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Magnetic Nanoparticles for PAHs Solid Phase Extraction

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In this paper a novel approach to the preparation of a solid-phase extraction sorbent, 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (TBCD)/magnetic nanoparticles, was developed. The four benzyl groups of TBCD provide the TBCD functionalized Fe_3O_4 with strong adsorption capacity for polycyclic aromatic hydrocarbons (PAHs), due to their π-π stacking interaction, which increases selectivity of the synthesized material to target analytes. The characterization indicated that the TBCD functionalized Fe_3O_4 nanoparticles rapidly and effectively pre-concentrate PAHs from water. Satisfactory precision and accuracy of the developed method were obtained at a low concentration of 5 ng L^{-1}.

The nanosized magnetic solid-phase extraction (MSPE) sorbent combines high surface area, typical of nanomaterials, acting as a platform for anchoring functional groups with strong adsorption ability, and the possibility for a rapid collection simply applying an external magnetic field due to the superparamagnetism.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) that consist of two or more benzene rings are among the most widespread organic pollutants. Moreover, they are carcinogenic, mutagenic, and teratogenic (Srogi, 2007). The US Environmental Protection Agency has taken PAHs on the priority pollutants list. Due to their direct threat to human health, more attention has been focused on the monitoring of PAHs in the natural environment (Huang et al., 2011). Among the current techniques for pre-concentration (Camel, 2000) solid phase extraction (SPE), in combination with HPLC, is the most usual one, as it. SPE has many advantages, such as high recovery, low consumption of organic solvents, and convenience of operation. However, there are still some drawbacks, such as low extraction efficiency for ultra-trace analytes, and long operation time when handling large volumes of water samples.

To overcome these disadvantages, magnetic solid-phase extraction (MSPE), a novel form of SPE, has been developed, based on the use of magnetic nanoparticles (Liu et al., 2012). In MSPE methods, functionalized magnetic nanomaterials are dispersed into samples to adsorb target compounds, then the sorbents are collected rapidly and conveniently with an external magnetic field and the adsorbed analytes are eluted with solvents. It is well known that a proper surface functionalization of Fe_3O_4 magnetic nanoparticles (MNPs) is very critical for the extraction efficiency. Typical modified groups (alkyl carboxylates, octadecylsilane, etc..) are hydrophobic and applied to extract hydrophobic PAHs from water samples, but these hydrophobic materials generally have low specificity to PAHs, and some natural hydrophobic organic matters in environmental water samples can also be adsorbed by sorbents and then affect the limits of detection (LODs). Today, the goal of MSPE is to design new magnetic sorbents with good stability, dispersibility and selective adsorption capability.

Herein, we propose the use of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (TBCD) modified MNPs for pre-concentration of PAHs in water. The nanoadsorbent was prepared by a bottom up chemical strategy, that provides experimental easiness and potential low-cost production (Altavilla et al., 2013; Sarno et al., 2014; Sarno et al., 2015a; Sarno et al., 2015b), together with excellent synthesis control of monodispersed size nanoparticles. A new facile functionalization approach was designed, developed and validated.

Two PAHs were chosen as target analytes because of their representative structures, including anthracene (Ant) and fluoranthene (FlA). The TBCD-functionalized MNPs were applied to extract trace level PAHs from water in 15 min. The separation efficiency of the proposed method was compared with the extraction efficiencies of other magnetic materials including Fe_3O_4/C (Zhang et al., 2010a), C_{10}–C_{18} carboxylates

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(Ballesteros-Gòmez et al., 2009), Fe_3O_4–C_{18} (Zhang et al., 2010b), Fe_3O_4-MPNP (Zhang et al., 2012a), Fe_3O_4/PC (Zhang et al., 2012b), Fe_3O_4/PDA (Wang et al., 2013a), Fe_3O_4@SiO_2-G (Wang et al., 2013b), in terms of amount of sorbent, extraction time, loading volume, Limit of detection (LOD), etc.. In particular, lower amount of TBCD-functionalized MNPs sorbent, that is able to work in a very short time, was needed if compared with other sorbents (Ballesteros-Gòmez et al., 2009; Zhang et al., 2010b; Zhang et al., 2012a; Zhang et al., 2012b).

