



# Comparison of different mesoporous silicas for off-line solid phase extraction of 17 $\beta$ -estradiol from waters and its determination by HPLC-DAD

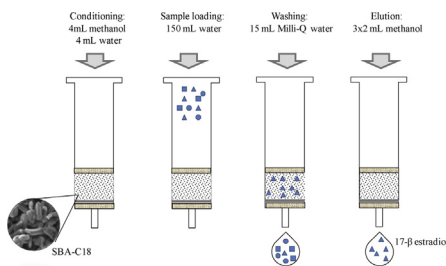
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## HIGHLIGHTS

- Mesoporous silicas were examined as sorbents for solid-phase extraction of 17 $\beta$ -estradiol in waters.
- SBA-C<sub>18</sub> had the highest adsorption affinity towards 17 $\beta$ -estradiol and under optimized conditions.
- 17 $\beta$ -Estradiol was determined by HPLC-DAD in drinking water with high recoveries and precision.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Functionalized (SBA-C<sub>18</sub> and SM-C<sub>18</sub>) and non-functionalized (SBA-15 and SM) mesoporous silicas were then examined as sorbents for solid-phase extraction of 17 $\beta$ -estradiol in aqueous media. Experiments were run in order to test critical factors affecting the procedure extraction efficiency, including the type of sorbent, the analyte concentration, the solvent and volume used for elution and the sample volume. Among the prepared materials, SBA-C<sub>18</sub> had the highest adsorption affinity towards 17 $\beta$ -estradiol and under optimized conditions (200 mg of sorbent, 150 mL of water sample, elution with 3 × 2 mL of methanol) this sorbent proved good extraction capacity and elution efficiency for this hormone from aqueous media (recovery near 100%). To evaluate the analytical applicability of the proposed method, it was applied to the determination of 17 $\beta$ -estradiol in drinking water by high performance liquid chromatography with a photodiode array detector. Calibration curves were shown to be linear between 1.25 and 100 mg L<sup>-1</sup> with correlation coefficients  $\geq 0.999$  ( $n = 5$ ) for 17 $\beta$ -estradiol. The instrumental detection and quantitation limits calculated were 0.38 and 1.25 mg L<sup>-1</sup>, respectively. The relative standard deviation obtained values were  $\leq 3\%$  and the mean recoveries obtained were of 82%. The results suggest that SBA-C<sub>18</sub> is a promising material for the off-line solid phase extraction of 17 $\beta$ -estradiol from waters.

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**Abbreviations:** ACN, acetonitrile; APTES, 3-aminopropyltriethoxysilane; BJH, Barret–Joyner–Halenda; C<sub>18</sub>, octadecyl-modified silica; CTAB, cetyltrimethylammonium bromide; DAD, photodiode array detector; DCM, dichloromethane; FTIR, Fourier transform infrared; HPLC, high performance liquid chromatography;  $k'$ , capacity factor;  $k_w$ , retention factor in water;  $K_{ow}$ , octanol–water partition coefficient; MeOH, methanol; PTFE, polytetrafluoroethylene; RSD, relative standard deviation;  $S_{BET}$ , BET surface area; SEM, scanning electron microscopy; SPE, solid-phase extraction;  $t_r$ , retention time;  $t_0$ , dead time; TEM, transmission electron micrograph; TEOS, tetraethylorthosilicate; TGA, thermogravimetric analysis; XRD, X-ray diffraction.

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## 1. Introduction

Recent advances in new materials research have had a direct impact on developments in analytical chemistry and could therefore be the key to improve current analytical techniques or develop new ones [1]. According to this, mesoporous silicas could be promising as sorbents due to its novel structure that combines uniform ordered structure, high pore volume, and high surface area. Likewise, subsequent chemical modification of these materials with organo-functional groups allows obtaining hybrid

mesoporous silicas, which are potentially useful in those processes where the specific and selective physisorption of different kinds of compounds is required to be obtained. As a result, hybrid mesoporous silicas could be considered of great value added in diverse aspects of human activity and can be used for environmental [2–4], analytical [5] and biomedical [6] applications, among others.

