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Nanofiber polymers as novel sorbents for on-line solid phase extraction in chromatographic system: A comparison with monolithic reversed phase C18 sorbent

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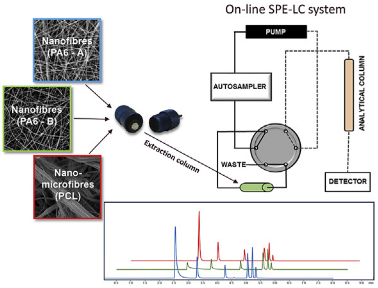
HIGHLIGHTS

- The nanofiber polymers showed to be promising sorbents for on-line solid phase extraction in chromatography systems.
- The approach enabled using of on-line nanofibrous extraction of different insecticides.
- Three different nanofibrous structures - polyamide 6, poly ε-caprolactone and polystyrene were tested.
- The reusability of nanofibrous extraction pre-columns was verified.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel application of nanofiber polymers in the wide area of a sample preparation techniques known as solid phase extraction has been studied. We demonstrated application of nanofibers as sorbents for use in a system including on-line extraction coupled with column-switching high performance liquid chromatography. Four types of nanofibers including polyamide 6 with two different surface densities, poly(ε-caprolactone), and polystyrene were tested. We found that three of them were very efficient extraction sorbents sufficiently stable for application in the on-line system. Our results confirmed that the extraction efficiency of the nanofibers depended on the type and chemistry of the spun polymer as well as on the fabrication process of the nanofibrous mats that affected their density, structure, surface density, and mechanical functionality. We also compared performance of all four nanofibers with a conventional monolithic reversed-phase C18 sorbent in terms of extraction efficiency using on-line solid-phase extraction-HPLC system. Polyamide 6 was found to be the best sorbent for lipophilic analytes with a retention and extraction efficiency for the target analytes comparable with that of the C18 monolith.

1. Introduction

Current trends of research in analytical chemistry are focused on the finding of new materials, their chemistry and physico-chemical properties, as well as their structural innovation to develop

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Abbreviations: PA6, polyamide 6; PCL, poly(ε-caprolactone); PS, polystyrene; LOD, limit of detection; PTFE, polytetrafluorethylene.

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sorbents for solid phase extraction (SPE). One of the novel but rarely described approaches with a great potential is the use of nanofibers as mats for solid phase extraction. Thanks to the small fiber size with diameters less than 1000 nm, nanofibers have a large surface area. Because of this unique property, they are affording a large extraction capacity. Several approaches to nanofibers have already been described. The most common way is electrospinning, during which the nanofibers are formed from a solution or melt of a polymer with help of a strong electrostatic field. The use of a syringe needle or a capillary spinner for forming nanofibers is called needle or needle-less electrospinning [1,2].

Sample pretreatment preceding the actual analyte determination is a crucial step of sample analysis, mainly when complex matrix measurements are desired. This sample pretreatment might be a complex procedure and typically includes multiple steps. Each of these steps represents a potential source of errors. Currently, SPE is one of the most often used methods in sample pretreatment techniques. Here, the analyte in a solution is reversibly bound to the sorbent via a variety of interactions that can be divided into three groups: polar, nonpolar, and ionic [3]. The type of sorbent and its structure are the most important factors that affect the extraction efficiency. Recently, the requirements for newly developing sample pretreatment techniques include minimizing the human error by reducing the number of steps. One of the options for the reduction in the number of steps is the on-line coupling of the sample pretreatment directly with analytical manifolds such as high-performance liquid chromatography system. This approach enables to carry out the pretreatment directly before analysis, and the treated sample is then injected in the chromatographic column without any further manipulation using a column switching valve. The on-line SPE-HPLC method usually consists of two steps and two different columns are applied for extraction and separation. In the first step, the sample is loaded in the extracting precolumn. Target analytes are selectively retained on the sorbent, and the remaining matrix and the following washing mobile phase are directed in the waste. The second step begins after the valve is switched to the second position and the analytes are eluted with the mobile phase from the precolumn in the chromatography column, where the separation occurs [4,5].

