Journal of Chromatography A, 1517 (2017) 203–208

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

An organically modified silica aerogel for online in-tube solid-phase microextraction

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ARTICLE INFO

Article history:
Received 25 May 2017
Received in revised form 18 July 2017
Accepted 23 July 2017
Available online 24 July 2017

Keywords:
Silica aerogel
Basalt fibers
In-tube solid-phase microextraction
High performance liquid chromatography
Estrogens
Online analysis

ABSTRACT

Aerogels have received considerable attentions because of its porous, high specific surface, unique properties and environmental friendliness. In this work, an organically modified silica aerogel was functionalized on the basalt fibers (BFs) and filled into a poly(ether ether ketone) (PEEK) tube, which was coupled with high performance liquid chromatography (HPLC) for in-tube solid-phase microextraction (IT-SPME). The aerogel was characterized by scanning electron microscopy (SEM) and fourier transform infrared spectrometry (FT-IR). The extraction efficiency of the tube was systematically investigated and shown enrichment factors from 2346 to 3132. An automated, sensitive and selective method was developed for the determination of five estrogens. The linear range was from 0.03 to 100 $\mu g\,L^{-1}$ with correlation coefficients (r) higher than 0.9989, and low detection limits (LODs) were 0.01–0.05 $\mu g\,L^{-1}$. The relative standard deviations (RSDs) for intra-day and inter-day were less than 4.5% and 6.7% (n = 6), respectively. Finally, the analysis method was successfully applied to detect estrogens in sewage and emollient water samples.

1. Introduction

Silica aerogels are interesting solid materials with many fascinating properties such as high porosity, low density and high specific surface [1–4]. These nano-sized framework compounds were prepared from sol-gels by replacing the solvent inside the pores with air. These properties make silica aerogels suitable for applications in adsorbents for organic analytes [5], sensors [6], thermal isolation [7], drug storage media [8] and catalysts [9]. Silanol groups are abundant on the surface of silica aerogels, which provide a potential basis for extensive modification of them. Nevertheless, the application of silica aerogels was hindered because of their disappointing mechanical strength, inherent hydrophilicity and tedious progress of drying behavior.

By introducing some flexible linking groups such as vinyl, ester and amine functional groups into silica aerogels, the structural strength and adsorbing performance can be improved significantly [10–13]. In the preparation process, the drying technology also plays a vital role in the formation of aerogel. Supercritical drying is an effective route to improve cavity growth morphology, avoid capillary stress and associated drying shrinkage [14]. Unfortunately, the costs of instrument, complexity and risks in operation process are destined to make this technology hardly to spread widely. Organic modification is an option to achieve the ambient pressure drying treatment and to reduce the difficulty of preparation [15]. Best of all, it could be employed as an effective extraction material due to a large number of adsorbent sites.

In-tube solid-phase microextraction (IT-SPME) can work with the adsorbent in a microtube coupled with HPLC for an automated analysis process [16–18]. It offers a prominent strategy to complete enrichment and separation of analytes in liquid samples, and sensitivity, repeatability and selectivity can be also improved significantly [19–23]. Furthermore, fibers into microtube can raise the utilization ratio of space [24,25], enhancing extraction efficiency and eliminating dead volume. Basalt fibers (BFs) are produced from molten volcanic rocks, and it is high tensile, easily modified and environmentally friendly [26]. In addition, silanol groups on BFs are plentiful and can be functionalized by a simple way. In this work, an organically modified silica aerogel coating with high surface and high-impact properties was synthesized on BFs for IT-SPME. The extraction performance of the aerogel coating was systematically investigated. An online analysis method was developed for five estrogens.

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http://dx.doi.org/10.1016/j.chroma.2017.07.075
0021-9673/

