], inductively coupled plasma-mass spectrometry (ICP-MS) [6], hydride generation atomic absorption spectrometry [7], and sequential multi-element flame atomic absorption spectrometry [8]. Among them, GFAAS has been popularly used for the determination of trace amounts of lead in various real samples due to its low detection limits, high sensitivity, and low cost [9]. However, the straight determination of trace concentration of lead in the presence of relatively high concentration of other diverse ions is a difficult task. Hence, separation and preconcentration steps are necessary prior to the lead detection, particularly when they exist at trace levels of concentration. A large number of sample enrichment procedures have been developed for the separation and preconcentration of lead ions, including dispersive liquid–liquid microextraction (DLLME) [10], single-drop microextraction (SDME) [11], cloud point extraction (CPE) [12], liquid–liquid extraction (LLE) [13], coprecipitation [14] and solid phase extraction (SPE) [15]. Recently, SPE technique has been widely applied as a preconcentration method due to being inexpensive, simple operation, high extraction efficiency, rapid phase separation and the ability of combination with different detection techniques in the form of on-line or off-line mode. In recent years, a novel SPE procedure, based on the use of magnetic or magnetizable materials called magnetic solid-phase extraction (MSPE), has also been developed. MSPE is based

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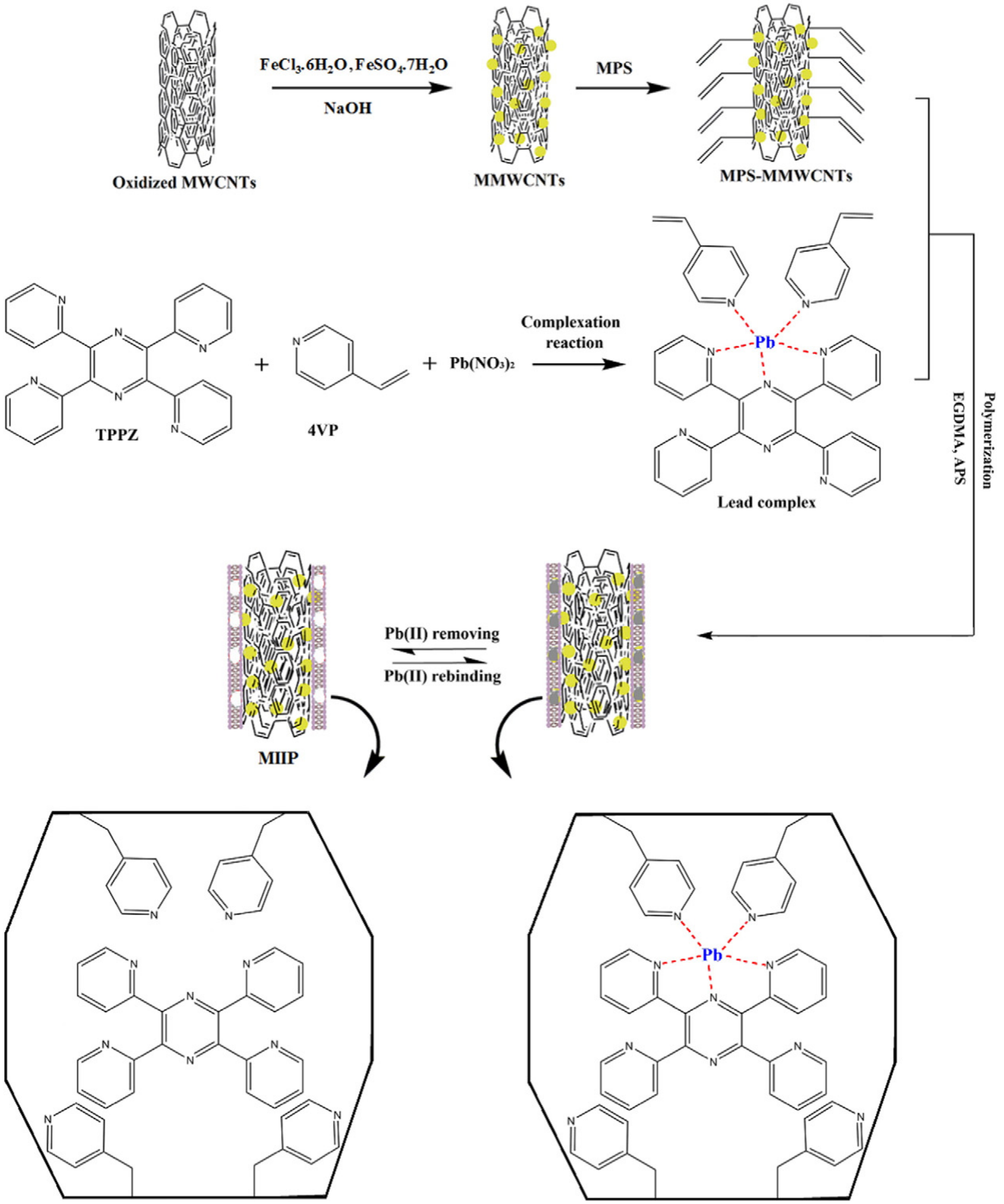
on the combination of inorganic magnetic materials and non-magnetic adsorbent materials. In MSPE methodology, separation of magnetic sorbent from the crude sample matrix can be easily achieved by the action of an external magnetic field [16]. The magnetic sorbent needs not be packed into the cartridge when using dynamic extraction mode, and no tedious centrifugation or filtration procedures are required after extraction when the static batch mode is employed. Their separation and collection are easier and faster than conventional SPE methods.

Ion imprinting technology based on the highly selective ion-imprinted polymers (IIPs) represents a new class of sorbents possessing selectivity and affinity for separation or preconcentration or removal of target ion [17]. Nowadays, IIPs are chosen as favorable sorbents owing to their low cost, ease of preparation, high selectivity, thermal and chemical stability, and feasibility of miniaturization. IIPs are prepared by formation of specific recognition sites in the framework of organic polymers and usually prepared by bulk polymerization method [18]. However, IIPs synthesized by this method suffer some disadvantages such as incomplete template removal, slow mass transfer, high crosslinking density and poor site accessibility for target species. To overcome these problems, the surface imprinting polymerization has been drawing more and more attention,



Scheme 1. Schematic depiction of the synthesis process of MIIPs.