The trace amounts of pharmaceuticals that have been detected in natural waters have attracted public attention and serious concern because of their potential adverse effects on the aquatic environment [7]. In that sense, recently mesoporous silicas have been investigated for adsorptive removal of selected emerging organic contaminants from aqueous media by batch adsorption experiments [3,4]. The results obtained in these studies suggest that mesoporous-silica-based materials are promising sorbents for removal of pharmaceuticals. Moreover, the pharmaceuticals that enter natural waters can ultimately transfer to our drinking water with potential impact on human health.

Estrogens are steroids that play important roles as sex hormones in animals. These hormones are powerful and can cause adverse reproductive and development alterations in aquatic organisms at very low concentrations in waters.  $17\beta$ -Estradiol, the most mammalian estrogenic hormone, is biodegraded to estrone, which degrades to estriol in the aquatic environment.  $17\beta$ -Estradiol, estrone and estriol have been detected at  $\text{ng L}^{-1}$  levels in natural waters and in influents/effluents of wastewater treatment plants. Even at such low concentrations, some of these compounds present activity as endocrine disrupters being responsible for the feminisation of certain aquatic organisms [7]. These compounds persist in drinking water due to incomplete removal with conventional drinking water treatments if its concentration in drinking water sources is very high [8]. The presence of important levels of estrogens in rivers, lakes, etc., can be a potential risk for the environment and in the future may be for humans, especially because synergistic and long-term effects are not fully understood [7].

Generally, the first goal of any chromatographic analysis is isolating the components of interest from the sample matrix into an injectable solution at detectable concentrations by the selected analytical separation technique. In many cases, the matrix is complex and interferes in the detection of low-level compounds. The proper sample treatment can considerably improve the limit of detection for the compounds of interest. Off-line solid-phase extraction (SPE) is nowadays one of the most used techniques for extracting such compounds from waters. It is very important to select a suitable sorbent for SPE in order to control parameters such as selectivity, affinity and capacity [9]. In this respect, although numerous types of materials have been used as sorbents in SPE (e.g. activated carbon, amorphous silica, chelating resins, etc.), many of these materials suffer from inherent problems such as low capacity, low selectivity, long equilibrium times, and mechanical and/or thermal instability, etc. In this context, and to avoid these limitations, the goal of some research groups in this field is to develop novel sorbent materials for SPE of different contaminants [10].

Regarding SPE of natural and synthetic estrogens, octadecyl-modified ( $\text{C}_{18}$ ) amorphous silica has been the SPE material most widely employed for extraction of these hormones from aqueous systems [11] and, in general, higher recoveries and larger breakthrough volumes have been reported with  $\text{C}_{18}$  type silicas than with commercial polymers [7,12]. For example, in a recent work of Kuster et al. [7] a reversed phase  $\text{C}_{18}$  based cartridge (LiChrolut RP-18) was preferred to a co-polymeric cartridge (Oasis HLB) due to its better performance for extraction of nineteen estrogenic compounds in environmental waters. In that respect, new promising sorbents prepared by functionalization of mesoporous silicas could be interesting for the SPE of toxic estrogens from waters due to their remarkable characteristics. However, to the best of our knowledge,

the use of hybrid mesoporous silica for SPE of estrogens in aqueous media has not been reported elsewhere yet.

In the present paper, two mesoporous silicas, denoted SBA-15 and SM, with different morphology and structure were prepared. Both mesoporous silicas were grafted with octadecylsilane groups by co-condensation (SBA- $\text{C}_{18}$ ) and post-synthesis (SM- $\text{C}_{18}$ ) methods. Functionalized and non-functionalized silicas were then examined as sorbents for SPE of  $17\beta$ -estradiol in aqueous media, prior to its determination by high performance liquid chromatography with photodiode array detection (HPLC-DAD).