2. Experimental Section

2.1 Preparation of Fe_3O_4@OA-OAL nanoparticles

The synthesis was carried out using standard airless procedures and commercially available reagents.

20 mL of the solvent (benzyl ether), 2 mmol of the precursor ($Fe(acac)_3$), 10 mmol of 1,2-hexadecanediol used for its high reducing ability, 6 mmol of oleic acid and 6 mmol of oleylamine used as surfactants, were mixed and magnetically stirred under a flow of nitrogen. The mixture was heated to 200°C for 120 min and then, under a blanket of nitrogen, heated to reflux (285°C) for another 120 min. The black-brown mixture was cooled to room temperature by removing the heat source. Under ambient conditions, ethanol was added to the mixture that was precipitated and separated via centrifugation. The black product was then dissolved in hexane. Transmission electron microscopy (TEM) images were acquired using a FEI Tecnai electron microscope operated at 200 KV with a LaB_6 filament as the source of electrons. XRD measurements were performed with a Bruker D8 X-ray diffractometer using CuKα radiation. The KBr technique was applied for determining the FT-IR spectra of the samples by using Vertex 70 apparatus (Bruker Corporation). Spectra were recorded the scanning range was from 4000 a 400 cm^{-1}. Thermogravimetric analysis (TG-DTG) at a 10 K/min heating rate in flowing air was performed with a SDTQ 600 Analyzer (TA Instruments).

2.2 Preparation of Fe_3O_4@OA-OAL_TBCD

The preparation of Fe_3O_4@OA-OAL functionalized TBCD nanoparticles is schematically illustrated in Figure 1. TBCD was chemical-bonded to the surface of the magnetic nanoparticles, prepared as described before, through quaternization reaction. An ethanol–tetrahydrofuran mixture (100 mL, 1:1, v/v), containing TBCD (90 mg), was placed in a reaction flask, and then the mixture was heated and refluxed at 80°C. TBCD dissolved totally in solution and the nanohybrid (60 mg) was added. The mixture was refluxed at 80 °C under stirring (400 rpm /min) for 24 h. After reaction, the product was isolated from the solution still hot by a magnet and finally washed with warm ethanol–tetrahydrofuran mixture (1:1, v/v), ethanol and water in turn. Then the final product was dried in vacuum at 60 °C for 24 h.

