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Evaluation of bi-functionalized mesoporous silica for solid-phase extraction of twelve endocrine disrupting compounds from water



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ABSTRACT

Mesoporous silica, bi-functionalized with octadecyl and aminopropyl groups was prepared and characterized. The adsorption capacity of the prepared silica for a mixture of twelve endocrine disrupting compounds in water was evaluated by solid-phase extraction and compared with a commercial phase. Analytes were determined by high performance liquid chromatography. Under optimized conditions, the material showed recoveries near 100% with standard deviations between 3 and 10%, with exception of estriol and prednisolone which showed recoveries of 66 and 82%, respectively.

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1. Introduction

Sample preparation is still a crucial step to achieve higher sensitivity and/or better selectivity in the analysis, especially for trace level analytes. In that sense, investigation and application of new materials has become a very interesting research area in field of Analytical Chemistry [1,2]. For example, a great range of new mesoporous materials are gaining interest in sample preparation because of their desired characteristics: (a) highly ordered and size-controlled mesoporous structures, (b) extremely high surface areas and large pore volumes, (c) very good thermal and chemical stability and (d) high flexibility in functionalization to enable the introduction of hydrophilic, hydrophobic, polar as well as charged functional moieties on surface [3].

The extraction and pre-concentration of trace contaminants onto solid stationary phases (solid-phase extraction, SPE) has proved to be an effective and valuable technique for sample preparation due to its flexibility, environmental friendly, and simplicity [4]. The most remarkable increase in the use of SPE has occurred in the last few years, with multiple improvements in terms of the introduction of new phases. In this respect, although numerous types of materials have been tested as stationary phases in SPE many of these materials suffer from inherent problems such as low capacity, low selectivity, long equilibrium time, and mechanical and/or thermal instability, etc. Regarding SPE of steroid and non steroid hormones (see [Supplementary materials 1](#)), octadecyl (C₁₈) modified amorphous silica has been the SPE phase most widely employed for extraction of these endocrine disrupting compounds (EDCs) from aqueous samples [5].

However, in some cases, different studies have demonstrated that with a C₁₈-SPE alone the extract obtained is not clean enough for direct injection on the instrument. For this reason, in order to obtain good recoveries some authors have combined in tandem C₁₈ and aminopropyl (NH₂) SPE cartridges for further cleaning of the C₁₈-SPE extract [6,7]. NH₂-SPE can effectively remove some matrix compounds extracted from the sample with the C₁₈-SPE cartridges, since these compounds can cause serious interferences in gas (GC) and liquid (LC) chromatography analysis. In this context, and to avoid an additional clean-up step to remove unwanted matrix components from the sample, the objective of the present paper was to prepare for the first time a new bi-functionalized mesoporous silica (with C₁₈ and NH₂ groups) and to study their applicability as sorbent for SPE of a mixture of twelve EDCs in aqueous media.

2. Experimental

Synthesis of bi-functionalized mesoporous silica (SBA-15-C₁₈-NH₂): 12 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was dissolved in 361 g of H₂O and 375 g of 2.0 M HCl solution with stirring at room T^o. After 22 mL of TEOS was added to that homogeneous solution. The resulting mixture was stirred at 40 °C for 3 h for prehydrolysis, and then 3.5 g of OTES and 2.8 mL of APTES was slowly added into the solution. Then, the mixture was stirred at 40 °C for 20 h, transferred into a polypropylene bottle and reacted under static condition at 50 °C for 2 h and 90 °C for 24 h. The solid product was recovered, washed with water, and dried at room temperature overnight. The template was removed from the synthesized material by refluxing in ethanol:H₂O (95:5, v/v) for 24 h. Finally, the material was dried at 50 °C for 24 h.