We found only a few papers that focused on the application of nanofibers as sorbents for SPE [6–14]. Moreover, authors of these studies carried out the extraction almost solely in the classical off-line mode, which is tedious and time-consuming. In contrast, direct extractions in column-switching mode, i.e. on-line SPE, using nanofibers was not described yet. This is not surprising because the coupling of the new type of extraction devices on-line to HPLC systems is not a trouble-free procedure. Typically, hardware modifications, flow inconsistencies, back pressure limitations, column and valve leaking, incompatibilities between extraction and separation materials, and pump pressurization are the most often encountered problems that can complicate method development and validation. Therefore, the number of papers published in the last decade using on-line extraction in chromatography system is rather limited. Most of them described the off-line extraction with nanofibers carried out primarily by using disc or pipette tips [6].

Ifegwu et al. studied selected nanomaterials for the determination of 1-hydroxypyren in urine. This study led to the conclusion that nanomaterials offer comparable results with C18 sorbents; however, the extraction time was shorter and the solvent consumption reduced [7]. Kang et al. studied extraction of several biologically active substances from water and plasma samples using polystyrene nanofibers. This study also confirmed the short extraction time and a decrease in solvent consumption when using nanofibers [8]. Other reports dealt with the determination of steroidal substances in aqueous solutions and saliva using nylon nanofibers [9] and polystyrene nanofibers [10–12]. Further studies were focused on the development of an extraction methodology for the determination of pollutants such as herbicides using polypyrrole fibers [13], chlorophenols using polyamide-polyethylene nanofibers [14] or multi-walled carbon nanotubes [15], and on the preparation of porous polystyrene nanofibers and their application for the determination of antibiotics in waste waters [16]. We found one work that concerned the on-line SPE nanofibrous extraction of the clodinafop herbicide from water and soil using polyamide nanofibers [14]. Another paper was focused on the production of polyamide nanofibers using magnetic and electric fields, and the resulting nanofibers were used for the on-line SPE extraction and HPLC [17].

Therefore, the first aim of this work was focused on using various polymers in nanofiber format for the solid phase extraction directly coupled to a chromatography system. The second aim was a comparison of the results obtained with the nanofibrous extraction with those obtained with a C18 sorbent that is commonly used for the solid phase extraction. The third, and the most important aim, was to describe and summarize the practical aspects, advantages, disadvantages, and troubles in the use of polymer nanofibers during the on-line SPE-HPLC method development. Two types of polyamide 6 differing in surface density, poly(ε-caprolactone), and polystyrene nanofibers were tested. The model analytes were selected from the group of pyrethroid and carbamate insecticides, which are frequently used for the protection of plants in agriculture and are frequent pollutants in water and soil. These analytes differed in physico-chemical properties such as log P. Thanks to this, the extraction performance of the nanofibers could be critically evaluated.

2. Experimental

2.1. Materials

All of the standards, carbaryl (purity $\geq$ 99%), fenoxycarb (purity $\geq$ 99), kadethrin (purity $\geq$ 90%), deltamethrin (purity $\geq$ 99%), and permethrin (purity $\geq$ 98%), as well as Chromasolv grade methanol and acetonitrile, poly(ε-caprolactone) (MW 45,000), and tetrahydrofuran were provided by Sigma-Aldrich (Prague, Czech Republic). The ultra-pure water was obtained using a Milli-Q (Millipore, Bedford, MA, USA). Absolute ethanol and chloroform, which were used for the production of the poly(ε-caprolactone) nanofibers, were purchased from Penta (Prague, Czech Republic). Nylon 6 (Ultramid B27) was purchased from BASF (Prague, Czech Republic). Polystyrene (Styron™ 634) was provided by Trinseo (Germany). A Chromolith® endcapped C18 column (10 × 4.6 mm) with a guard cartridge kit was purchased from Merck (Darmstadt, Germany).

2.2. Instrumentation and software

Analyses were carried out using a Nexera X2 chromatographic UHPLC system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC-30AD solvent delivery pumps, an SIL-30AS autosampler, a DGU-20 A5R degassing unit, a CBM-20A communication module, a SPD-M30A DAD detector, and a CTO-20AC column oven. A FCV-12AH high pressure six-port column switching valve was also used. Shimadzu LC Lab-Solutions version 5.57 software (Shimadzu Corporation, Kyoto, Japan) handled the system control, data acquisition, and evaluation. The nanofibers were produced using a laboratory machine Nanospider NS1WS500U (Elmarco, Czech Republic). Electron scanning microscope VEGA3 (Tescan) and software NisElements (Nikon) were used for morphologic analysis of nanofibers.

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