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Magnetic solid phase extraction and gas chromatography–mass spectrometrical analysis of sixteen polycyclic aromatic hydrocarbons

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ABSTRACT

Fluorenyl functionalized superparamagnetic core/shell magnetic nanoparticles (MNPs, Fe_3O_4@SiO_2@Flu) were prepared and characterized by transmission electron microscope, X-ray diffraction and infrared spectroscopy. The MNPs having an average diameter of 200 nm were then used as solid-phase extraction sorbent for the determination of 16 priority pollutants polycyclic aromatic hydrocarbons (PAHs) in water samples designated by United States Environmental Protection Agency (U.S. EPA). The main influencing parameters, including sorbent amount, desorption solvent, sample volume and extraction time were optimized. Analyses were performed on gas chromatography–mass spectrometry (GC–MS) using selected ion monitoring (SIM) mode. Method validation proved the feasibility of the developed sorbents for the quantitation of the investigated analytes at trace levels. Limit of detection ranging from 0.5 to 4.0 ng/L were obtained. The repeatability was investigated by evaluating the intra- and inter-day precisions with relative standard deviations (RSDs) lower than 13.1%. Finally, the proposed method was successfully applied for the determination of PAHs in water samples with the recoveries in the range of 96.0–106.7%.

1. Introduction

It is well known that water pollution has become an important problem related to public health. Among the pollutants, polycyclic aromatic hydrocarbons (PAHs) have raised global concerns because of their widespread distribution and carcinogenic toxicity [1]. The U.S. EPA has formulated regulations for the monitoring and control of PAHs and has developed methods for their measurement in air, water, food, and other matrixes [2]. The EPA has designated 16 PAHs as priority pollutants [3], and eight of them are considered to be possible carcinogens, namely: benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, indenol[1,2,3-cd]pyrene and benzo[g,h,i]perylene [4].

PAHs in different matrices were characterized and quantified mainly by HPLC or GC-based methods, such as Method 610 which deals with the measurement of these PAHs in wastewater by either HPLC/UV and FLD or gas chromatography with flame ionization detection (GC/FID) [5]. Method 8100 analyzes PAHs by GC/FID [6]. Methods 525, 625, and 8270 which analyze several PAHs and many other environmental pollutants in drinking water, wastewater, and solid wastes, respectively, by GC/MS [7–9]. Method 8275 which is a thermal extraction coupled with capillary GC/MS procedure for the quantitative determination of targeted PCBs and the 16 EPA priority pollutants PAHs in soils, sludges, and solid wastes [10].

However, the trace content in surface water makes the determination of PAHs a challenging task. Effective extraction and preconcentration techniques prior to instrumental analysis are often required. The widely used pre-treatment method at present for PAHs from aqueous samples are mainly sorbent based techniques, such as solid phase extraction (SPE) [11–14], micro-solid-phase extraction (μ-SPE) [15], and magnetic solid-phase extraction (MSPE) [16–29]. MSPE is a procedure for the preconcentration of target analytes from large volumes by using magnetic or magnetizable sorbents [30], which can be easily separated from sample solutions by an external magnetic field without the need of additional centrifugation or filtration. Moreover, since the sorbent can be dispersed in sample solution, the contact surface between analytes and sorbents is very large, which results in a rapid mass transfer and rapid extraction equilibrium. For the above reasons, MSPE has attracted increasing interests and found wide applications in the field of sample preparations.

Several MNPs were synthesized for the extraction of U.S. EPA 16 PAHs, they are C_{18} functionalized Fe_3O_4 nanoparticles

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(magnetic C_{18}) [31], diphenyl functionalization of Fe_3O_4 MNPs (Fe_3O_4 diphenyl) [32], carbon–ferromagnetic nanocomposite (carbon–Fe_3O_4) [33] and *n*-octadecylphosphonic acid modified mesoporous MNPs (OPA/MMNPs) [34]. Generally, π–π conjugative effect and hydrophobic interaction were contributed to adsorb PAHs. To the best of our knowledge, there is no report about preparation of condensed cyclic structural MNPs, and their application as SPE sorbents for adsorption of PAHs. Also, there is lack of report about the adsorption capacity of the MNPs. In the present study, a new kind of MNPs termed as fluorenyl functionalized magnetic silica nanoparticles (Fe_3O_4@SiO_2@Flu) was developed to extract PAHs from water samples. Fe_3O_4@SiO_2@Flu MNPs were synthesized by coating/modification magnetite Fe_3O_4 nanoparticles with silica, subsequently 3-isocyanatopropyltriethoxysilane and finally 9-fluorenylmethyl chloroformate. To our knowledge, this study is the first report with respect to the introduction of fluorenyl to functionalize MNPs for the extraction of PAHs. Due to the condensed cyclic structure, rich π-electrons exist on the surface of fluorenyl, which leads to the adsoption of PAHs through the π–π conjugative effect. Finally, adsorption capacity of Fe_3O_4@SiO_2@Flu was studied, and the sorbents was used for enrichment of PAHs from environmental water samples.

2. Experimental

2.1. Reagents and materials

All reagents were procured from major suppliers. Tetraethoxysilane (TEOS, 99%), 3-aminopropyltriethoxysilane (APTES, 99%) and 9-fluorenylmethyl chloroformate were obtained from Adamas Reagent Ltd. (Switzerland). HPLC grade methanol, *n*-hexane and acetonitrile (99%) were bought from Merck (Darmstadt, Germany). Ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$, 99%), ferrous sulfate heptahydrate ($FeSO_4\cdot 7H_2O$, 99%), ammonia (26%), hydrazine hydrate (99%), isopropanol (99%), triethylamine (99%), toluene (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Ultrapure water was used through the experiment which was prepared using a Milli-Q system water purification system (Millipore Inc., USA).

