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# Polyaniline-nylon-6 electrospun nanofibers for headspace adsorptive microextraction

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ABSTRACT

A headspace adsorptive microextraction technique was developed using a novel polyaniline-nylon-6 (PANI-N6) nanofiber sheet, fabricated by electrospinning. The homogeneity and the porosity of the prepared PANI-N6 sheet were studied using the scanning electron microscopy (SEM) and nanofibers diameters were found to be around 200 nm. The novel nanofiber sheet was examined as an extracting medium to isolate some selected chlorobenzenes (CBs), as model compounds, from aquatic media. The extracted analytes were desorbed using μL-amounts of solvent and eventually an aliquot of extractant was injected into gas chromatography–mass spectrometry (GC–MS). Various parameters affecting the extraction and desorption processes were optimized. The developed method proved to be convenient and offers sufficient sensitivity and a good reproducibility. Limits of detection achieved for CBs with the developed analytical procedure ranged from 19 to 33 ng $L^{-1}$, while limits of quantification were from 50 to 60 ng $L^{-1}$. The relative standard deviations (RSD) at a concentration level of 0.1 ng $mL^{-1}$ and 1 ng $mL^{-1}$ were in the range of 8–14% and 5–11% ($n = 3$), respectively. The calibration curves of analytes were investigated in the range of 50–1000 ng $L^{-1}$ and $R^2$ between 0.9739 and 0.9932 were obtained. The developed method was successfully applied to the extraction of selected CBs from tap and river water samples. The relative recovery (RR) percentage obtained for the spiked real water samples at 0.1 ng $mL^{-1}$ and 1 ng $mL^{-1}$ level were 93–103% and 95–104%, respectively. The whole procedure showed to be conveniently applicable and quite easy to handle.

## 1. Introduction

Because of the low concentrations of environmental pollutants in water samples, it is necessary to apply a preconcentration step prior to the instrumental analysis. The traditional sample preparation methods such as liquid–liquid extraction (LLE) and solid phase extraction (SPE), consume large amounts of samples and organic solvents, while they are time consuming and tedious. Recent approaches based on the sorptive and adsorptive microextraction, provide advantages of being solvent-less or little solvent usage, lower sample consumption, higher sample preparation speed and ease of operation [1]. The common aspects in the microextraction strategies are mostly focused on miniaturized sorbent amount and the extraction device geometry which often lead to the extraction of small fraction of the analytes from the sample into the extracting phase [2]. In order to increase the sensitivity of solid phase microextraction (SPME), which is due to its lower sample capacity, other approaches including stir bar sorptive extraction (SBSE) were developed to provide higher mass of sorbent in the sorptive extraction manner [3,4]. Although these approaches were used to improve different aspects of the whole extraction procedure, the fundamental bases are rather similar [5].

Another strategy to improve the sensitivity of the microextraction methods relies on the usage of nanostructured materials in which the interactions between the desired analytes and the sorbent are increased. This could be due to the enhancement of surface to volume ratio as the size of the sorbent particles is reduced extensively [6–8]. An emerging method for preparing nano-dimensional sorbents is electrospinning [9]. This methodology is a convenient technique for fabricating fibrous sorbent with controllable diameter, functionality and high surface to volume ratio [10–12]. In this technique by applying high voltages to a viscous polymeric solution, when the electrostatic repulsive force overcomes the surface tension of the polymeric solution, a charged polymeric jet ejects from the solution and afterwards flies toward the collector and forms the fibrous material with diameters in the scale of nano-to-micrometer. The electrospun sorbents were used in SPE [13–16], micro-SPE [10], SPME [17–19] and membrane extraction [20] of some organic and inorganic compounds.

In this work, polyaniline (PANI) was synthesized inside the nylon-6 (N6) solution as a carrier polymer, and a composite of polyaniline-nylon-6 (PANI-N6) was electrospun into the fibrous

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sheet with nano-scale dimensions. Then, the prepared composite was applied for the headspace adsorptive microextraction of some selected chlorobenzenes (CBs), as model compounds, to evaluate its extraction applicability.

## 2. Experimental

### 2.1. Reagents

The CB compounds 1,4-dichlorobenzene (14DCB), 1,2-dichlorobenzene (12DCB), 1,2,4-trichlorobenzene (124TCB), 1,2,3-trichlorobenzene (123TCB) and 1,2,3,4-tetrachlorobenezne (1234TeCB) were purchased from Merck (Darmstadt, Germany). Standard solution (2000 mg L$^{-1}$) of CBs mixture was prepared in HPLC-grade methanol (Merck) and stored in the refrigerator. The working standard solutions were prepared weekly by diluting the standard solution with methanol, and more diluted working solutions were prepared daily by diluting this solution with double distilled water (DDW). Ammonium peroxodisulphate and sodium chloride were purchased from Merck. Aniline was obtained from Merck and distilled before use. Nylon-6 (N6) was purchased from Kolon Industries Inc. (Seoul, Korea) and formic acid was obtained from Riedel-de Haën (Seelze-Hannover, Germany). All solvents used in this study were of analytical reagent grade or HPLC grade.