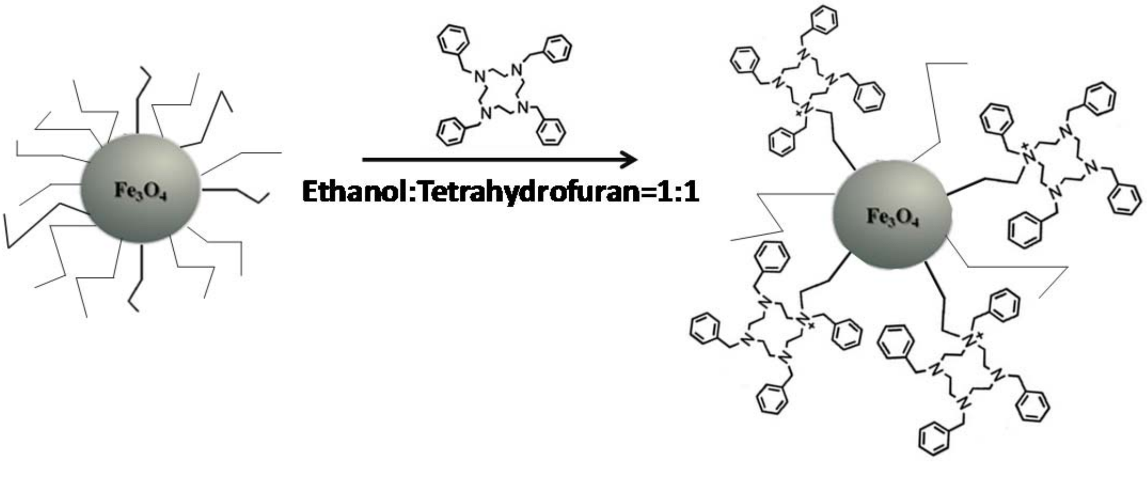

Figure 1: Preparation scheme of Fe_3O_4@OA-OAL_TBCD

2.3 Extraction procedure

The whole extraction procedure is depicted in Figure 2. Firstly, 80 mg of TBCD-functionalized magnetic nanoparticles were cleaned and activated with acetonitrile and distilled water in sequence. Then 200 mL of sample solution spiked with PAHs (5 ng/L) was added. To ensure maximum capture of the target PAHs, the mixture was sonicated at room temperature for 5 min to disperse the magnetic nanoparticles in solution.

Then the TBCD-functionalized MNPs were separated rapidly from the solution under an external magnetic field within 10 min. After the supernatant solution was discarded, PAHs were eluted from the sorbents with 4x 2 mL of acetonitrile. The eluent was collected and evaporated to about 100 mL under a gentle nitrogen flow at 30°C and then re-dissolved to 200 mL by acetonitrile. Finally, the PAHs eluting solution was analysed by gas chromatography.

Determination of PAHs was carried out by gas chromatography-mass spectroscopy (GC-MS, ThermoFisher). The analysis conditions were set as follows: run time, 16.5 min; injector temperature, 200 °C; 80°C for 1min+from 80°C to 185°C 10°C/min+185°C for 5 min, 1 mL/min.