## 2. Experimental

### 2.1. Reagents and materials

Tetraethylorthosilicate (TEOS) 98% ( $M=208.33 \text{ g mol}^{-1}$ ,  $d=0.934 \text{ g mL}^{-1}$ ), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO20PO70EO20, Pluronic 123,  $M_{\text{av}}=5800 \text{ g mol}^{-1}$ ,  $d=1.019 \text{ g mL}^{-1}$ ), cetyltrimethylammonium bromide (CTAB) 98%, ( $M=364.46 \text{ g mol}^{-1}$ ), octadecylsilane 97% ( $M=284.61 \text{ g mol}^{-1}$ ,  $d=0.795 \text{ g mL}^{-1}$ ), dimethyloctadecylchlorosilane, ( $M=347.09 \text{ g mol}^{-1}$ ) and 3-aminopropyltriethoxysilane (APTES) 99% ( $M=221.37 \text{ g mol}^{-1}$ ,  $d=0.949 \text{ g mL}^{-1}$ ) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Organic solvents (toluene, diethyl ether and ethanol) were purchased from SDS (Peypin, France). Hydrochloric acid 35% ( $M=36.45 \text{ g mol}^{-1}$ ,  $d=1.19 \text{ g mL}^{-1}$ ) was purchased for Panreac (Castellar del Vallès, Barcelona, España). HPLC-grade solvents acetonitrile (ACN), methanol (MeOH) and dichloromethane (DCM) were purchased from Sigma-Aldrich. Stock standard solutions of  $1000 \text{ mg L}^{-1}$  were prepared by diluting adequate amounts of  $17\beta$ -estradiol (1,3,5-estratriene-3,17- $\beta$ -diol, 98%, Sigma-Aldrich) in methanol and stored at  $-20^\circ\text{C}$ . Working solutions were prepared at various concentrations by appropriate dilution of the stock solution in methanol ( $0.5\text{--}10 \text{ mg L}^{-1}$ ). All working solutions were filtered through a  $0.45 \mu\text{m}$  pore size nylon filter membrane before analysis. Water (resistance  $18.2 \text{ M}\Omega \text{ cm}$ ) used in the preparation of mobile phase and spiked water samples was obtained from a Millipore Milli-Q-System (Billerica, MA, USA). All other reagents were at least of analytical grade.

### 2.2. Synthesis of SBA-15 and SBA- $\text{C}_{18}$ mesoporous silicas

SBA-15 mesoporous silica was prepared as follows: 12 g of Pluronic 123 was dissolved in 361 g of  $\text{H}_2\text{O}$  and 375 g of 2.0 M HCl solution with stirring at room temperature. After, 22 mL of TEOS was added to that homogeneous solution with stirring at room temperature. The resulting mixture was stirred at  $40^\circ\text{C}$  for 3 h for prehydrolysis and then transferred into a polypropylene bottle and reacted at  $90^\circ\text{C}$  under static condition for 24 h. The solid product was recovered by filtration, washed with water, and dried at room-temperature overnight. The template was removed from the synthesized material by refluxing in 95% ethanol for 24 h. Finally, the material was filtered, washed several times with water and ethanol, and dried at  $50^\circ\text{C}$ . Octadecyl-functionalized SBA-15 mesoporous silica (denoted SBA- $\text{C}_{18}$ ) was prepared in a similar way but after prehydrolysis 6.9 g of octadecylsilane was slowly added into the solution.

### 2.3. Synthesis of SM and SM- $\text{C}_{18}$ spherical mesoporous silica

Spherical mesoporous silica (denoted SM) was prepared according to the method of Ma et al. [13]. Typically, 18 g of Pluronic 123 and 3 g of CTAB were dissolved in a solution formed by mixing 360 mL of 2 M HCl, 180 mL  $\text{H}_2\text{O}$  and 150 mL ethanol. Then, 60 mL of TEOS were added in the aqueous solution at room temperature under

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