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# Solid phase extraction of magnetic carbon doped $Fe_3O_4$ nanoparticles

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ABSTRACT

Carbon decorated $Fe_3O_4$ nanoparticles ($Fe_3O_4$/C) are promising magnetic solid-phase extraction (MSPE) sorbents in environmental and biological analysis. $Fe_3O_4$/C based MSPE method shows advantages of easy operation, rapidness, high sensitivity, and environmental friendliness. In this paper, the MSPE mechanism of $Fe_3O_4$/C nanoparticles has been comprehensively investigated, for the first time, through the following three efforts: (1) the comparison of extraction efficiency for polycyclic aromatic hydrocarbons (PAHs) between the $Fe_3O_4$/C sorbents and activated carbon; (2) the chromatographic retention behaviors of hydrophobic and hydrophilic compounds on $Fe_3O_4$/C nanoparticles as stationary phase; (3) related MSPE experiments for several typical compounds such as pyrene, naphthalene, benzene, phenol, resorcinol, anisole and thioanisole. It can be concluded that there are hybrid hydrophobic interaction and hydrogen bonding interaction or dipole–dipole attraction between $Fe_3O_4$/C sorbents and analytes. It is the existence of carbon and oxygen-containing functional groups coated on the surface of $Fe_3O_4$/C nanoparticles that is responsible for the effective extraction process.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) as the products of incomplete combustion or pyrolysis of organic material are widespread in the environment [1–3]. Concerns are being raised because of their toxicity. Some of them are the significant sources of persistent organic pollutants (POPs) due to persistence and bioaccumulation [4]. Therefore, sensitive determination of PAHs in environmental samples is essential to control environmental pollution.

Trace analysis of pollutants in environmental samples generally requires a pretreatment step to isolate and enrich the target analytes before instrumental determination. Solid-phase extraction (SPE) is one of the most commonly used techniques for the preconcentration of PAHs [5,6]. SPE has been widely exploited due to its strong separation capacity, high enrichment factor, minimal sample and solvent consumption, low cost and easy automation [7]. Nowadays, a new mode of SPE, magnetic solid-phase extraction (MSPE) has gained more attention in trace analysis. Various functionalized magnetic materials such as carbon materials [8–15], inorganic silica materials [16], metal oxides [17], organic polymers [18], surfactants [19,20], metal-organic frameworks [21] and ionic liquids [22] coated $Fe_3O_4$ nanoparticles have been prepared and used as appropriate sorbents in MSPE technique. The magnetic nanomaterials are dispersed into sample solutions to adsorb target analytes, subsequently the materials are collected rapidly and conveniently with a magnet, and then the adsorbed analytes are eluted with organic solvents. Compared with traditional SPE, MSPE adsorbents combine numerous advantages such as large surface area, unique magnetic property, convenient functional modification, high separation efficiency, high reusability and environmental friendliness. Carbon materials are well known for their high adsorption capacity for organic compounds. Many research groups have explored amorphous carbon [11,12,14], $C_8$ [13], $C_{18}$ [10], graphene [9], graphene oxide [15] and activated carbon [8] as outside coating materials of magnetic nanoparticles. Zhang et al. [11] successfully synthesized superparamagnetic $Fe_3O_4$/C sorbents by hydrothermal reaction of glucose with iron resource and applied them for MSPE of PAHs from large volumes of environmental waters. Moreover, Shen et al. [14] used $Fe_3O_4$/C sorbents in the clean-up and enrichment of PAHs from tree leaves. The new magnetic sorbent combines the merits of good repeatability, strong adsorption/desorption ability and high recovery for PAHs. However, there is no more detailed research about the mechanism of why the carbon coated $Fe_3O_4$ particles can adsorb/desorb PAHs. In this present work, the adsorption/desorption mechanism of $Fe_3O_4$/C to PAHs and other compounds has been elucidated by comparison in adsorption/desorption property with activated carbon, and retention behavior of the nanoparticle directly used as the chromatographic stationary phase, as well as various spectroscopic

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characterizations. It is found that there is hydrophobic interaction coupled with hydrogen bonding or dipole–dipole interaction between $Fe_3O_4$/C nanoparticles and analytes.

## 2. Experimental

### 2.1. Materials and reagents

Ferric trichloride ($FeCl_3 \cdot 6H_2O$), sodium acetate anhydrous and ethylene glycol (Analytical reagent grade) were purchased from Nanjing Chemical Regent Company (Nanjing, China). Glucose, uracil, resorcinol, phenol, benzene, anisole, thioanisole, and naphthalene (Analytical reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Fluorene (Flu), anthracene (Ant), pyrene (Pyr), benz[b]anthracene (BbA) and benzo(a)pyrene (BaP) were purchased from Alfa Aesar (Tianjin, China). Activated carbon powders (Analytical reagent grade), AC1 (about 50 μm in size) and AC2 (about 200 μm in size), were obtained from Zhuxi Activated Carbon Reagent Co. (Changzhou, China) and Alfa Aesar (Tianjin, China), respectively. HPLC-grade acetonitrile was obtained from Fisher Scientific Corporation (Fair Lawn, NJ, USA). Purified water (Wahaha Group Ltd., Hangzhou, China) was used throughout the experiment. Water samples were obtained from different districts of Nanjing. Rain water was collected in our downtown campus in Gulou District (Nanjing) in January 2012. Tap water was taken from our laboratory in the downtown campus. Lake water was acquired from Xuanwu Lake (Xuanwu District, Nanjing). All water samples were collected randomly and filtered through 0.45 μm membranes to remove suspended particles. The filtered water samples were analyzed within 24 h.

