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Thermo-responsive polymer tethered metal-organic framework core-shell magnetic microspheres for magnetic solid-phase extraction of alkylphenols from environmental water samples

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ABSTRACT

In this work, the thermo-responsive polymer PNIPAM tethered to Fe_3O_4@SiO_2@MOF core-shell magnetic microspheres was first synthesized by a surface-selective post-synthetic strategy and underwent highly efficient magnetic solid-phase extraction (MSPE) of alkylphenols from aqueous samples. Alkylphenols, including 4-*tert*-octylphenol (OP) and 4-*n*-nonylphenol (NP), were selected as target compounds. The sample quantification was carried out using LC–MS/MS in multiple reaction monitor (MRM) mode. Under optimal working conditions, the developed method showed good linearity in the range of 5–1000 ng L^{-1}, a low limit of detection (1.5 ng L^{-1}), and good repeatability (relative standard deviation, <8%, n = 5) for NP and OP. Owning to the hydrophilic/hydrophobic switchable properties of the nanocomposite, high recoveries (78.7–104.3%) of alkylphenols were obtained under different extraction conditions. The levels of OP and NP in environmental samples collected from local river, lake and pond waters were analyzed using the developed method. It was believed that the synthesized material with the thermo-responsive coating, large surface areas and magnetic properties should have great potential in the extraction and removal of alkylphenols from environmental samples.

1. Introduction

Solid-phase sorption-based extraction techniques have been widely used in the sample pretreatment process [1]. The interactions between the sorbent and the target analytes play a critical role in the extraction process [2]. Due to the designable nature of nanomaterials, many novel nanomaterial-based sorbents have been fabricated and used to improve the performance of the extraction techniques. Recently, metal-organic frameworks (MOFs) have attracted great attention and have been explored as a sorbent in extraction techniques [3–7]. For example, Yan and coworkers have systemically investigated the performance of MOFs as SPE sorbents and stationary phases of GC capillaries and HPLC columns [8–11]. Lee et al. used MIL-101 and ZIF-8 as sorbents for micro-solid-phase extraction (μ-SPE) of acid drugs and organochlorine pesticides from water samples [12,13]. Ouyang and coworkers have utilized MIL-101 (Cr) and isoreticular bio-MOF 100–102 as the fiber coating of solid-phase microextraction (SPME) for determination of organic pollutants [14,15]. We have explored the application of MIL-53(Al) as a sorbent for SPME of PAHs and membrane funnel-based spray ionization mass spectrometry analysis of bovine serum albumin tryptic digest [16,17].

Alkylphenols have changeable charge properties and switchable hydrophilic/hydrophobic properties under different conditions [18]. Taking 4-*n*-nonylphenol (NP) as an example, the phenolic hydroxyl group may be deprotonated or protonated, which makes NP negatively charged or electron neutral at different pHs. The pristine form of NP is more hydrophobic due to the nature of the nonyl group, while the NP becomes more hydrophilic with deprotonation of the phenolic group under alkaline conditions. The alkylphenols are endocrine disruptors and have been detected in water samples. Therefore, it is quite interesting and necessary to develop a sorbent that could satisfy the requirement of alkylphenol extraction under different conditions.

One of the important properties of MOFs is their availability of in-pore functionality and outer-surface modification [19,20]. In this work, a thermo-responsive polymer tethered to Fe_3O_4@SiO_2@MOF core-shell magnetic microspheres is synthe-

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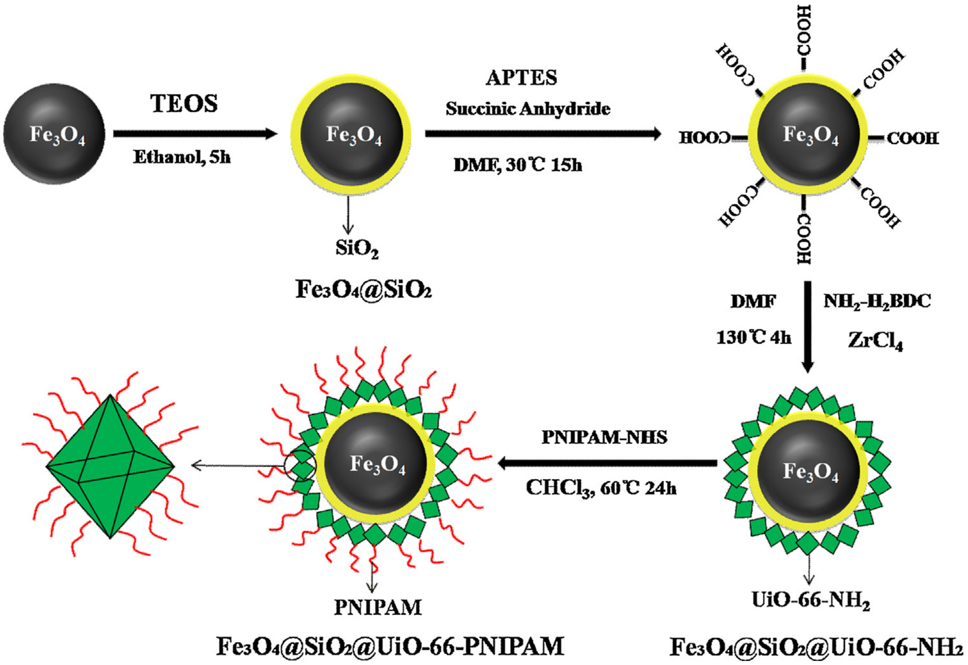

