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Electrospun decyl-3-methylimidazolium mono bromate/polyamide nanofibers as solid-phase microextraction coating

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ABSTRACT

In the current study, electrospun-based ionic liquid (IL) doped polyamide (PA) nanofibers were prepared and used as the coating material of solid phase microextration device in the fiber geometry. Addition of IL, decyl-3-methylimidazolium mono bromate, increased the conductivity of the PA solution facilitating the electrospining process. The scanning electron microscopy images of decyl-3-methylimidazolium mono bromated/polyamide nanofibers showed the decreased diameter of the nanofibers in the range of 35–160 nm compared to the PA nanofiber. The factors affecting the structure of nanofibers (*e.g.* ratio of decyl-3-methylimidazolium mono bromate to PA, coating time and applied voltage) were studied. In addition, influential parameters of extraction/desorption performance such as ionic strength, extraction time, and desorption time and temperature were studied. The limit of detections and limit of quantifications were obtained in the range of 0.75–0.9 and 2–5 ng L^{-1}, respectively, demonstrating high efficiency of the prepared nanofiber. The developed method also showed good repeatability, RSD 4–9% ($n = 3$), for the spiked aqueous solution at concentration level 150 ng L^{-1} of chlorobenzenes, and linearity,R = 0.996, in the range of 5–5000 ng L^{-1}.

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1. Introduction

Determination of pollutants in water samples has gained high attention due to the harmful impact on public and environment health. An efficient sample preparation technique is required to clean-up and pre-concentrate the compounds to meet the maximum contaminate limits (MCL) provided by United States Environmental Protection Agency and other environmental agencies. The conventional sample preparation methods such as solid phase extraction (SPE) and liquid-liquid extraction (LLE), consume large amounts of organic solvents which are toxic resulting in waste generation [1–3]. In addition, they need large volume of sample to meet the required MCLs. Minimizing the sample preparation steps by integration of extraction and pre-concentration in a single step and eliminating the solvent evaporation and reconstitution steps is an effective way to reduce the cost and time of analysis and providing green approaches. Solid phase microextraction (SPME) is a miniaturized sample preparation method introduced in 1990s as a green alternative to traditional sample preparation techniques. Apart from integration of clean-up and preconcentration steps, SPME is easily coupled to gas chromatography (GC) and liquid chromatography (LC) [4–6]. Fused-silica was initially used as substrate of SPME fibers, limited its application to 20–30 runs due to the physical limitation. Currently, fused silica core was replaced with metal alloy in commercially available fibers. In addition, a number of home-made metal wire/tubing-based SPME fibers including stainless steel [7], zinc [8,9], aluminium [10], copper [11], gold [12], platinum [13], titanium [14] and NiTi alloy [15] were developed to increase lifetime of the fibers. The novel application of SPME coatings are mostly focused on improving thermal, mechanical and chemical stability and development of material with higher sensitivity.

Recently, electrospinning technique has been used to prepare nano-structured coating materials providing several advantages including higher extraction efficiency.For example, polyacrylic acid (PAA)/poly (vinyl alcohol) nanofibrous mats were prepared by electrospining and it was offered a reduced pressure drop during the extraction/desorption process compared to a conventional particle-packed SPE method [16]. The electrospinning is a convenient technique to prepare nanofiber polymers with adjustable

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polarities, porosities and diameters. They have malleability to conform to a wide variety of sizes and shapes. The composition of polymer nanofibers with the desired functionalities and properties is controlled by changing the concentration of monomer and electrospining parameters. The electrospinning process is based on similar principle as electrospray ionization mass spectrometry [17]. Viscosity and charge density of the polymer solution are two critical parameters to fabricate uniform bead free nanofibers. The high viscosity of a certain concentration needs a great effort to be spun while reducing viscosity using low concentration solution leads to the formation of unfavourable beads. To adjust the solution viscosity surfactants are usually considered as favourable compounds. The volumetric charge density of the solution depends on the applied voltage and ionic conductivity. Higher voltage leads to higher energy consumption and also needs a more powerful power supply [18]. For this reason, ionic conductivity is the most important factor as the more ionic conductivity result in the more charge accumulation. By increasing the volumetric charge density in solution, much more charge can be accumulated and transferred through the polymer surface and lessen forces are needed to form the jet [19]. Ionic liquids (ILs) are recently used in electrospinning technique to improve the conductivity of the polymer solution, also, to change the structure and properties of nanofibers.