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Characterization of SBA-15-C₁₈-NH₂: X-ray diffraction (XRD) patterns of the silicas were obtained on a Philips Diffractometer model PW3040/00 X'Pert MPD/MRD at 45 kV and 40 mA, using Cu-K α radiation ($\lambda=1.5418$ Å). Scanning electron microscopy (SEM) was carried out on a XL30 ESEM Philips with an energy dispersive spectrometry system. Transmission electron microscopy (TEM) was carried out on a TECNAI 20 Philips, operating at 200 kV. N₂ gas adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2020 analyzer. Proton-decoupled ²⁹Si MAS-NMR spectra were recorded on a Varian-Infinity Plus 400 MHz Spectrometer operating at 79.44 MHz proton frequency. Cross polarization ¹³C MAS-NMR spectra were recorded on a Varian-Infinity Plus 400 MHz Spectrometer operating at 100.52 MHz proton frequency. Elemental analysis was performed with a LECO CHNS-932 analyzer. Thermogravimetric analyses (TGA) were carried out using a Setsys 18 A (Setaram) analyzer (from 25 to 800 °C at 10 °C per min).

SPE experiments: To prepare the SPE cartridges, 100 mg of ExtraBond^R C₁₈ commercial amorphous silica (500 m²/g, 50 μ m particle diameter, 60 Å pore diameter, 17% C) or SBA-15-C₁₈-NH₂ were packed into a 6 mL syringe type cartridge (65 mm length, 11 mm diameter) plugged with porous PTFE disks at both ends. To prevent the material lost during sample loading, a 0.45 μ m pore size nylon filter membrane was also inserted at the bottom of the mesoporous silica bed (see [Supplementary materials 2](#)). Sample loading was carried out with a Supelco VisiprepTM DL solid phase extraction vacuum manifold 12 port model connected to a vacuum pump at 7.6 psi. The resulting extracts were evaporated and reconstituted with 1 mL of MeOH. HPLC analyses were performed on a Varian ProStar (Varian Ibérica, Madrid, Spain) chromatographic system (see [Supplementary materials 3](#)). Recoveries were calculated by comparison of the areas of spiked Milli-Q water samples with the areas of simulated samples, prepared in the same way but spiked with the analytes at the end of the SPE process.

3. Results and discussion

Mesoporous silica characterization: XRD pattern of the SBA-15-C₁₈-NH₂ displayed a well-resolved pattern at low 2θ values with a very sharp (1 0 0) diffraction peak at 0.79°, and a weak diffraction peak (1 1 0) at 1.55°. d_{100} -spacing value and unit cell parameter

(a_0) were 97 and 129 Å, respectively. These patterns were similar to the pure SBA-15 [8], indicating that the prepared bi-functionalized silica contain well-ordered hexagonal arrays of one-dimensional channel structure. The N₂ adsorption–desorption isotherms for mesoporous silicas are shown in [Supplementary materials 4](#). For these materials the isotherms are type IV according to the I.U.P.A.C. classification and have an H1 hysteresis loop that is representative of materials with pores of constant cross-section. The Brunauer–Emmett–Teller specific surface area (S_{BET}), pore volume and BJH (Barrett–Joyner–Halenda) pore diameter of this material were 526 m²/g, 0.66 cm³/g and 76 Å, respectively (see [Supplementary materials 5](#)). SEM images showed a cylindrical shape with an average particle size of 1.7 μ m \times 270 nm ([Fig. 1a](#)). TEM images demonstrated a clear arrangement of hexagonal pores with uniform size for both materials ([Fig. 1b](#)). The ²⁹Si MAS-NMR spectra in the solid state for SBA-15-C₁₈-NH₂ ([Fig. 2a](#)) revealed that Q⁴ sites ((SiO)₄Si), ascribed to surface silicon atoms with four siloxane bonds, was the most abundant site. The spectra of the bi-functionalized silica showed two more peaks assigned to T³ (R(SiO)₃Si) and T² (R(SiO)₂SiOH) sites at –67 and –58 ppm, respectively, which verified the anchoring of the NH₂ groups to the SBA-15 surface [8]. The ¹³C MAS-NMR spectra ([Fig. 2b](#)) clearly displayed peaks at 28, 19 and 14 ppm, corresponding to the carbon atoms on the C₁₈ group (–(CH₂)₁₆–, –CH₃ and Si–CH₂–, respectively). Additional peaks at 10, 21 and 42 ppm appeared in the spectrum, corresponding to the C atoms on the Si–CH₂–CH₂–CH₂–NH₂ group in sequence from left to right [8,9]. Elemental analysis was carried out to determine the amount of organic groups incorporated in the silica, calculated from the % C and % N in this material (see [Supplementary materials 6](#)). In addition, the TGA curves showed that an exothermic degradation process occurs between 200 and 600 °C, attributed to the decomposition of C₁₈ and NH₂ groups, with a total weight loss of about 20%.

