



# In situ preparation of core–shell magnetic porous aromatic framework nanoparticles for mixed–mode solid–phase extraction of trace multitarget analytes

Yanlong Chen<sup>a,1</sup>, Wenfen Zhang<sup>a,1</sup>, Yanhao Zhang<sup>c,1</sup>, Zhifen Deng<sup>a</sup>, Wenjie Zhao<sup>b,\*</sup>,  
Huifang Du<sup>a</sup>, Xue Ma<sup>a</sup>, Dan Yin<sup>a</sup>, Fuwei Xie<sup>d</sup>, Yu Chen<sup>a</sup>, Shusheng Zhang<sup>a,\*\*</sup>

<sup>a</sup> College of Chemistry and Molecular Engineering, Zhengzhou University, Kexue Road 100, Zhengzhou 450001, PR China

<sup>b</sup> School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China

<sup>c</sup> State Key Laboratory of Environmental and Biological Analysis, Department of Chemistry, Hong Kong Baptist University, Hong Kong, PR China

<sup>d</sup> Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, PR China

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## ABSTRACT

This study reports a novel strategy for the preparation of porous aromatic framework (PAF-6) coated magnetic nanoparticles (PAF-6 MNPs) using cyanuric chloride as a planar trigonal basis upon which to build a linear piperazine linker unit. The PAF-6 MNPs were examined as an efficient solid-phase extraction (SPE) sorbent for enrichment of trace organic pollutants including phenol, 2,4,6-trinitrophenol, naphthalene, naphthol, bisphenol A, 2,4-dichlorophenol and 3-nitrochlorobenzene in water. The high-performance liquid chromatography detection limits of such analytes were in the range of 0.08–5.02 ng/mL and recoveries were found to be 84.0–94.0% in well water, tap water, river water and wastewater. The main toxic components of cigarette smoke, including phenolic compounds and benzo[a]pyrene, are efficiently adsorbed by PAF-6 MNPs, and over 50% of such toxins are removed. Theoretical computations were performed to understand the molecular interaction mechanism between PAF-6 and such analytes. The results demonstrate that the PAF-6 MNPs sorbents show excellent adsorption of phenols, polycyclic aromatic hydrocarbons and nitroaromatics based on multiple  $\pi$ - $\pi$  stacking and hydrogen-bond interactions. These results suggest that the PAF-6 MNPs can be applied to extraction, removal and determination of diverse trace multi-target analytes from complex media.

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## 1. Introduction

Solid-phase extraction (SPE) is a well-accepted method [1–9] which is supplanting the conventional liquid–liquid extraction (LLE). Recently, graphene [10], calixarene [11], metal-organic frameworks (MOFs) [12,13], covalent-organic frameworks (COFs) [14], porous organic frameworks (POFs) [15,16] and/or their functionalized Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) [17–19] have been as SPE sorbents due to their large specific surface area, special space configuration, quantum size effect and/or super-paramagnetism.

These SPE sorbents can obtain a better adsorption and purification for different target analytes. Nevertheless, development of versatile SPE sorbents to meet the requirement of diverse kind of multi-target analytes in complex and actual applications remains a challenge.

In recent years, mixed-mode SPE and/or sorbents [20–28] have displayed great potential to deal with the analysis of multi-target species in complex matrices. These sorbents included the commercially available Oasis HLB, Oasis MAX and Oasis MCX, and other synthetic sorbents. For example, magnetic material of polymeric ionic liquid-based has been used as SPE sorbent to adsorption and determination organophosphate pesticides and PAHs [26], and magnetic tetraazacalix[2]arene[2]triazine SPE sorbent for simultaneous extraction and determination of trace analytes [27]. Ding's group [28] using MOFs@graphene SPE sorbent for determination of nonsteroidal anti-inflammatory drugs and selective enrichment of proteins. Although MOF-based SPE sorbents have been used suc-

\* Corresponding author at: Henan University of Technology, Zhengzhou 450001, Henan, PR China.

