Testing of nylon 6 nanofibers with different surface densities as sorbents for solid phase extraction and their selectivity comparison with commercial sorbent

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ABSTRACT

Nylon 6 nanofibers were tested for their ability to serve as a sorbent for solid phase extraction (SPE). The regular nanostructure providing a great sorption area and amidic functionality should lead to the assumption that nylon 6 nanofibers could be used as a novel sorbent with great potential for sample pre-treatment. However, due to the substantial differences between classical particle sorbents used for solid phase extraction and nanofibers, it is necessary to evaluate this novel approach. This article describes three types of laboratory fabricated nylon 6 nanofibers with different surface density ($5.04\,\mathrm{g\,m^{-2}}$, $3.90\,\mathrm{g\,m^{-2}}$ and $0.75\,\mathrm{g\,m^{-2}}$) and corresponding surface areas for solid phase extraction of several groups of compounds with different structural and physicochemical properties (parabens, steroids, flavonoids and pesticides). The nanofibers were created by needleless electro-spinning. Extraction columns were manually packed in classic 1- or 3-mL plastic syringe cartridges with 26–30 mg of nanofibers and the column bed was sealed with polypropylene frits. The SPE procedure followed a typical five-step protocol and the collected eluates were analyzed by HPLC with UV detection. Extraction recovery was used as a parameter to evaluate the behavior of the analytes within the SPE process. Under this set condition, the recovery of the SPE process ranged from 23.1% to 125.8%. SPE showed good repeatability (0.58–11.87% RSD) and inter-day reproducibility (3.86–9.79% RSD). The achieved results were compared with SPE using a classic particle sorbent column. Good mechanical and chemical stability of nanofibers was proved. Scanning electron microscope was used for the evaluation of morphological changes in nanostructure. Nylon 6 nanofibers proved being a cost-effective sorbent for repeated use in SPE. Nylon 6 nanofibers have great potential in miniaturized SPE enabling users to overcome troubles with high back-pressure.

1. Introduction

Sample pre-treatment is an essential step when performing analyses and is often necessary before the determination. The process typically consists of multiple steps and each step is a possible source of error. Nowadays, solid phase extraction (SPE) is the most frequently used technique for sample pre-treatment. SPE is used to eliminate interferences and sample matrix issues that could negatively affect the determination of target analytes. Very important factors that influence extraction recovery and sample clean-up efficiency include the type and structure of the SPE sorbent.

Recent trends in the SPE techniques have been focused on finding of new types of materials that have greater sorption area and selective extraction properties. The extraction of e.g. highly polar compounds

and macromolecules from aqueous samples still remains challenging. Therefore, the main task for many researchers is to find a suitable substitution of non-specific (surface-modified silicas and porous polymers) sorbents for compound-specific and class-specific sorbents. Surfactant-modified sorbents, mixed-mode polymeric sorbents, molecular recognition sorbents (molecularly-imprinted sorbents, aptamers and immunosorbents) and nanostructured materials are among the new class-specific and compound specific sorbents for SPE [1,2].

Another task is to find sorbents with improved chemical, mechanical and thermal stability as well as sorbents with advantageous particle size and morphology suitable for higher mass-transfer rates. Nanostructured materials are being extensively studied for their potential use in analytical chemistry, including their use as sorbents in SPE. Recent research has been focused on nanostructured materials

such as carbon nanotubes, electrospun nanofibers, dendrimers and magnetic nanoparticles [1]. Nanofibers have great sorption capacity thanks to their large surface area (small fiber diameter) and they might prove to be promising sorbents with great potential for SPE. Sorbents with large surface area enhance extraction capacity and sorption kinetics.

The most often-used process when forming nanofibers is called electrospinning. Two types of electrospinning have been developed: needle electrospinning (conventional), which uses a syringe needle as a fiber generator, and needleless electrospinning, which uses a roller or a cylinder. Nanofibers are created from a polymer solution or melt due to the strong electrostatic field between the two electrodes - needle/roller and the opposite electrode [3]. Needleless electrospinning has made mass production of nanofibers possible [4]. Optimization of the production parameters has led to the production of nanomaterials with improved physicochemical properties, mechanical strength, etc. One of the advantages of nanomaterials is their potential for derivatization and functionalization [1,2]. In the literature that has been published over the last decade, several works that describe the use of nanofibers as a sorbent for solid phase extraction have been found. The team of O.C. Ifegwu tested different types of nanofibers for the determination of 1-hydroxypyrene in urine. Their work described the influence of sorbent geometry on separation and recovery [5]. Asiabi M. et al. described the extraction of tetrahydrocannabinol from whole blood using electrospun composite chitosan nanofibers containing iron nanoparticles [6]. Another group studied the possibility to use polystyrene nanofibers to extract several biologically active substances from plasma or water samples [7]. Further studies have dealt with the determination of steroidal substances in saliva or in water using polystyrene nanofibers [7–9] or nylon nanofibers [10]. Other studies have also focused on the development of extraction methodologies using nanofibers for the determination of pollutants in environmental samples [11–13]. Most of the published works have tested nanofibers made by needle electrospinning.