### 2.2. Apparatus

An Agilent (Palo Alto, CA, USA) 6890 plus series GC equipped with a split/splitless injector and an Agilent 5973 mass selective detector system were used. The MS was operated in the EI mode (70 eV). Helium (99.999%) was employed as carrier gas and its flow rate was adjusted to 1 mL min$^{-1}$. The separation of CBs was performed on a 30 m × 0.25 mm HP-5 MS column (0.25 μm film thickness). The GC column temperature was first started at 50 °C and held for 5 min, then increased by 30 °C min$^{-1}$ to 80 °C and held for 1 min, then ramped at 20 °C min$^{-1}$ to 200 °C for 5 min. The injector temperature was set at 250 °C in the splitless mode for 1 min. The GC–MS interface, ion source and quadrupole temperatures were set to 280, 230 and 150 °C, respectively. The selected ion monitoring (SIM) mode, considering two characteristic ions for each compound (Table 1), was used for quantitative analysis. The surface morphology of the fabricated nanofiber sheet was investigated by a TSCAN VEGA II XMU SEM instrument (Brno, Czech Republic). All samples were heated in a homemade glass water bath connected to a refrigerated circulating water bath (RTE-8, Neslab Instruments Inc., Portsmouth, NH, USA) and stirred using a magnetic stirrer (Baird & TatLook, London, England). A Brandenburg (West Midlands, England) regulated power supply was used for electrospinning. A KDS100 syringe pump (KdScientific Co., Holliston, MA, US) was used for the polymer solution delivery in the electrospinning process.

**Table 1**
The selected ions, scan start times and retention times of CB mixtures studied by GC–MS.

| Compounds | Selected ions ($m/z$) | Scan start time (min) | Retention time (min) |
|---|---|---|---|
| 14DCB | 146, 148 | 3 | 5.89 |
| 12DCB | 146, 148 | 3 | 6.30 |
| 124TCB | 180, 182 | 8 | 8.99 |
| 123TCB | 180, 182 | 8 | 9.76 |
| 1234TeCB | 214, 216 | 12 | 12.98 |

### 2.3. Electrospinning of PANI-N6

Firstly, an amount of 0.25 g N6 was dissolved in 1 mL of formic acid. Then, an amount of 0.1 g ammonium peroxodisulphate was added to this polymeric solution. After dissolving the salt, the aniline monomer (0.5 g) was added to the solution and the mixture was stirred to obtain a homogenous solution. After that, 0.5 mL of this solution was withdrawn by a 2.5 mL syringe which was eventually transferred to a syringe pump. A piece of aluminum foil (10 × 10 cm) was employed as a collector electrode. The collector and the polymer containing syringe needle were connected to the high voltage power supply terminals.

The distance between the needle and the collector was set at 10 cm. Fig. 1 shows the schematic diagram of the apparatus used in the electrospinning process. A voltage of 16 kV was applied for the nanofibers production while a flow rate of 1.5 μL min$^{-1}$ was set for the syringe pump to deliver the polymer solution. All fibers were electrospun for 12 h to achieve the desired coating thickness. The electrospinning experiments were performed under the ventilation. After the electrospinning experiment, the collector foil was separated from the power supply and afterward a sheet with a typical dimension of 1 × 1 cm, was cut from the central part of the Al foil using a predesigned template and employed for extraction.

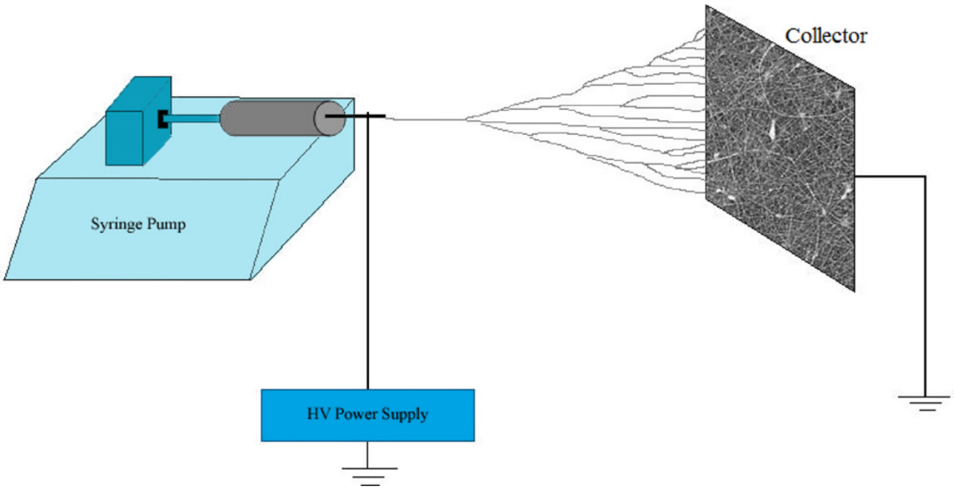

**Fig. 1.** Scheme of the electrospinning set up.