



Selective determination of aromatic acids by new magnetic hydroxylated MWCNTs and MOFs based composite

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ABSTRACT

A novel, efficient, and high-selectivity magnetic solid-phase extraction (MSPE) adsorbent based on Fe₃O₄ nanoparticles, hydroxylated multi-walled carbon nanotubes (MWCNTs-OH) and metal-organic frameworks (MOFs) was prepared and applied for trace aromatic acids determination in solid samples by applying a template-free in situ strategy. The morphology, configuration and magnetic behavior of the adsorbent were characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra, and vibrating sample magnetometer (VSM). The adsorbent can achieve the selective extraction of aromatic acids from the aromatic mixture in apple samples, which was mainly promoted by intermolecular hydrogen bonding and π - π electron-donor-acceptor (EDA) interaction. The potential application of the adsorbent was evaluated by MSPE of trace 1-naphthylacetic acid (NAA), cinnamic acid (CA) and terephthalic acid (TPA) from apple samples under the optimal conditions which were investigated. Satisfactory linearities were obtained in a range of 5–500 ng/g and the recoveries of three aromatic acids at three spiked levels ranged from 91.2% to 98.0% with the relative standard deviations (RSD) of less than 5.5%. The limits of detection (LODs) for CA, TPA and NAA were 0.17, 0.61, and 0.86 ng/g. The satisfactory results confirmed the great potential of the novel adsorbent for the selective extraction of aromatic acids from complex sample matrices.

1. Introduction

Aromatic acids are ubiquitous in environment and human activities and widely used as pharmaceuticals, chemical raw materials, food additives, and pesticides like aspirin, benzoic acid, sorbic acid and dicamba, etc. The excess use of some aromatic acids will lead to a great threat to the ecological environment and human health, such as naphthylacetic acid (NAA) and terephthalic acid (TPA), whereas some others are benefit for the human being, for instance, cinnamic acid (CA), so the development of sensitive and selective method for separation, enrichment and determination of aromatic acids are of great urgency and significant importance. NAA, a naphthalene-derived plant growth regulator, is widely used in fruits and vegetables owing to their structure similarities with the indoleacetic acid, the first plant auxin [1], the residual of which in plant is detrimental to the health of human beings and animals due to its potential toxicity [2]. TPA, used in various applications such as manufacturing of chemical industry materials, food additives, medicines, and pesticides, is dangerous for

human and microorganisms due to its toxic nature [3]. CA, a phytotoxic allelochemical produced in plant root exudates, is derived from the L-phenylalanine ammonia-lyase reaction inside the plant and commonly presents in many fruits and vegetables, which exhibits hepatoprotective, antimalarial, and antioxidative activities [4,5]. Aromatic acids are generally occurring at trace concentrations in sample and interfered by many coexisting substances, which make their analysis extremely difficult. Therefore, it is indispensable to develop an appropriate sample pretreatment technique for both enriching and purifying aromatic acids prior to final analysis.

The sample preparation step in an analytical process typically consists of a basic, important and dominant extraction procedure that results in the isolation and enrichment of analytes of interest from a sample matrix [6,7]. As a classical sample preparation technique, solid-phase extraction (SPE) has been widely applied throughout the years, and varieties of innovative SPE methods have been designed and developed to tackle the issues and challenges faced in practical applications [8–11]. Magnetic solid-phase extraction (MSPE) is one

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of these methods, in MSPE, the magnetic or magnetically modified adsorbents are generally directly dispersed in the sample solutions to quickly extract analytes since they can be readily recovered by an external magnet without the need of additional filtration or centrifugation procedures, which makes the extraction process easier and faster [9]. Various materials have emerged as promising adsorbents in SPE to handle the emerging chemicals, including carbon nanomaterials (CNs) [12–14], metal organic frameworks (MOFs) [15,16] and others [17,18]. Carbon nanotubes (CNTs), with their unique structures leading to extraordinary properties, have been attracting considerable attentions worldwide in analytical science [19,20]. These properties, especially high surface area, ability to establish π - π interactions and easiness to be functionalized with covalent and non-covalent modification modes, predispose CNTs to be good adsorbents in SPE [21]. It was proposed that CNTs can exhibit superior affinities to analytes through hydrogen-bonding interactions, π - π electron-donor-acceptor (EDA) interactions, and hydrophobic interactions [22–24]. MOFs represent a class of hybrid materials constructed from metal clusters and bridging-ligands [25], which have attracted immense attention for applications in a number of fields related to porous materials due to their unique properties including diverse and tunable porosities, desirable functionality and large surface area [26]. Various specific properties of MOFs and their derivatives, such as IRMOF1 [27], ZIF8 [28], MIL101(Cr) [29], MOF508 [30], ZIF67 [31] and Co-MNPC [32], have been successfully explored as the adsorbents in SPE and other adsorbent-based extraction methods. More recently, studies have been conducted to explore the potential application prospects of MOFs/CNs composites in analytical science. Zhang et al. introduced an unbreakable and thickness-controlled MOF-199/CNTs coating for sampling ethylene mainly based on "molecular sieving" effect [16], and Wu et al. proposed an approach by immobilizing of MOF-5/ionic liquid functionalized graphene (MOF-5/ILG) composite on etched stainless steel for enrichment of antibiotics [33]. The type of hybrid composites can be considered as excellent candidates for enrichment and detection of trace analytes by combining the versatile properties of both CNs and MOFs.