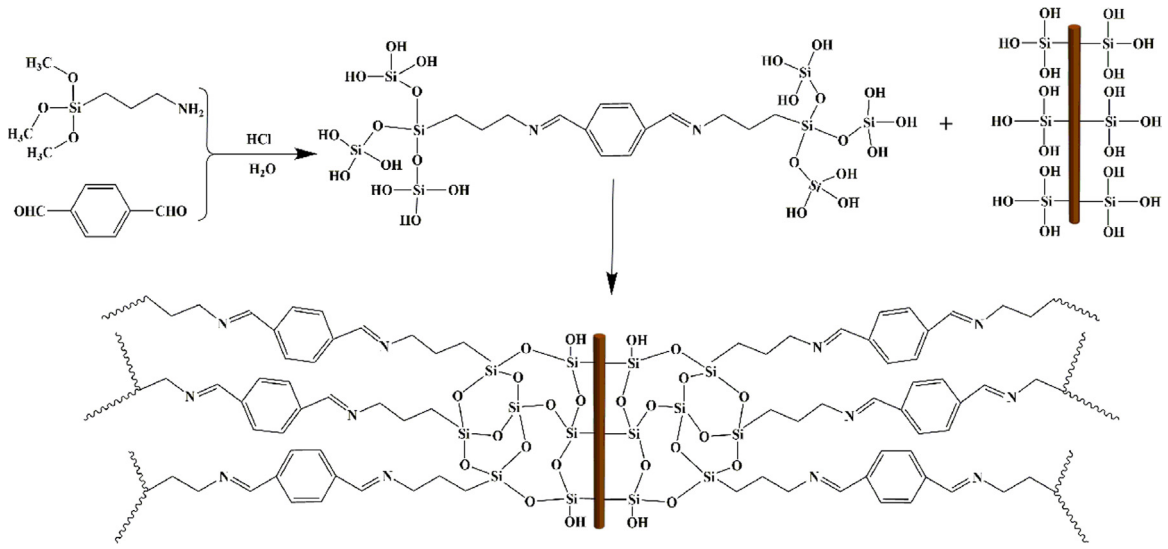

Fig. 1. Synthesis reactions of organically modified silica aerogel coating on BFs.

2. Experimental

2.1. Reagents and apparatus

(see Supplementary material)

2.2. Sample preparation

(see Supplementary material)

2.3. Synthesis of organically modified silica aerogel on the fibers for IT-SPME device

25 cm BFs (108.4 mg) were sonicated in acetone and water for 30 min in turn. Then the fibers were activated with a mixed solution of hydrogen peroxide (4%) and sulfuric acid (1.2 mol L^{-1}) at 40 °C for 10 min. In reaction solution, *p*-phthalaldehyde (0.5233 g) was dissolve into ethanol (2 mL), and then 20 mL hydrochloric acid (1.5 mol L^{-1}) and 3-aminopropyl trimethoxysilane (9.1105 g) were added immediately. The BFs were immersed into the reaction solution, and the reaction system was placed at 40 °C for 20 h. As shown in Fig. 1, —CHO groups of *p*-phthalaldehyde and —NH_2 groups of 3-aminopropyl trimethoxysilane are polymerized together via the imino bond. And the hydrolysis of the methoxy group can be combined with the dehydration of the silanol groups of BFs to form a strong Si—O—Si bond. The excess reagent and water scattered in the wet gel were substituted by ethanol twice, and each time was sustained for 5 h. After being heated at 80 °C for 24 h, the organically modified silica aerogel on BFs was obtained finally. The installation of the extraction device is shown in Fig. 2a–b. A bundle of BFs modified with aerogel coating (114.3 mg, 52 cm) was placed into a PEEK tube (25 cm) by traction with a thread.

2.4. Online IT-SPME-HPLC procedure

The schematic diagram of the equipment can be seen in Fig. 2c. Two important steps including extraction and desorption can be generalized in the automatic analysis processes, and the complete and detailed processes were described in Supplementary material S2.4.

3. Results and discussion

3.1. Characterization of aerogel coating

The morphological properties of the BFs and the aerogel coating functionalized BFs were investigated by SEM. As shown in Fig. 3a–b, the surface of BFs is quite smooth. It can be seen from Fig. 3c–d, the surface of aerogel coating functionalized BFs is obviously rough. The coating possesses a homogeneous, porous 3D framework structure, which is beneficial to get high extraction efficiency. In order to demonstrate the chemical structure of aerogel, the FT-IR spectrum was applied to characterize it (Fig. S1). Strong absorption peak at 1450 cm^{-1} is attributed to the C=C stretching vibrations in the benzene. The —OH group peak and the —CH_2- group peak are clearly observed at 3440 cm^{-1} and 2933 cm^{-1}, respectively. The peak at 455 cm^{-1} is attributed to the O—Si—O bending vibration. The peaks about 798 cm^{-1} and 1100 cm^{-1} are attributed to the Si—O—Si symmetric stretching vibration and antisymmetric stretching vibration, respectively. The adsorption band at 695 cm^{-1} is attributed to the out-of plane bending vibration of C—H in benzene ring. The peak at 1670 cm^{-1} is assigned to the stretching vibration of C=N that connected to benzene, suggesting that *p*-phthalaldehyde and 3-aminopropyl trimethoxysilane were chemically bonded to each other sucessfully.

3.2. Validation of extraction ability of aerogel coating

To validate the extraction efficiency derived from the aerogel coating on BFs, two IT-SPME devices with and without the aerogel coating were compared through extracting 30 mL working solution of estrogens. The extraction device with aerogel coating (Fig. S2a) reveals excellent extraction performance. In contrast, the extraction efficiency of the BFs without aerogel coating (Fig. S2b) is very poor for analytes. It is indicated that the excellent extraction performance is derived from the aerogel coating.

3.3. Optimization of extraction and desorption conditions

The influence of sampling rate was investigated in the range of 0.50–2.00 mL min^{-1}. As shown in Fig. 4a, the peak areas of the five analytes change little with increasing the sampling rate from 0.50 to 1.25 mL min^{-1}. While the sampling rate increases beyond 1.25 mL min^{-1}, the downward trend can be observed easily. In