### 2.2. Apparatus

A KQ3200DE ultrasonic bath with temperature control (Kunshan Shumei Ultrasonic Instrument, Suzhou, China) was used to disperse the nanoparticles in solutions. The pH was controlled by a Mettler Toledo SevenMulti pH meter (Mettler-Toledo, Shanghai, China). The magnetism measurement of $Fe_3O_4$ and $Fe_3O_4$/C nanoparticles was examined using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, San Diego, CA, USA) at room temperature. Fourier transform infrared (FT-IR) spectra (4000–400 $cm^{-1}$) in KBr were recorded on a Nicolet-6700 spectrometer (Nicolet, Madison, WI, USA). The morphology and microstructure of $Fe_3O_4$ and $Fe_3O_4$/C nanoparticles were characterized by high resolution transmission electron microscopy (HRTEM) on a JEM-200CX microscope (JEOL, Tokyo, Japan) operating at a 200 kV accelerating voltage. The samples for TEM were obtained by drying sample droplets from water dispersion onto a 300-mesh Cu grid coated with a lacey carbon film, which was then allowed to dry prior to imaging. The X-ray diffraction (XRD) spectra were collected on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (Shimadzu, Kyoto, Japan). Energy dispersive X-ray spectrometry (EDX) was carried out with an EX250 spectroscope (Horiba, Kyoto, Japan) attached to an S-3400N II scanning electron microscope (SEM, Hitachi, Tokyo, Japan). The carbon content (C%) of $Fe_3O_4$/C nanoparticles was determined by Vario MICRO elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). An Nd-Fe-B magnet (8.0 mm × 6.0 mm × 1.6 mm) was used for magnetic separation. The concentrations of PAHs and other analytes were quantitatively analyzed by high performance liquid chromatography (HPLC) on an Agilent 1200 equipped with a vacuum degasser (G1322A), a quaternary pump (G1311A), an auto-sampler (G1329A), a diode array detector (DAD) (G1315A), a fluorescence detector (FLD) (G1321A) and an Agilent ChemStation (Agilent, Palo Alto, CA, USA).

### 2.3. Preparation of $Fe_3O_4$/C nanospheres

The preparation of $Fe_3O_4$ and $Fe_3O_4$/C magnetic nanoparticles was based on the previously reported methods [11,14,23–26] with minor modifications. Briefly, $FeCl_3 \cdot 6H_2O$ (1.35 g) and ethylene glycol (40 mL) were mixed and stirred for a period of time until $FeCl_3$ was dissolved completely, and then sodium acetate anhydrous (3.6 g) was added and reacted vigorously to acquire a transparent solution. Then the mixture was transferred to a Teflon-sealed autoclave at 198 °C for 6 h. The obtained products were cooled naturally, washed several times with water and ethanol, and finally dried at 60 °C for use. As-prepared $Fe_3O_4$ nanoparticles (100 mg) were first washed with water several times. Then, the washed magnetic nanoparticles were dispersed in 15 mL of 0.5 mol $L^{-1}$ glucose solution under vigorous stirring. After stirring for another 30 min, the solution was transferred to a Teflon-sealed autoclave and kept at 180 °C for 4 h and then cooled naturally. The obtained $Fe_3O_4$/C products were separated by a magnet and washed several times with water and ethanol. At last, they were dried at 60 °C for future use.

### 2.4. MSPE experiments

The MSPE procedures for PAHs referred to the previously reported work [11] with minor modifications. Briefly, 1 mL 1.0 mol $L^{-1}$ ammonium acetate buffer solution and 100 mL water sample were transferred into a beaker to obtain the sample solution with pH 7.0. Afterwards, 25 mg of the prepared $Fe_3O_4$/C magnetic nanoparticles was added into the beaker and the mixture was stirred vigorously for 10 min to make the sorbents dispersed uniformly in the solution. Subsequently, an Nd–Fe–B strong magnet was put under the bottom of the beaker to separate the sorbents from the solution. The solution became limpid and the upper clear liquid was decanted 10 min later. After drying by air, the adsorbed target compounds from water sample were eluted from the sorbents with 2 mL acetonitrile. After sonification for 2 min and magnetic separation for 2 min, the supernatant was filtered for HPLC analysis.

### 2.5. HPLC analysis

The chromatographic column used for HPLC analysis of PAHs was a Welch Materials XB-C18, 5 μm, 150 mm × 4.6 mm i.d. (Welch, Shanghai, China). A mobile phase of acetonitrile–water (80:20, v/v) was employed at a flow rate of 1.0 mL $min^{-1}$. The injection volume was 10 μL. The time-programmed excitation/emission wavelengths for fluorescent detection were set as following: 0 min, 260/323 nm (for Flu); 4.9 min, 253/404 nm (for Ant); 6.0 min, 240/385 nm (for Pyr); 8.0 min, 270/480 nm (for BbA); 10.0 min, 290/410 nm (for BaP).

### 2.6. Adsorption of activated carbon for PAHs

To reveal the difference in adsorption/desorption ability between $Fe_3O_4$/C nanoparticle and activated carbon to PAHs, 25 mg of activated carbon was also used as absorbent in the overall SPE procedure and HPLC-FLD analysis of Flu, Ant, Pyr, BbA and BaP. The initial concentrations of the analytes were 1.6 μg $L^{-1}$. Filtration of activated carbon was implemented instead of magnetic separation for $Fe_3O_4$/C. The concentrations of Flu, Ant, Pyr, BbA and BaP in raffinates after adsorption with activated carbon and $Fe_3O_4$/C, and those in eluents with acetonitrile were determined by HPLC according to the procedure in Section 2.5, respectively.