Generally, CNTs-based adsorbents have poor selectivity to aromatic compounds with different substituents. In this work, a novel magnetic hydroxylated multi-walled carbon nanotubes and poly-zeolite imidazolate frameworks based composite (Fe_3O_4 -MWCNTs-OH@poly-ZIF67) was designed for trace aromatic acids by applying a template-free in situ strategy. The prepared composite, combining the favorable characteristics of single Fe_3O_4 nanoparticles, MWCNTs-OH and ZIF67, not only shows superparamagnetic property, but also exhibits excellent adsorption affinity to aromatic acids. To evaluate the adsorption performance of Fe_3O_4 -MWCNTs-OH@poly-ZIF67 in SPE, several aromatic compounds with significant structural characteristics were selected as model analytes to carry out the extraction experiments prior to their determination by high-performance liquid chromatography-ultraviolet detection (HPLC-UV). Effects of critical experimental parameters on the extraction efficiencies were investigated, and the mechanism of selective extraction of aromatic acids was evaluated based on hydrogen-bonding interaction, π - π EDA interaction, Lewis acid-base interaction and other weak intermolecular interactions. As an example of applications, the composite was successfully applied to the analysis of trace NAA, TPA and CA from apple samples.

2. Experimental

2.1. Reagents and materials

CA, TPA, NAA and perylene (PLE) were purchased from Aladdin Industrial Corporation (Shanghai, China). 4-Hydroxybenzoic acid (HBA), benzophenone (BPO), phenol (Phol) and benzene (PhH) were gained from Kishida Chemical Co. Ltd. (Hangzhou, China). 1-Pyrenebutyric acid (PBA) was purchased from TCI Development Co.,

Ltd. (Shanghai, China). Phenylacetic acid (PA), 2-methylimidazole (2-MIM) and cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Aldrich Chemical Co., Ltd. (Shanghai, China). MWCNTs-OH (OD, 10–20 nm; -OH content, 3.06 wt%; length, 10–30 μm ; purity > 95 wt%) were purchased from Chengdu Organic Chemical Co., Ltd. (Chengdu, China); Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from Beijing Chemicals Corporation (Beijing, China). All reagents were of analytical reagent grade unless otherwise mentioned and were used directly without further purification. Standard stock solutions of CA, TPA and NAA (each at 100.0 $\mu\text{g}/\text{mL}$) were prepared in methanol and stored in brown flasks at 4 °C. All the working solutions were freshly prepared by appropriate dilution of the stock solutions with ultrapure water to give the desired concentrations.

2.2. Instruments

Liquid chromatographic system consisted of Waters 1525 HPLC system and 2998 diode array detection system. A reversed phase Redclassical C18 column (250 mm \times 4.6 mm id, 5 μm) was used for separations. The mobile phase consisted of (A) methanol and (B) 0.1% acetic acid in water in the ratio of 30:70 (v/v) at a flow rate of 1.0 mL/min. The UV detection wavelengths were chosen at 277, 241, 222, 259, 255, 254, 271, 254, 275 and 251 nm for CA, TPA, NAA, PA, HBA, BPO, Phol, PhH, PBA and PLE, respectively. Fourier transform infrared (FTIR) spectra were recorded on an IFS120HR spectrometer (Bruker, Germany). Magnetic properties of the materials were conducted with a 3473-70 vibrating sample magnetometer (VSM) (Gmw Associates, USA). Scanning electron microscopy (SEM) images were acquired by a MIRA3 SEM instrument (TESCAN, Czech Republic). Transmission electron microscope (TEM) images were observed on a Tecnai-G2-F30 field TEM instrument (FEI, USA). X-ray diffraction (XRD) measurements were performed on an X'pert PRO X-ray diffraction using Cu K α radiation (Philips, Netherlands). Thermogravimetric analysis was studied by a thermal gravity analyzer (TGA) (Netzsch, Germany). Sample preparation was conducted with a JY99-IIDN ultrasonic cell crusher (SCIENTZ, China).

2.3. Synthesis of Fe_3O_4 -MWCNTs-OH@poly-ZIF67

Fe_3O_4 enclosure MWCNTs-OH (Fe_3O_4 -MWCNTs-OH) was prepared via a simple chemical co-precipitation method with slight modification as follows [34]. MWCNTs-OH (250 mg) was well-dispersed in 30 mL of deoxygenated water in a 250 mL three-necked round-bottomed flask equipped with a Schlenk line by ultrasonication for 20 min, then a 30 mL mixture solution containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (151 mg, 0.559 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (55 mg, 0.277 mmol) was added to the MWCNTs-OH suspension under mechanical stirring. Subsequently, ammonia solution (10 mL, 5 wt%) was added dropwise at 70 °C, and the mixture was kept vigorously stirring for 2 h. All the reaction processes were performed under nitrogen atmosphere. In the presence of $\text{NH}_3 \cdot \text{H}_2\text{O}$, Fe^{2+} and Fe^{3+} jointly participate in the chemical co-precipitation reaction and finally generate Fe_3O_4 as described by the following equation:



After that, the black composite (Fe_3O_4 -MWCNTs-OH) was obtained by filtration and then washed by ultrapure water and ethanol repeatedly until the pH level of the eluents became 7.0. Then the composite was dried under vacuum at 65 °C overnight for the next procedure. The approach followed is to synthesize of the desired composite (Fe_3O_4 -MWCNTs-OH@poly-ZIF67). The composite obtained previously (Fe_3O_4 -MWCNTs-OH) (300 mg) was added to a mixture solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (300 mg, 1.031 mmol) and 2-MIM (180 mg, 2.192 mmol) under mechanical stirring. Subsequently the

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