Optimization of the SPE: The adsorption of the twelve EDCs onto SBA-15-C₁₈-NH₂ and ExtraBond^R C₁₈ is shown in [Supplementary materials 8](#). As it can be seen, SBA-15-C₁₈-NH₂ sorbent proved good extraction capacity and elution efficiency for the target EDCs, so a cartridge with 100 mg of this sorbent retained between 66 and 114% of the analytes from 50 mL of 1 mg/L in Milli-Q water. The repeatability of the procedure was good, with standard deviation (SD) between 1 and 8% ($n=3$). On the other hand, under similar conditions, ExtraBond^R C₁₈ was not capable of extracting most of these compounds satisfactorily, with recoveries lower

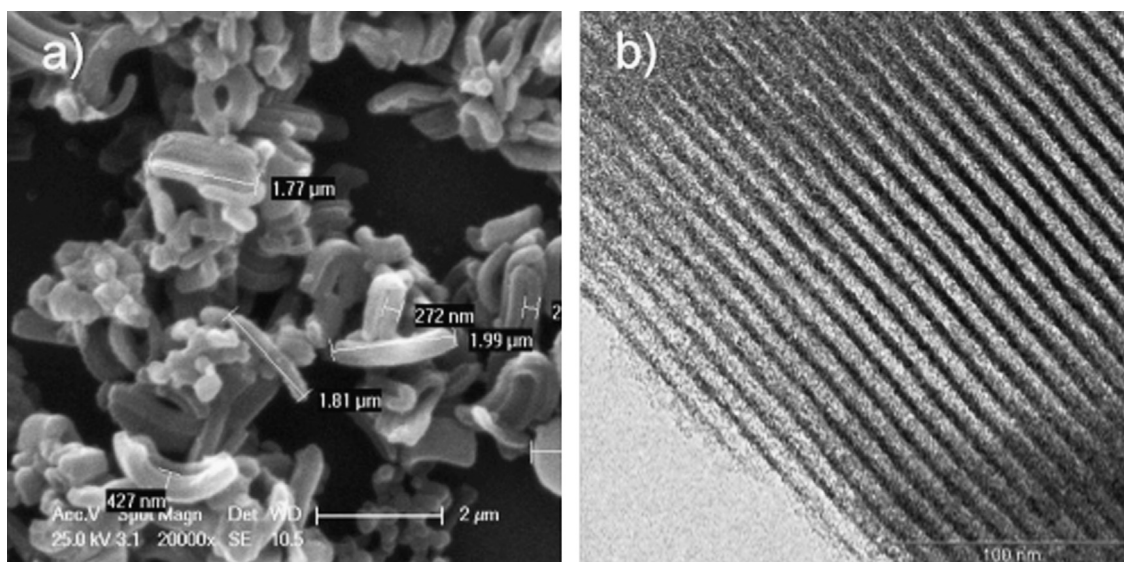


Fig. 1. (a) SEM image of SBA-15-C₁₈-NH₂. (b) TEM image of SBA-15-C₁₈-NH₂.

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