\*\* Corresponding author.

E-mail addresses: [wjiezhang@126.com](mailto:wjiezhang@126.com) (W. Zhao), [zsszz@126.com](mailto:zsszz@126.com) (S. Zhang).

<sup>1</sup> These authors contributed equally and should be considered co-first authors.

cessfully for sample preparation and analysis, they still have some limitations such as inferior chemical stability, weaker coordinative interaction and higher cost of synthesis. In contrast POFs, especially porous aromatic frameworks (PAFs) have unique molecular architectures, simple structural regularity, homogeneous porous distribution and high surface areas, high hydrothermal stability, a specific hydrophobic-hydrophilic nature,  $\pi$ - $\pi$  conjugated array systems and a highly charged low-density network [29,30]. These advantages make them outstanding SPE sorbents with which to extract hydroxylated PAHs [16] and metal ions [31] using different building units and functionalized groups.

Cancers caused by environmental water pollution is a global problem [32,33]. The cost-effective and energy-efficient reduction and simultaneous determination of trace chemical carcinogens in water is challenging. Organic pollutants, including pesticides, pharmaceuticals, industrial chemicals, hormones and waste gas in the river, have raised significant attention about possible negative influence on aquatic ecosystems, and even on human health [33–36] (Fig. 1). For instance, phenol and naphthol are heavily used in medicine and dye production [37], and bisphenol A, a component of plastics has caused wide public concerns as an endocrine disruptor [38]. Concerns also surround 2,4,6-trinitrophenol and 3-nitrochlorobenzene, models for nitrobenzene pollutants [39,40], 2,4-dichlorophenol, an intermediate in synthesis of herbicide and a known carcinogen [41], and naphthalene, a model for various PAHs pollutant [42]. Recently, major concern in this area is focused on the two types of adsorbing materials, activated carbons and zeolites [43]. Activated carbons are the adsorbent materials most widely used to adsorb toxic compounds from water, while they have some shortcomings, such as their slow uptake of the pollutants and the poor adsorptive power of various kind of hydrophilic analytes [43]. To fulfil current needs ultimately requires robust analytical methodologies to monitor broad range of chemicals at relatively low levels. Cigarette smoke composed of thousands of chemical compounds, is a complex mixture; it includes nicotine, gaseous compounds, and tar with its many carcinogens [42,44–46]. Inhaling toxic substances such as Bap and phenols may cause cancer and any diseases [47,48] and adsorption and removal of toxins from cigarette smoke is one of the most important challenges for manufacturers and users of tobacco products. Consequently, development of versatile adsorbents that can be used various kinds of multitargets and analytes is of great necessity.

In the present work, we controlled the reaction temperature and used cyanuric chloride (CC), piperazine and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  microspheres to prepared of a novel PAF-6 coated  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  MNP adsorbent via one-step polymerization (Fig. 2, PAF-6 MNPs). PAF-6 MNPs were prepared without use of metal catalysts, in a reaction which is mild and inexpensive, and gives a high yield. PAF-6 is assembled with piperazine and triazine groups to build a framework with repeated 12-ringsunits. These aromatic rings and nitrogen atoms have multipoint recognition sites. In view of its biocompatibility, lack of toxicity, chemical stability [49,50], and high porosity, PAF-6 and PAF-6 MNPs are expected to be valuable SPE sorbents capable of interacting with many different analytes with various polarities. The new core-shell sorbent, PAF-6 MNPs, core-shell structured with a functional shell (PAF-6) and a magnetically responsive core have comprehensive advantages of good adsorption capacity and magnetic separation. PAF-6 MNPs were used for adsorption of trace organic pollutants such as phenol, 2,4,6-trinitrophenol, naphthalene, naphthol, bisphenol A, 2,4-dichlorophenol and 3-nitrochlorobenzene in water (Fig. 1). At the same time, the technique was used to identify the main toxic components in cigarette smoke, i.e. phenol, *m*-cresol, *p*-cresol, *o*-cresol, hydroquinone, resorcinol, pyrocatechol and benzo[a]pyrene using this novel sorbent. The satisfactory results obtained showed

that PAF-6 MNPs might be applied to the determination of diverse trace multi-target analytes in complex samples.