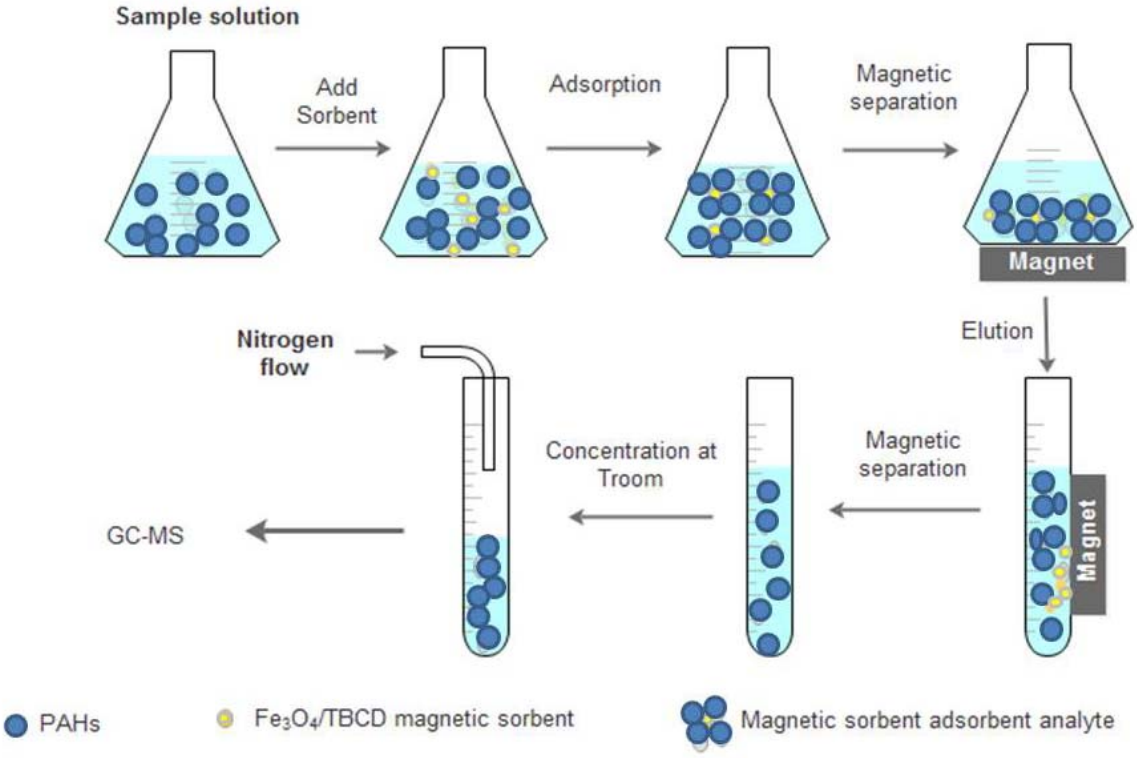

Figure 2: Scheme of the process extraction

3. Results and discussion

The monodispersed nanoparticles of Fe_3O_4 have been obtained successfully as confirmed by TEM analysis. Figure 3 shows TEM images of the Fe_3O_4 nanoparticles at two different magnifications. The images revealed the formation of nanoparticles with highly uniform size that, once deposited over a copper grid, tend to self-organize in a regular hexagonal layer. The particle size distribution, obtained from statistic analysis of over 400 nanoparticles, indicates that the average diameter of inorganic core is d = 10 nm with σ = 1.22 nm.

X-ray diffraction analysis of the reaction product, after washing, confirms that they are magnetite crystals (Sarno et al., 2015) and that the mean crystal sizes, as determined by Debye-Scherrer equation, was 9.95 nm.

