Implementing a superhydrophobic substrate in immersed solvent–supported microextraction as a novel strategy for determination of organic pollutants in water samples

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ABSTRACT

In this research, a new approach for extraction and determination of polycyclic aromatic hydrocarbons from sea and rain water samples was developed by implementing a superhydrophobic substrate and consuming the least amount of solvent. This version of solvent–supported microextraction enabled us to perform the procedure in the immersion mode with the slightest troubles arising from water leakage into the gas chromatography. The superhydrophobic property leads to the fixation of extracting solvent on the substrate surface during water sampling. To prepare a superhydrophobic substrate, a piece of melamine foam was coated by tannic acid and silica nanoparticles using methyltrimethoxysilane and tetramethyl orthosilicate. The morphology of the prepared foams was studied by scanning electron microscopy. The developed solvent–supported microextraction method in combination with gas chromatography–mass spectrometry was applied to the isolation and determination of some typical polycyclic aromatic hydrocarbons from aquatic media. Influential parameters such as substrate nature, extractive solvent, eluting solvent and its quantity and extraction time were investigated. The limits of detection and quantification of the method under the optimized conditions were 0.01–0.11 $\mu g\,L^{-1}$ and 0.03–1.01 $\mu g\,L^{-1}$, respectively. The relative standard deviations at the concentration level of 20 $\mu g\,L^{-1}$ were between 3% and 14% ($n = 3$). The linearity of calibration curves ranged from 0.03 to 60 $\mu g\,L^{-1}$. The implementation of the solvent-supported method to the analysis of real water samples was quite successful and the relative recoveries were between 88% and 107%.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed mainly by the incomplete combustion of fossil fuels and coal, petrochemical cracking processing and the degradation of lubricating oils and dyes. Some PAHs are classified as probable human carcinogens and show tumorigenic activity and endocrine-disrupting activity in mammals. So it is necessary to monitor their distribution, source apportionment, determination and potential risk assessment (Montuori et al., 2016; Poerschmann and Schultze-Nobre, 2014; Hou et al., 2018; Qiao et al., 2018). Because of the low concentrations of environmental pollutants such as PAHs in water samples, it is essential to perform a preconcentration step prior to the instrumental analysis. Recently, various methods are developed and used for extraction and determination of environmental pollutants from aquatic media (Megson et al., 2016). The analyte and sample matrix types are critical parameters in order to adapt an appropriate method. Two general approaches based on the implementation of solid (Rabii

et al., 2014) and liquid phase (Campillo et al., 2017), are usually considered. Most extraction methodologies on the base of this classification are introduced and developed. As far as the solid–based methods are concerned, solid phase extraction (SPE) (Rabii et al., 2014), solid phase microextraction (SPME) (Bielská et al., 2014), micro extraction by packed sorbent (MEPS) (Soleimani et al., 2017) are being used while single drop microextraction (SDME) (Li et al., 2013), dispersive liquid–liquid microextraction (DLLME) (Arain et al., 2016) are common strategies in the liquid–based methods. These two categories have different operational principles, while adsorption and partition are the dominant mechanisms. For solid–based methods, mechanism of the entrapment is limited to the surface of sorbent while in the liquid–phase systems, diffusion of analyte through the liquid phase plays the major role. The simultaneous use of both solid and liquid phases in the extraction process appears to enhance the overall efficiency, synergistically. Recently, combination of solid–phase extraction with liquid phase extraction has been developed as a new approach to achieve greater

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efficiencies. Some works such as low–density magneto fluid dispersive liquid–liquid microextraction (LMF–DLLME) (Shen et al., 2013), magnetic nanoparticle assisted dispersive liquid–liquid microextraction (Pérez et al., 2016) and solid phase extraction combined with dispersive liquid–liquid microextraction (SPE–DLLME) (Zhao et al., 2016; Liang et al., 2016) are the typical developed methods on this regard. A liquid (organic) drop is usually suitable for entrapment of analytes and by its fixation as a thin film layer on a porous substrate, the accessible sites for extraction is expected to be enhanced. Within the initial duration of extraction, chemical species are transferred from sample solution into the sorbent phase while the phase transition rate depends on the interface between the donor and acceptor phases. By increasing this parameter, the extraction time is expected to be shortened. Simultaneous use of characteristic solid and liquid phases seems to be an appropriate approach to benefit from both phases for extraction of pollutants from aquatic media. When the solid surface is coated by a liquid, both partition in liquid phase and adsorption on the solid surface become prominent and combination of these mechanisms leads to more available sites for the entrapment process. Apparently this justification was a driving force for some researchers to incorporate both SDME and SPME as a single extraction methodology (Saraji and Farajmand, 2012; Zhang et al., 2014; Zhang and Lee, 2013). The use of solid materials with high surface area, leads to the increased adsorption of the extractive solvent and subsequent enhancement in the extraction performance. Since most of environment pollutants, such as PAHs, have non–polar structures, the solid phase is preferentially coated by non–polar organic solvents. The superhydrophobic materials with rough surfaces and low surface energy are appropriate candidates for this intention. That is why these interesting materials, due to their high oil absorption capacity, have been used in oil/water separation (Lee et al., 2011). More recently, superhydrophobic materials have been successfully used as the extractive phase in needle trap microextraction (Baktash and Bagheri, 2017; Bagheri et al., 2017) and μ-solid phase extraction (μ-SPE) (Bagheri et al., 2016).