As far as we know, there are only a limited number of studies that describe the influence of the electrospinning process on extraction abilities. In our present work, we tested three different types of nylon 6 nanofibers created by needleless electrospinning. The first aim of the presented work focused on testing nylon 6 nanofibers as the solid phase mats for extracting selected biologically active substances. The second aim of this study was the description of the influence of the fabrication properties of the nanofibers on extraction recovery (analyte retention). The third aim was to summarize and discuss practical aspects, troubles, advantages and disadvantages of using nylon 6 nanofibers as a sorbent in the SPE procedure.

2. Materials and methods

2.1. Chemicals

All tested substances (purity ≥ 99%) as well as all solvents (acetonitrile Chromasolv, methanol Chromasolv, ammonium acetate, formic acid, and acetic acid) used for SPE testing, for HPLC determination and to produce nanofibers were provided by Sigma-Aldrich (Prague, Czech Republic). The nylon 6 material for nanofiber fabrication (Ultramid B27) was provided by BASF (Prague, Czech Republic). The ultra-pure water was purified through a Milli-Q (Millipore, Benford, MA, USA).

2.2. Instrumentation and software

The solid phase extractions were performed using a vacuum SPE manifold Visiprep (Sigma-Aldrich, Prague, Czech Republic). Oasis HLB® 1 mL SPE columns were provided by Waters (Prague, Czech Republic). Empty SPE cartridges were provided by Waters and Sigma-Aldrich. HPLC determinations were performed using a Shimadzu LC-2010C system (Shimadzu Corporation, Kyoto, Japan) equipped with a UV–VIS

Table 1
Standard solutions composition.

Analyte	Solvent of standard stock solution [1 g L^{-1}]	Concentration	Solvent of model sample	Solvent of working standard solution
Methylparaben	ACN	4 mg L^{-1}	H$_2$O	ACN
Ethylparaben				
Propylparaben				
Butylparaben				
Triamcinolone	ACN: MeOH (1:1)	20 mg L^{-1}	H$_2$O	ACN
Hydrocortisone	ACN			
Triamcinolone acetonide	ACN			
Hydrocortisone acetate	ACN:H$_2$O (4:1)			
Estradiol	ACN			
Testosterone	ACN			
Ethinylestradiol	ACN			
Estrone	ACN: MeOH (1:1)			
Progesterone	ACN			
Rutin	MeOH	4 mg L^{-1}	H$_2$O	MeOH
Naringin	MeOH			
Kaempferol	MeOH			
Luteolin	MeOH			
Hesperidin	MeOH: DMSO (4:1)			
Quercetin	MeOH			
Naringenin	MeOH			
Hesperetin	MeOH			
Fenoxycarb	MeOH	4 mg L^{-1}	MeOH:H$_2$O (1:3)	ACN
Trans-permethrin	MeOH			
Cis-permethrin	MeOH			
Hydroxypyrene	MeOH	4 mg L^{-1}	MeOH:H$_2$O (1:3)	ACN

detector. The system control and data evaluation were performed using Shimadzu LC Class VP software version 6.13 (Shimadzu Corporation, Kyoto, Japan). All the HPLC analyses were performed using a Supelco Discovery HS C18 (100 × 4.6 mm, 5 μm) analytical column (Sigma-Aldrich, Prague, Czech Republic). Preparation of the nanofibers was carried out using a Nanospider NS1WS500U laboratory machine (Elmarco, Czech Republic).

2.3. Preparation of standard solutions

Individual standard stock solutions were prepared by dissolving 1 mg of each substance in 1 mL of organic solvent (methanol or acetonitrile). For further details, see Table 1. All standard stock solutions were stored at 4 °C in the dark. Working standard solutions were prepared on the day of measurement by diluting the standard stock solutions in organic solvent used as the elution solvent (acetonitrile or methanol). These working standard solutions were directly injected to the HPLC system (without performed SPE procedure) and used as comparative solutions for evaluating SPE recovery (considered as 100%).

2.4. Preparation of model samples

The testing of the extraction properties of nanofibers was accomplished using model samples (aqueous samples) with model analytes selected from the groups of parabens, steroids, flavonoids, insecticides and hydroxypyrene. Model samples were prepared on the day of measurement. Ultra-pure water was used to dilute the standard stock solutions. Model samples containing insecticides and hydroxypyrene were diluted with 33% methanol in water (v/v). The effect of pH of the sample on extraction recovery was tested with flavonoids using sample