Fig. 1. Synthetic procedures for $Fe_3O_4@SiO_2$@UiO-66-PNIPAM core–shell magnetic microspheres.

sized by surface-selective post-synthetic strategy and undergoes highly efficient MSPE of alkylphenols from environmental water samples. As representatives of alkylphenols, 4-*tert*-octylphenol (OP) and NP, which have been reported to be widespread, are selected as target compounds. Structurally, they both have alkyl and phenolic hydroxyl groups; bisphenol A and phenol, which lack the hydrophobic groups and have smaller log K_{OW}, are used for comparison.

2. Experimental

2.1. Reagents and materials

All reagents were analytical grade. Iron (III) chloride hexahydrate ($Fe_3Cl{\cdot}6H_2O$) (99%), ethyl alcohol, ethylene glycol, *N*,*N*-dimethylformamide (DMF) and acetic acid were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium acetate trihydrate (NaAc) was obtained from Kermel Chemical Reagent Company (Tianjin, China). Ammonia solution (25%) and chloroform were obtained from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Tetraethyl orthosilicate (TEOS), succinic anhydride (99%) and zirconium chloride ($ZrCl_4$) (98%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). 2-Aminoterephthalic acid (99%), poly (*N*-isopropylacrylamide) (PNIPAM) and ester-terminated *N*-hydroxy-succinimide (NHS) were obtained from Sigma-Aldrich Co., Ltd. (Shanghai, China). (3-Aminopropyl) triethoxysilane (98%) (APTES) was supplied by Macklin Biochemical Co., Ltd. (Shanghai, China). De-ionized water ($18.2\,M\Omega\,cm^{-1}$) obtained from a Millipore Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare aqueous solutions for further experiments. The standards of bisphenol A (BPA), 4-*tert*-octylphenol (CAS No. 140-66-9) and 4-*n*-nonylphenol (CAS No. 140-40-5) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). 4-Nonylphenol 2,3,5,6-d4 and bisphenol A-d16 (Sigma-Aldrich, USA) were used as internal standards of BPA and NP. A working standard ($100\,ng\,mL^{-1}$ in methanol) was prepared weekly. Methanol, acetone, acetonitrile and *n*-hexane were obtained from Tedia Company Inc. (USA).

2.2. Instrumentation

The morphology of the synthesized crystals was observed with scanning electron microscopy (SEM)(SWPRA^{TM} 55, Carl Zeiss Micro Imaging Co., Ltd., Germany). Transmission electron microscopy (TEM) was observed on a JEOL Ltd. JEM-2010 spectrometer. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Magna 750 FTIR spectrometer. Powder X-ray diffraction (PXRD) pattern was acquired at room temperature (298 K) on a Bruker SMART APEX CCD-based diffractometer. ^1H nuclear magnetic resonance (NMR) was performed on a Bruker DRX-600 spectrometer. The Brunauer-Emmett-Teller specific surface areas of typical products were measured using an ASAP 2020 porosimeter (Micromeritics, USA). The magnetization curves were obtained at room temperature on an MPMS-SQUID-VSM (Quantum Design, USA). Thermogravimetric analysis (TGA) was performed on ~25–30 mg of powdered sample loaded inside a platinum crucible on a Stanton Red croft TG-DSC instrument. All samples were heated at a ramp of 5 °C per minute–700 °C under N_2 and O_2 with flow rates at 20 and 5 mL per minute, respectively.

2.3. Synthesis procedure

For the synthesis of PNIPAM-tethered $Fe_3O_4@SiO_2$@MOF core-shell magnetic microspheres, UiO-66, was used as a model MOF. To allow the coupling of ligand with the polymer, 2-amino-benzenedicarboxylic (H_2N-H_2BDC) with an amine group was selected as the ligand [21]. The synthetic procedure of the nanocomposite was shown in Fig. 1. Fe_3O_4 and $Fe_3O_4@SiO_2$ magnetic particles were synthesized according to the previously reported method with a minor modification; the detailed procedure was described in the supplementary information [22].

2.3.1. Synthesis of $Fe_3O_4@SiO_2$@UiO-66-NH_2 core-shell microspheres

$Fe_3O_4@SiO_2$@UiO-66-NH_2 microspheres were fabricated via facile hydrothermal synthesis. Typically, carboxylate-terminated $Fe_3O_4@SiO_2$ microspheres (10 mg), $ZrCl_4$ (46.61 mg, 0.20 mmol), 2-aminoterephthalic acid (36.23 mg, 0.20 mmol) and acetic acid