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A comparison study of nanofiber, microfiber, and new composite nano/microfiber polymers used as sorbents for on-line solid phase extraction in chromatography system

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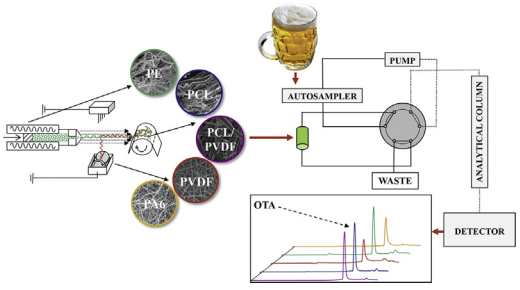
HIGHLIGHTS

- Five different nanofibrous and composite nano/microfibrous polymers were tested.
- Promising composite sorbent for on-line extraction was created by melt-blown and electrospun technology.
- Composite polymer consisted of polycaprolactone microfibers/polyvinylidene difluoride nanofibers.
- It showed extremely good stability in organic solvents and under the high-backpressure.
- The new nanofibrous extraction was tested for ochratoxin A in beer for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

Three different approaches has been used to obtain nano/micro fibers and their diversity and extraction properties were examined. The effect of their structure on stability in an ultra-high-performance liquid chromatography (UHPLC) system during on-line SPE procedure was monitored. Five types of various nano/micro fiber polymers were used as sorbents: polyamide 6 nanofibers, polyvinylidene difluoride nanofibers, polyethylene microfibers, and two new polycaprolactone microfiber/nanofiber and polycaprolactone microfibers/polyvinylidene difluoride nanofibers composite polymers. The fiber polymers were filled in a cartridge directly connected to the UHPLC system and tested. For each polymer, the optimal conditions of the on-line extraction were found and potential applicability on real samples was tested. The determination of ochratoxin A (OTA) in beer matrix was chosen as a case study. Relevant factors such as the mechanical and chemical stability of the nano/microfibers, filling the cartridges, fiber reusability and the possibility and the repeatability of all processes were involved in the proposed study. A new nano/micro composite sorbent consisting of polycaprolactone microfibers/polyvinylidene difluoride nanofibers was chosen as the most suitable sorbent for the on-line extraction of OTA from a beer matrix. The tested validation parameters had the value of intra-day precision lower than 1.48%,

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linearity in the range from 0.5 to 100 μg L^{-1} with $r^2 \geq 0.9999$ for standard and matrix calibration curve, and recovery in the range 99.1–103.9% at five concentration levels. Long-term precision evaluated for 31 analyses over the period of three months did not exceed 2.9% RSD. It confirmed the column reusability and perfect stability of nano/micro composite sorbent in the presence of organic solvents and after repeated injection of a complex beer matrix.

1. Introduction

The fabrication, application, and possible utilization of nanofibers in different areas of advanced technologies and everyday use have been hot topics in recent years. Nanofibers possess large surface area resulting from their small size. The surface area of nanofiber polymers can be controlled and their properties can be changed in a wide range of ways. Nanofiber polymers can have different physicochemical properties and can contribute to different interactions [1]. All these facts make nanofibers attractive for researchers in different areas. For example, in analytical chemistry, nanofibers are tested as perspective sorbents for solid phase extraction (SPE) [2]. Nowadays, nanofibrous SPE is a promising, new, and innovative approach using polymer fibers as sorbents with suitable physicochemical properties and large sorption capacity that requires small volumes of samples and solvents. The large surface area enhances the sorption capacity and reaction kinetics with the target analytes. Therefore, polymer nanofibers exhibit a good potential in this field due to their versatility, stability, and reusability.

Various approaches have been tested by different research groups over the past decade and the most suitable ways and arrangements of using nanofibers as sorbents for SPE have been developed [3–6]. However, the use of nanofibers as sorbents in different SPE manifolds also presents certain problems. Several factors affect the extraction properties of the nanofibers and all of them have to be considered when developing an extraction procedure.