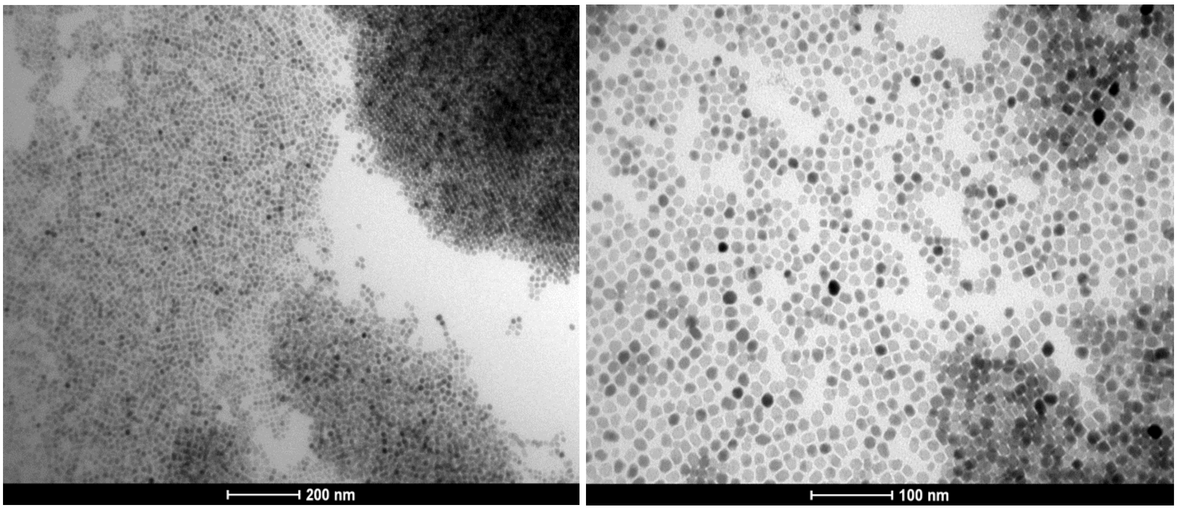

Figure 3. TEM images of the Fe_3O_4 nanoparticles at different magnification

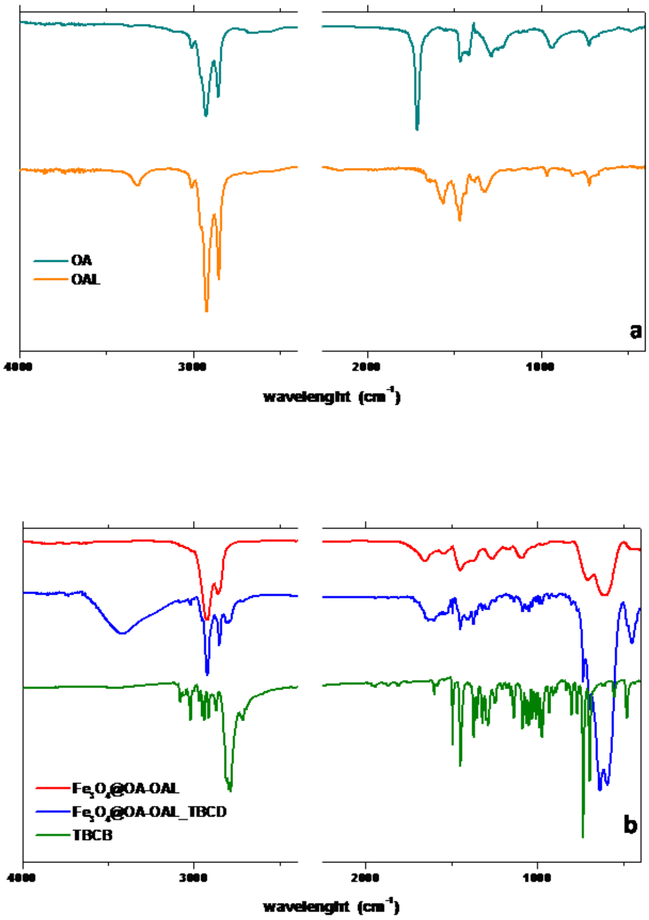

Figure 4. FTIR spectra of oleic acid and oleylamine (a), Fe_3O_4@OA-OAL, Fe_3O_4@OA-OAL_TBCD and TBCD (b), in the range 400-4000 cm^{-1}.

To investigate whether the surface of the nanoparticles was capped with oleic acid and oleylamine FT-IR spectra were acquired on OA, OAL and nanoparticles (Figure 4a). Oleic acid shows a strong absorption peak of carbonyl stretch band around 1710 cm^{-1}. The band at 1285 cm^{-1} exhibited the presence of C-O stretch and the bands at 1462 and 937 cm^{-1} are the in-plane and out-plane bands of O-H (Altavilla et al., 2011). The strong band at 2855 and 2923 cm^{-1} belong to methylene and methyl symmetric stretching vibration, respectively. The spectrum of oleylamine shows the characteristic peaks of the oleic group in the 2750-3000 cm^{-1} region, the v(C=C) stretch mode at 1647 cm^{-1}, and the peak at 1468 cm^{-1} due to the (C-H) bending mode. In addition, there are characteristic signals of the amine group: the peak at 3319 cm^{-1} due to the v (N-H) stretching mode of the primary amine, the peak at 1560 cm^{-1} due to the -NH_2 scissoring mode, and the peak due to the -NH_2 bending mode at 968 cm^{-1} (Altavilla et al., 2011), as well as a C-H (C>7) flexural vibration in the range of 720 cm^{-1}. It is possible to observed the Fe_3O_4 typical peaks due to the ν1 (Fe-O) and ν2 (Fe-O) bonds at 635 and 590 cm^{-1}. Two new bands at 1541 and 1649 cm^{-1} appear in the Fe_3O_4@OA-OAL spectrum characteristic (Figure 4b) of the asymmetric ν_{as}(COO-) and the symmetric ν_s(COO-) stretch, instead. Moreover, the presence of oleylamine as capping agent (Figure 4b) on the nanoparticles surface is confirmed by the peak characteristics of the oleic group in the 2750-3000 cm^{-1} region, the v (C=C) stretch mode at 1647 cm^{-1}, and the peak at 1468 cm^{-1} due to the (C-H) bending mode. Indeed, the as prepared nanoparticles result hydrophobic, becoming much more hydrophilic and dispersible after anchoring the TBCD. The IR spectrum of Fe_3O_4@OA-OAL-TBCD is also reported in Figure 4b (blue trace), peaks at 3079 cm^{-1} and 3019 cm^{-1} appear corresponding to the C–H stretching vibration of benzenoid ring (compare with green trace of free TBCD), indicating the success of our quaternization reaction functionalization approach, which allows to directly use the organic chains around the nanoparticles performing a dual function: to control the magnetite size and anchor TBCD.