610/8100 PAH standard solution was bought from ANPEL Laboratory Technologies (Shanghai) Inc. The PAH standard solution contains naphthalene (Nap), acenaphthylene (Aceny), acenaphthene (Acen), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), chrysene (Chr), benzo[a]anthracene (B[a]A), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene (I[1,2,3-cd]P), dibenzo[a,h]anthracene (D[a,h]A) and benzo[g,h,i]perylene (B[ghi]P), each at 2 mg/mL in benzenen/methylene dichloride (1/1, v/v). The PAH stock solution was prepared in methanol at a concentration of each at 2 μg/mL, and kept at 4 °C in darkness. PAH working solutions were prepared by proper dilution of the stock solution.

Tap water, river water and waste water were used for real sample investigation. Tap water was taken from our lab tap after flowing for 10 min. River water sample was collected from the Ganjiang River in Nanchang (Jiangxi, China) and collected at 10 cm depth below the water surface. Waste water sample was collected from water treatment plants effluents (Jiangxi, China). Water samples were analyzed within 24 h.

2.2. Instrumentations and analytical conditions

The size and morphological characterization of the particles were observed by transmission electron microscopy (TEM, JEM-2100F, JEOL Co., Tokyo, Japan). Fourier transform infrared spectra (FTIR) were recorded on Vertex 70 (Bruker Optics, Germany). After being dried at 80 °C in a vacuum oven for 12 h, samples were mixed with KBr to fabricate a KBr pellet for FTIR analysis. PAHs were extracted from water samples with the assistance of an ultrasonic instrument KQ-600KDE. The magnetic property was analyzed using a vibrating sample magnetometer (VSM, Model 7410, Lake Shore Cryotronics, Inc., Westerville, OH, USA).

Analyses were conducted using an Agilent 7890A GC (Agilent Technologies, USA) system coupled to an Agilent 5975C mass spectrometer (Agilent Technologies, USA). Helium (purity 99.999%) was employed as the carrier gas at a flow rate of 1.8 mL/min. Samples (1 μL) were injected in splitless mode. The injector temperature was set at 280 °C and the interface temperature maintained at 280 °C. The chromatographic separation of the PAHs was performed on a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column (Agilent). The GC oven was initially held at 80 °C for 1 min and increased to 250 °C at 25 °C/min and held for 6 min, then increased to 300 ◦C at 10 °C/min and held for 2 min. Preliminarily, full scan electron ionization data were acquired to determine appropriate masses under the following conditions: ionization energy: 70 eV, mass range: 35–350 amu, scan time: 3 scan/s. PAH standards and samples were finally analyzed in selective ion monitoring (SIM) mode for quantitative determination of the analytes. The masses monitored were as follows: 3–5 min, *m*/*z* 128, 127, 102 for naphthalene; 5–6 min, *m*/*z* 152, 154 for acenaphthylene and acenaphthene; 6–7 min, *m*/*z* 166, 165 for fluorene; 7–8 min, *m*/*z* 178 for phenanthrene and anthracene; 8–10 min, *m*/*z* 202, 203, 200 for fluoranthene and pyrene; 10–13 min, *m*/*z* 228, 226, for chrysene and benzo[a]anthracene; 13–18 min, *m*/*z* 252 for benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene; 18–22 min, *m*/*z* 276, 278 for indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene. The solvent delay time was 3 min (to bypass the solvent peak). For all the investigated analytes the corresponding ion ratios were used for confirmation purposes. Signal acquisition and data processing were performed using the Agilent MSD Chemstation (G1701EA, Agilent Technologies).

2.3. Preparation of Fe_3O_4@SiO_2@Flu magnetic nanoparticles

2.3.1. Preparation of Fe_3O_4 MNPs

The Fe_3O_4 MNPs were prepared by chemical co-precipitation. Briefly, $FeCl_3\cdot 6H_2O$ (4.0 g) was dissolved in deionized water (30 mL) in a three-necked round bottom flask, followed by addition of hydrazine hydrate (2 mL) and $FeSO_4\cdot 7H_2O$ (10.90 g) to prepare a stock solution. Afterwards, ammonia solution (35 mL 26.5% w/w) was added into the stock solution under vigorous stirring, followed by dropwise addition of ammonia solution (26.5% w/w) until the solution pH reached 9. The solution was stirred at room temperature for 30 min, aged at 80 °C for 60 min, and then cooled to room temperature. The product was magnetically collected, and washed with water, finally vacuum-dried at 60 °C for 12 h.

2.3.2. Encapsulation of the MNPs with silica (Fe_3O_4@SiO_2)

Nanoparticles (1 g) were dispersed in a mixture of 2-propanol (100 mL) and ultrapure water (8 mL), sonicated for 15 min, then added with ammonia solution (10 mL, 26.5% w/w) and TEOS (8 mL) sequentially. After stirring the mixture for 12 h at 45 °C, the MNPs were collected by a magnet, washed with water and ethanol respectively, and vacuum-dried at 60 °C for 12 h. Through this procedure, the ferro-MNPs were encapsulated with a layer of mesoporous silica.

2.3.3. Preparation of fluorenyl coated MNPs (Fe_3O_4@SiO_2@Flu)

The preparation scheme of Fe_3O_4@SiO_2@ Flu is depicted in Fig. 1. Firstly, the above Fe_3O_4@SiO_2nanoparticles (3 g) were