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A magnetic-based dispersive micro-solid-phase extraction method using the metal-organic framework HKUST-1 and ultra-high-performance liquid chromatography with fluorescence detection for determining polycyclic aromatic hydrocarbons in waters and fruit tea infusions

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ABSTRACT

A hybrid material composed by the metal-organic framework (MOF) HKUST-1 and Fe_3O_4 magnetic nanoparticles (MNPs) has been synthetized in a quite simple manner, characterized, and used in a magnetic-assisted dispersive micro-solid-phase extraction (M-d-μSPE) method in combination with ultra-high-performance liquid chromatography (UHPLC) and fluorescence detection (FD). The application was devoted to the determination of 8 heavy polycyclic aromatic hydrocarbons (PAHs) in different aqueous samples, specifically tap water, wastewaters, and fruit tea infusion samples. The overall M-d-μSPE-UHPLC-FD method was optimized and validated. The method is characterized by: its simplicity in both the preparation of the hybrid material (simple mixing) and the magnetic-assisted approach (~10 min extraction time), the use of low sorbent amounts (20 mg of HKUST-1 and 5 mg of Fe_3O_4 MNPs), and the low organic solvent consumption in the overall M-d-μSPE-UHPLC-FD method (1.5 mL of acetonitrile in the M-d-μSPE method and 2.8 mL of acetonitrile in the UHPLC-FD run). The resulting method has high sensitivity, with LODs down to 0.8 ng L^{-1}; adequate intermediate precision, with relative standard deviation values (RSD) always lower than 6.3% (being the range 5.9–9.0% in tap water for a spiked level of 45 ng L^{-1}, 6.1–14% in wastewaters for a spiked level of 45 ng L^{-1}, and 7.2–17% in fruit tea infusion samples for a spiked level of 45 ng L^{-1}); and adequate relative recoveries, with average values of 82% in tap water, and 94% and 75% in wastewater and fruit tea infusion samples, respectively, if using the proper matrix-matched calibration.

1. Introduction

The utilization of nanoparticles (NPs, 1–100 nm) is quite advantageous for chemical analysis given the intrinsic characteristics of these materials: high superficial area, unique reactivity, high chemical stability, and easiness of functionalization, among others [1,2]. Magnetic nanoparticles (MNPs) are a kind of NPs presenting superparamagnetism. The magnetic solid phase of MNPs mainly consists of iron minerals and magnetic iron oxides such as magnetite (Fe_3O_4) [3]. The use of MNPs has really increased the applicability of magnetic-facilitated extraction procedures since 1996 [4]. Analytical extraction approaches based on MNPs (using bare or coated MNPs to extract analytes) are advantageous over more classical solid-phase extraction approaches (SPE). Thus, MNPs-based extraction methods avoid filtration and centrifugation steps, because the extractant sorbent can be easily separated from the remaining components of the sample with the application of an external magnetic field [4–6]. The utilization of dispersive micro-SPE (d-μSPE) with the help of any agitation system (vortex, ultrasounds, stirring...), rather than static μSPE (sorbent amounts < ~500 mg), facilitates the transfer of the analytes to the sorbent material while reducing extraction times [7].

Bare MNPs are scarcely used in analytical extraction methods due to their high chemical reactivity, tendency to aggregation,

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easily oxidation in air, and quick biodegradation. Thus, coated and/or functionalized MNPs are commonly used [4–6] because they present higher chemical and colloidal stability. Besides, they have wider extraction capabilities, because other sorbent materials are incorporated generating a hybrid material. More common hybrid materials for magnetic-based d-μSPE include silica ($Fe_3O_4@SiO_2$) [8,9], surfactants [10,11], molecular imprinted polymers (Fe_3O_4@MIPs) [12,13], and carbon nanotubes (Fe_3O_4@CNTs) [14,15].

Metal-organic frameworks (MOFs) are a group of materials that are starting to receive increasing attention in analytical chemistry [16,17] given their outstanding properties: permanent nanoscale porosity, good thermostability, high surface area, impressive tuneability (almost infinite combination of metals and organic linkers), and uniform structure cavities [18]. Thus, several MOFs have been proposed as sorbent materials in SPE [19,20], d-μSPE [7,21], and solid-phase microextraction (SPME) [22–24].

MOFs have also been proposed in combination with MNPs in magnetic-based d-μSPE (M-d-μSPE) approaches, mainly for the determination of metals [25–29]. Regarding the determination of organic compounds, it has been mainly described the use of $Fe_3O_4@SiO_2$@MOF [30–34]. The use of MNPs without silica has only been reported for polychlorinated biphenyls (PCBs) with the MOF MIL-100 [35] and using a prior functionalization of Fe_3O_4 with mercaptoacetic acid (30 min each cycle, 30 cycles overall), and for organophosphorus pesticides with the MOF MIL-101 [36] and using the solvothermal method without any functionalization (~20 h). Recently, Maya et al. combine the MOF MIL-100 with Fe_3O_4 immobilized in a micro-syringe [37].

The present work reports the utilization of the MOF HKUST-1 in combination with MNPs, in a M-d-μSPE method with ultra-high performance liquid chromatography (UHPLC) and fluorescence detection (FD) for the determination of 8 heavy polycyclic aromatic hydrocarbons (PAHs). The analytical applications is carried out with environmental waters (tap water and wastewaters), and with fruit tea infusion in which PAHs have been reported [38,39]. It is important to highlight that the preparation of the hybrid material HKUST@Fe_3O_4 is accomplished without ensuring any kind of chemical binding through a reaction: both materials are simply mixed with the aqueous sample. Thus, the overall method is quite simple, not only for the use of a magnetic-based approach but also for the easiness of preparation of the hybrid sorbent material.