1-decyl-3-methylimidazolium bromide (ILs) was selected to reduce the surface tension of the solution. Also using long chain alkyl halides, the ionic ILS can have more surfactant effect. The specific conductivity for 1-decyl-3-methylimidazolium bromide at 24.6 °C was measured 1141 μS cm^{-1}. Therefore, reduction in viscosity and surface tension are ideal to fabricate nanofibers with higher aspect ratio so with increase its special surface, its absorbent properties will increase. The effect of ILs concentration on solution viscosity and nanofibers diameters was considered by He et al. [20]. Luo et al. [21], studied the relation between the morphology of the polybutylene succinate-co-terephthalates and viscoelastic behaviour. Wang et al. [22], considered the rheological properties of 8–20 wt% of concentrated solutions of polyacrylonitrile/1-butyl-3- methylimidazolium chloride under different temperatures and polyacrylonitrile molecular weights Different processing factors including polymer concentration, solution flow rate, distance between the needle and collector and the applied voltage are affected on the fiber'diameters.

In this work, the effects of ionic liquid on decyl-3-methylimidazolium mono bromate as well as other influencing factors on the structure and morphology of the electrospun nanofibers were investigated. The nanofiber was developed as SPME coating for the pre-concentration of CBs pollutants from environmental water samples.

2. Experimental

2.1. Reagents

Chemicals such as monochlorobenezne (MCB), 1,2-dichlorobenzene (12DCB), 1,4-dichlorobenzene (14DCB), 1,2,4-trichlorobenzene (124TCB), methanol and NaCl were analytical grades and purchased from Merck (Darmstadt, Germany). Stock solution of CBs was prepared in methanol at 1000 mg L^{-1} concentration and stored in 4 °C. Working solutions were prepared daily by diluting stock solutions with double distilled water. The working solutions were daily prepared by diluting the stock solution with double distilled water. Nylon 6 (N6) was from Kolon industries Inc. (Korea) and formic acid prepared from Riedel-de Haen (Seelze-Hannover, Germany). Ethyl acetate, 1-bromodecane and 1-methylimidazole also were purchased from Merk (Darmstadt, Germany).

Table 1
The selected ions of CBs compounds studied by GC–MS.

Compound	Selected ions (*m*/*z*)
MCB	77, 112
14DCB	146, 148
12DCB	146, 148
124TCB	180, 182

2.2. Apparatus

Hewlett-Packard (HP, Palo Alto, USA) GC equipped with a split/splitless injector and mass-selective detector system in EI mode (70 eV) were used for CBs analysis. A glass inlet liner was deactivated by trimethylchlorosilane and used. The analytes separation was performed by a capillary column HP-5 MS (60 m, 0.25 mm i.d.) with 0.25 μm film thicknesses. The Helium (99.999%) gas was applied as carrier gas with flow rate of 1 mL min^{-1}. The oven program was set as follow; temperature held at 50 °C for 2 min, increased to 150 °C at a rate of 15 °C min^{-1} and then raised to 250 °C at 25 °C min^{-1} and kept at this temperature for 3 min. The injector temperature was set at 200 °C and all injections were carried out on the splitless mode for 3 min. To obtain the highest sensitivity, the MS detection was operated using time-scheduled selected ion monitoring (SIM) based on the selection of some mass peaks of the highest intensity for each compound. Table 1 list the retention times and selected masses of studied compounds.

2.3. Synthesis of decyl-3-methylimidazolium mono bromate

The equal molar of 1-methylimidazole and 1-bromodecane were added into a round-bottomed flask fitted with a reflux condenser for about 24 h at 70 °C with stirring until two phases formed. The top phase layer containing the unreacted starting materials was decanted and removed and then, ethyl acetate (a volume approximately equal to half of the bottom phase) was added under mixing. The ethyl acetate was then decanted and the process was repeated two more times to remove the unreacted materials.

2.4. IL/PA coating by electrospinning

Electrospinning solutions were prepared by dissolving PA (15 w/v%) in a formic acid solvent. Then, different concentration of decyl-3-methylimidazolium mono bromate was added to the polymer solution and stirred for 20 min to obtain a homogeneous solution. To prepare electrospun nanofibers, loaded in a syringe, the polymer solution was pumped at a flow rate of 0.5 mL min^{-1} While, an electric field of 16 kV was applied to syringe needle tip and collector metal. The polymer jets were generated from the needle and nanofibres were formed on the collector metal. All electrospinning experiments were performed under the same processing condition.

2.5. Extraction procedure

A home-made SPME holder was used for extraction/desorption of cholrobenzene from water samples. The SPME fiber containing IL/PA coating was first conditioned in the GC inlet at 180 °C for 5 h. Extraction was conducted by exposing the SPME fiber to headspace (HS) of 4 mL of spiked sample in a 7-mL vial under stirring at maximum rate. When equilibrium of analytes between sample and SPME fiber was reached, SPME fiber was retracted into the needle and inserted in the GC inlet for 3 min to desorption and further analysis of the target compounds.

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