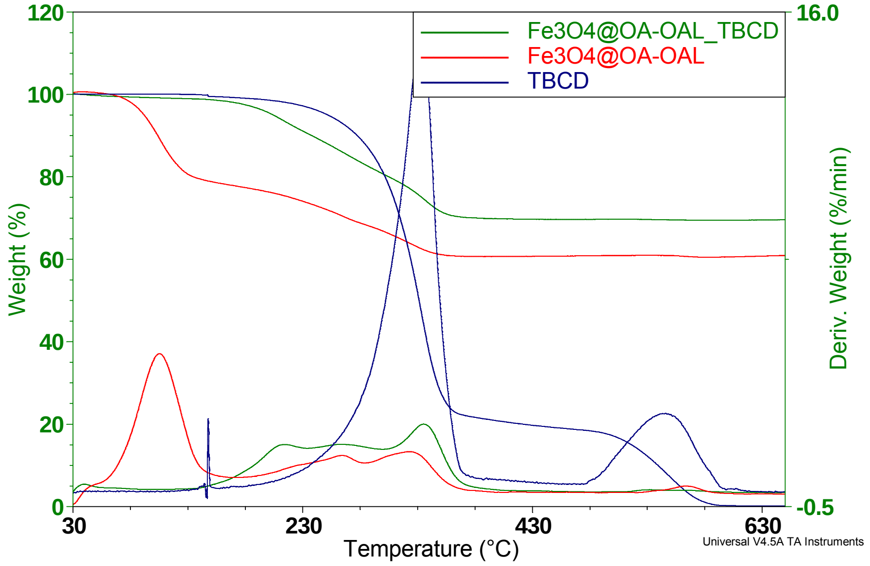

Figure 5: TG-DTG analysis in air of Fe_3O_4@OA-OAL, Fe_3O_4@OA-OAL_TBCD and TBCD

TG-DTG measurements in air can be used to identify the relative amounts of: (i) coating agents on the surface of the nanoparticles, (ii) oxidized nanoparticles that constitute the residue, and (iii) TBCD. Air flow TG-DTG of Fe_3O_4@OA-OAL, Fe_3O_4@OA-OAL_TBCD and TBCD are shown in Figure 5. From room temperature to 400°C, after water release accounting for about 20 wt. %, a weight loss due to organic chains release (19.2 wt.%) happens for Fe_3O_4@OA-OAL (red traces), indicating that the inorganic core is the 57 wt. % of Fe_3O_4@OA-OAL. The presence of TBCD in Fe_3O_4@OA-OAL_TBCD is confirmed by the pronounced weight loss centered at 350°C. In particular, TBCD constitutes the 8.1 wt.% of Fe_3O_4@OA-OAL_TBCD.

Finally, we have evaluated, with the help of GC-MS, in our experimental condition (low amounts of PAHs) a separation efficiency of 92%, for our Fe_3O_4@OA-OAL_TBCD adsorbent. These preliminary results indicate that the magnetic adsorbent nanocomposite prepared can enrich the PAHs from water sample efficiently.

4. Conclusion

In this research, magnetic nanoparticles, functionalized with TBCD by a new and easy approach, were synthesized and applied to enrich trace level PAHs from water in a short extraction time. The nanoparticles have highly uniform size (d = 10 nm with σ = 1.22 nm) and tend to self-organize in a regular hexagonal layer due to the capping organic layer. Moreover, the organic chains can be directly use to anchor TBCD through a quaternization reaction.

The performances of the method indicate that it has a great prospect in pre-concentrating and detecting trace pollutants in real samples.

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