The type and chemistry of the polymer are the first aspects which have to be contemplated. A wide range of polymers covering a large variety of chemistries are available. The most frequently used polymers are polyamide, polystyrene, and polyetherimide [7–13]. The relative ease with which these polymers can be modified enables the preparation of a large range of copolymers and composite materials differing in chemistry. This variability then provides many yet-unexplored options [3,5,14–18], e.g. creation of new coated nanofibers with unique chemical characteristics.

The fabrication of nanofibers is the next important parameter. Several approaches towards fiber production have been designed. Typically, electrospinning and the melt-blown technologies are the most commonly used. Electrospinning uses a strong electrostatic field for forming the nanofibers. Due to the small diameter of these nanofibers, they are not stable, and their three-dimensional structure can collapse. That is why electrospun nanofibers are mostly used in the format of a 2D cloth (sheet). Nanofibers in this format can be conveniently used as membranes for filtration or extraction. These extraction techniques should be used only in off-line mode to avoid some problems. An on-line connection with a suitable flow analytical method such as liquid chromatography is problematic or impossible because the flat layout is not compatible with the LC system. Also, packing the sheets in the SPE cartridges for on-line coupling is less reproducible and often adds large void volume in the system.

The meltblown technology enables the production of a three-dimensional porous structure of the fibers in both nano and micro dimensions. Polymers used for the preparation of fibers using the meltblown technology typically have a lower melting temperature than the polymers used for electrospinning. The three-dimensional structure of microfibers is stable and can withstand even the high pressure applied in UHPLC. Furthermore, the porous structure provides for other advantages such as the low contribution of the cartridge filled with fibers to the overall back pressure in the on-line SPE UHPLC system.

Microfibers can be used alone as sorbents for on-line SPE-UHPLC, or they can provide a scaffold for nanofibers that are not able to create a stabile three-dimensional porous structure. The combination of micro and nanofibers can create a unique composite material with sorption properties depending on the chemistry of the polymer used and on the method of fabrication. Bonding nanofibers to a microfiber scaffold created from the same type of polymer can enlarge the active surface. This increase then enhances the extraction capacity and the speed of extraction. Using a different type of polymer for preparation of the nanofibers leads to a dual chemistry composite polymer with modified extraction properties. Combining the meltblown and electrospun fibers is a way to innovate nanofibrous sorbents for solid phase extraction and successfully apply them in high-pressure systems. Only a few reports describing the preparation and use of composite polymer fibers prepared via this approach have been published [19–21].

The next important aspect that cannot be neglected is the arrangement of the nanofibers. For solid phase extraction procedures, the nanofibers can be used in the format of discs and membranes [5,8–10,16,22,23], layers covering steel wires [14,24], and filled in cartridges and pipette tips [3,17,25].

As it was mentioned, using nanofibers as sorbents for on-line solid phase extraction coupled with liquid chromatography (on-line SPE-HPLC) remains a quite challenging task. On-line connections simplifying the analysis of real samples with a minimal demand for the operator's skills, and improving the repeatability of the whole process are desirable. A handful of reports dealing with the application of the polymer nanofibers, mostly using polyamide 6, in on-line method, have been published [13,14,25,26].

Our current study concerns use of new nanofiber sorbents for on-line SPE-UHPLC. We also compare various types of polymers including microfibers, nanofibers, and composite structures, prepared using three different approaches. The effect of the structure of our fibers on extraction of real samples and their suitability for the determination of ochratoxin A (OTA) in beer was elucidated. This work also deals with some practical problems related to the development of the on-line SPE-UHPLC method such as the reproducibility of nano/microfiber packing, flow and back pressure inconsistency, the reuse of extraction column, and the long-term stability of the tested polymers. Complete method validation for on-line SPE determination of OTA in beer samples was carried out for the most suitable nanofiber sorbent.