2. Experimental

2.1. Chemicals, reagents, materials and samples

The eight PAHs studied in this work were: benzo[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaPy), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiPer), and indeno[1,2,3-cd]pyrene (I(1,2,3-cd)Py). BaA, BbF, BaPy, DahA and I(1,2,3-cd)Py were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany) as individual standard solutions in acetonitrile with a concentration of 10 mg L^{-1}. Chy (98%) and BghiPer (98%) were supplied as solids by Aldrich (Milwaukee, Wisconsin, USA). BkF (99%) was supplied as solid by Fluka Chemika (Buchs, Switzerland). These solids were used to prepare standard solutions with concentrations of 80 mg L^{-1} for BkF, 92 mg L^{-1} for Chy, and 80 mg L^{-1} for BghiPer, all kept at 4 °C and also protected from light. These eight standard solutions were used to prepare a mixture standard solution in acetonitrile (ACN) with all 8 PAHs with a concentration of 1 mg L^{-1}. Such standard mixture solution was used to spike water (ultrapure water, tap water or wastewaters) and fruit-tea infusion samples, as well as to prepare working aqueous standard solutions of all PAHs at μg L^{-1} levels.

Ultrapure Milli-Q water was obtained by a water purification system A10 MilliPore (Watford, UK). ACN was obtained from VWR (Llinars del Vallés, Spain) with LC-MS purity grade. Hexane was acquired to Sigma–Aldrich (Steinheim, Germany) with Chromasolv® grade. Trichloromethane (TCM) and dichloromethane (DCM) were supplied by Panreac (Barcelona, Spain) with pro-analysis purity grade.

HPLC mobile phases were filtered before use using Durapore® membrane filters of 0.20 μm, supplied by Sigma–Aldrich.

Absolute ethanol PRS 99.5%, supplied by Panreac, copper (II) nitrate hemipentahydrate and benzene-1,3,5-tricarboxylic acid (trimesic acid) (95%), supplied by Sigma–Aldrich, were utilized in the synthesis of HKUST-1.

Iron (III) chloride hexahydrate ($FeCl_3·6H_2O$) (≥99%), iron (II) chloride tetrahydrate ($FeCl_2·4H_2O$) (≥99%), sodium hydroxide (≥98%), and hydrochloric acid (≥37%), all from Sigma–Aldrich, were required in the synthesis of Fe_3O_4 magnetic nanoparticles.

0.2 μm syringe Milex® Durapore® PVDF (Polyvinylidene fluoride) were purchased from Sartorius Stedim Biotech (Goettingen, Germany), and used before any UHPLC injection of samples and standards

A prism (5 cm × 2 cm × 2 cm) NdFeB magnet was purchased to ENES Magnesy Pawel Zientek (Warszawa, Poland).

Tap water was taken at the laboratory and three wastewaters were supplied by an environmental monitoring laboratory belonging to the University. Wastewaters were directly sampled at the wastewater treatment plant. In all the cases, sampling was carried out while avoiding the formation of bubbles, and using clean amber glass bottles of 100 mL in volume. Samples were also maintained in a portable fridge until they reached the laboratory, and then maintained in the dark at 4 °C for no more than 48 h, before being analyzed.

Three fruit-tea samples were bought in a local supermarket, being its fruity content specifically composed of: apple, elder flower, mallow flower, plum and lemon (fruit-tea 1); guarana, ginger and raspberry (fruit-tea 2); and wild fruits (fruit-tea 3). The preparation of the infusion tried to mimic the common preparation of tea infusions in the Canary Islands, which is quite simple [38]. Thus, 100 mL of bottled water was boiled in a glass vessel, and then one commercial packet bag of the fruit-tea (about 1.5 g) was placed in the vessel for 10 min, until it almost reached room-temperature. Afterwards, the infusion was filtered through 0.2 μm and kept in the dark at 4 °C for no more than 48 h before being analyzed. In some experiments, the filtered infusion sample was spiked with PAHs.

2.2. Synthesis of Fe_3O_4 MNPs

α-Fe_3O_4 (magnetite) MNPs were synthesized through a modification of the alkaline co-precipitation of Fe(II) and Fe(III) method initially developed by Kang et al. [40]. Briefly, 2.0 g of $FeCl_2·4H_2O$ and 5.2 g of $FeCl_3·6H_2O$ were dissolved in 25 mL of ultrapure water containing 0.85 mL of concentrated HCl, with a nitrogen atmosphere. Then, 250 mL of 1.5 mol L^{-1} NaOH was added dropwise under vigorous stirring in nitrogen atmosphere. Once the reaction was complete, the black precipitate of MNPs was separated from the reaction medium using a strong magnet. MNPs are then washed with 200 mL of ultrapure water (previously degassed) five times. The final product is re-suspended in 200 mL of ultrapure water, obtaining an estimated Fe_3O_4 MNPs concentration of ~10 mg mL^{-1}.

2.3. Synthesis of HKUST-1

HKUST-1 was prepared according the procedure of Wang et al. in 2002 [41] by mixing 0.630 g of trimesic acid in 15 mL of ethanol and 1.255 g of $Cu(NO_3)_2·2.5H_2O$ in 15 mL of deionized water, with