## 2. Experimental

### 2.1. Reagents and materials

Analytical grade iron chloride hexahydrate ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ), polyethylene glycol, ethylene glycol, sodium acetate (NaOAc), toluene, hydrochloric acid (HCl), sodium hydroxide (NaOH), acetone ( $\text{Me}_2\text{CO}$ ) and ethanol (EtOH) were purchased from Henan Chemical Reagents Co. Ltd (Henan, China). HPLC grade methanol (MeOH) and acetonitrile (MeCN) were purchased from Dikma (Sigma, Germany). Activated carbon powder (with mesh size of 50, analytical grade) was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Ultrapure water used for the experiments by Milli-Q system (Millipore, USA).

Phenol, 2,4,6-trinitrophenol (TNP), naphthalene (Naph), naphthol (Nap), bisphenol A (BPA), 2,4-dichlorophenol (2,4-DCP), 3-nitrochlorobenzene (3-NCB), tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), benz[a]pyrene (Bap), *m*-cresol, *p*-cresol, *o*-cresol hydroquinone, resorcinol and pyrocatechol were supplied by Aladdin (Shanghai, China).

### 2.2. Apparatus

Fourier-transform infrared (FT-IR) analysis was measured using a Nicolet 6700 spectrometer (Thermo, USA). X-ray diffraction (XRD) spectra were collected on an ARL X'TRA diffractometer with Cu  $K\alpha$  radiation (ARL, Switzerland). Scanning electron microscopy (SEM) images were collected by a S-4300 SEM instrument (Hitachi, Japan). Transmission electron microscopic (TEM) properties were studied with an H-7500 TEM instrument (Hitachi, Japan). The magnetization curves were presented at ordinary temperature on a LDJ 9600-1 vibrating sample magnetometer (VSM) (LDJ Electronics, USA). The surface area and pore properties analysis was performed on an Autosorb-1 MP gas adsorption instrument (Quantachrome, USA).

High performance liquid chromatography (HPLC) analysis was carried out with an Agilent system (Agilent 1260, USA) with UV detector (UVD) and fluorescence detector (FLD) which used in all the experiments. The detailed analysis methods for trace organic pollutants, phenolic compounds, and Bap are described in the Supporting Information (SI).

### 2.3. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PAF-6}$ MNPs

$\text{Fe}_3\text{O}_4$  were synthesized by solvothermal reduction method [51].  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  nanoparticles were synthesized by a previously described method [52,53]. The detailed synthetic method for nanoparticles can be seen in SI. Cyanuric chloride (CC), piperazine and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  microspheres were prepared via a one-step polymerization, as shown in Fig. 2. To a 250 mL round-bottom flask,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (1.0 g), CC (1.5 g) and *N,N*-dimethylethylamine (1.8 mL) were added in anhydrous 1,4-dioxane (100 mL). The solution was kept at 0 °C, and piperazine (1.0 g) in anhydrous 1,4-dioxane (40 mL) was added dropwise. After ultrasonic degassing, the solution was evaporated under  $\text{N}_2$ . In order to improve the reaction yield, the temperature was programmed as follows: the polymerization was first carried out at 0 °C for 4 h, then the temperature was increased to 50 °C where it was maintained for 4 h. Finally, the reaction was kept at 95 °C for 24 h. The obtained product was collected by magnetic adsorption, washed thoroughly with  $\text{Me}_2\text{CO}$ ,  $\text{H}_2\text{O}$ , THF and MeOH, a, respectively, to obtain PAF-6 MNPs.

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