In this project, a superhydrophobic melamine formaldehyde (MF) foam was prepared and used as a probe in solvent–supported microextraction (SSME). The foam synthesized in such way to hold large quantities of extractive solvent to improve the overall performance. The MF foam was coated by tannic acid (TA) and functionalized by silica nanoparticles using methyltrimethoxysilane (MTMS) and tetramethyl orthosilicate (TMOS). After examining the morphological structures, their entrapment capabilities were compared and eventually, the developed SSME method was implemented to the isolation of PAHs from aquatic media.

2. Experimental

2.1. Materials

Chromatographic grade methanol, propanol, 1-octanol, iso-octane, toluene, cyclohexene was purchased from Merck (Darmstadt, Germany). Reagents of TA, MTMS (98%), TMOS (98%), $FeCl_3 \cdot 6H_2O$ were also purchased from Merck. NH_4OH (25%) was purchased from Kian Kaveh Azma, Iran. Naphthalene, anthracene, fluorene, acenaphthylene, acenaphthene and linden were purchased from Merck (Darmstadt, Germany). The stock solution of these compounds was prepared in methanol at concentration of $400 \, mg \, L^{-1}$ and stored at 4 °C. The working solutions from each compound were prepared by diluting the stock solution with methanol and more diluted working solutions were prepared daily by their subsequent dilution with double distilled water.

2.2. Instrumental

A gas chromatograph model Agilent 6820, with a split–splitless injection port and flame ionization detection (FID) system, was used for evaluation survey. Separation of analytes was carried out on a capillary column HP–5 MS (30 m 0.32 mm i.d.) with 0.25 μm film thickness (Hewlett-Packard, Palo Alto, CA, USA). The carrier gas was nitrogen (99.999%) at a flow rate of $0.5 \, mL \, min^{-1}$. The gas chromatograph was operated in the splitless mode and the split valve was kept closed for 1 min. The column was held at 70 °C for 1 min, increased to 280 °C at a rate of $40 \, °C \, min^{-1}$, and then was kept at this temperature for 5 min. The injector and detector temperatures were set at 270 and 290 °C respectively. For quantitation purposes, a Hewlett–Packard (HP, PaloAlto, USA) HP 6890 plus series GC equipped with a split–splitless injector and a HP 5973 mass-selective detector system were used. The MS was operated in the electron ionization mode (70 eV). Helium (99.999%) at the flow rate of $1 \, mL \, min^{-1}$ was employed as the carrier gas. The separation of model PAHs was performed on a 30 m 0.25 mm HP–5 MS column (0.25 μm film thickness). The column was held at 70 °C for 1 min, increased to 280 °C at a rate of $40 \, °C \, min^{-1}$ and was kept at this temperature for 1 min. The injector temperature was set at 270 °C while the GC–MS interface, ion source and quadrupole mass analyzer were set at 280, 230 and 150 °C, respectively. The detection method was programmed for SIM considering two or three characteristic ions for each compound. All samples were extracted from 25 mL clear glass vials with a PTFE-faced septum and aluminum cap. Samples were stirred using ZAG Shimi (Tehran–Iran) magnetic stirrer. For aspirating the sample into the pipette tip an Ismatec BVP peristaltic pump (Switzerland) was used.

2.3. Fabrication of the superhydrophobic foams

Several pieces of MF foams were added to 100 mL aqueous solutions of $FeCl_3 \cdot 6H_2O$ (0.1 g) and TA (0.4 g) and stirred for 5 min (Huang et al., 2015). Then, they were washed with methanol several times and dried at 60 °C. To salinize the substrate and creating superhydrophobic properties, a 40–mL solution of MTMS (2 mL) and TEOS (0.08 mL) in methanol was prepared and 5 mL NH_4OH solution (25%) was added. In the following, pieces of MF and MF coated by TA (MF-TA) were added and the solution was stirred for 24 h. Then, the prepared foams were washed with methanol for several times and dried at 60 °C. By adapting this protocol, the MF and the MF-TA foams were coated by the silica nanoparticles (MF-Si, MF-TA-Si).

2.4. The extraction process

To use the prepared foams as the substrates for holding the extractive solvent, and evaluating their superhydrophobic properties, the same quantity (0.004 g) from MF, MF-TA, MF-Si and MF-TA-Si was placed in a pipette tip and washed by methanol and dried at 80 °C and then connected to a peristaltic pump to deliver the relevant samples, extractive and eluting solvents. This setup improved the elution efficiency and decreased the eluting solvent consumption.

To perform the analysis, a 30–μL portion of the extractive solvent passed through the pipette tip for 3 times in a forward/backward motion and then washed by 3 mL water in order to remove the excess solvent amounts. A 10–mL water sample was placed in a 25–mL glass vial and was cyclically passed through the micropipette tip containing the prepared foams at $2.4 \, mL \, min^{-1}$ for 15 min. Then, N_2 was employed for a short while to remove the remaining water. For elution step, 25 μL of the appropriate solvent, containing $500 \, \mu g \, mL^{-1}$ linden as the internal standard was pumped through the pipette tip and an aliquot of 2–μL of the eluting solvent was injected into the GC–MS system.

3. Results and discussion

3.1. The superhydrophobic substrate and extractive solvent

For creation of superhydrophobic substrates, the desired surfaces must have sufficient roughness and low energy. The MF foam possesses