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Core–shell electrospun polybutylene terephthalate/polypyrrole hollow nanofibers for micro-solid phase extraction

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ABSTRACT

In the present work, a new micro-solid phase extraction (μ-SPE) sorbent as an extracting medium based on core–shell nanofibers was synthesized by electrospinning. The core–shell nanofibers of polyvinylpyrrolidone-Polybutylene terephthalate/polypyrrole (PVP-PBT/PPy) were electrospun and subsequently, modified hollow nanofibers were prepared by removing the central PVP moiety. Moreover, conventional PBT/PPy was also prepared for the comparison purposes. The homogeneity and the porous surface structure of the core–shell nanofibers were confirmed by scanning electron microscopy (SEM). The applicability of the fabricated nanofibers-coating was examined by immersed μ-SPE of some selected triazine herbicides from aqueous samples and wheat grains. Subsequently, the extracted analytes were transferred into a gas chromatography (GC) after solvent desorption. Influencing parameters on the morphology of nanofiber such as elctrospinning parameters and the weight ratio of components were optimized. In addition, effects of different parameters influencing the extraction efficiency including extraction temperature, extraction time, ionic strength, sample pH, desorption temperature, and desorption time were investigated and optimized. Eventually, the developed method was validated by gas chromatography–mass spectrometry (GC–MS). At the optimum conditions, the relative standard deviation values for real water samples spiked with the selected triazines at 1 ng mL^{-1} were 4–8% ($n = 3$) and the limits of detection for the studied compounds were between 50 and 90 ng L^{-1}. The calibration curves for the selected triazines were in the range of 0.3–500 ng mL^{-1} and regression coefficients (R^2) were between 0.9985 and 0.9996.

1. Introduction

Sample preparation has remained a key step to achieve higher sensitivity *via* bringing the analytes of interest to a small-scale volume. A great deal of improvements in sorbent-based extraction techniques has been implemented during the last two decades, which led to the emerged miniaturized extraction techniques. Solid-phase extraction is a well-established process in which the compounds of interests are isolated from the bulk of sample by a solid sorbent. More techniques such as solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE) and μ-SPE have been introduced as efficient micro-oriented extraction techniques. The μ-SPE approach is a miniaturized equilibrium-based microextraction technique and is an alternative to the conventional SPE for the extraction purposes in which small amounts of sorbent is being used [1]. Similar to SPME, μ-SPE can be operated in two modes of (i) immersion and (ii) headspace. After immersed extraction, the μ-SPE sorbent is withdrawn from the sample vial, rinsed with the distilled water to remove any salts and other interfering components, cleaned by a paper tissue to remove water, and then desorbed by tiny amount of solvent. Various sorbents have been used for extraction of different analytes from biological and environmental samples. Many types of materials such as multi-wall carbon nanotube [1], C_{18} [2,3], molecularly imprinted polymer (MIP) [4], magnetic nanocomposite [5], carbon coated titanium dioxide nanotubes [6] and conductive polymers [7] have been used as the extracting media. These methods have been applied to the analysis of various compounds such as organophosphorous pesticides from sewage sludge [1], ketoprofen and ibuprofen from wastewater [2], phenolic compounds from environmental water samples [4], volatile aromas of liquid essential oils from Bulgarian rose and Provence lavender [8], carbamate pesticides in soil samples [3], naproxen and ketoprofen in saliva and urine samples [6] and triazine herbicides in aquatic media [7]. Among different types of sorbents used for the extraction of organic analytes, conducting polymers [9,10] have attracted a great deal of attentions.

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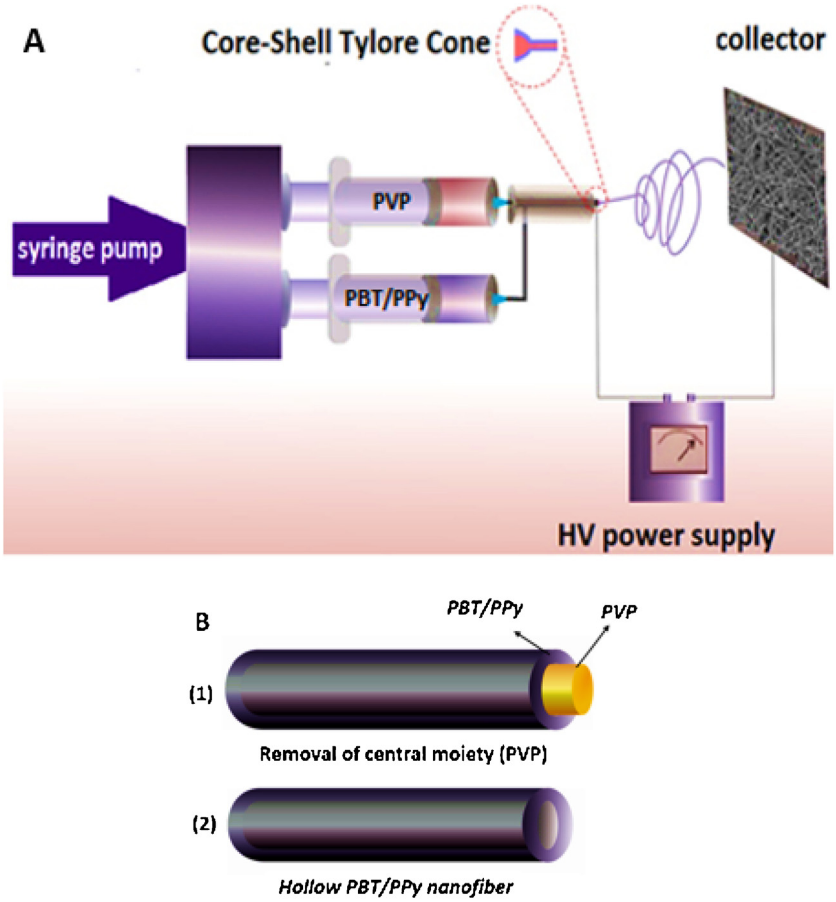

Fig. 1. Schematic diagram of the homemade core–shell electrospinning setup (A), PBT/PPy hollow nanofiber obtained from core–shell PVP-PBT/PPy nanofibers (B).

In recent years electrospun nanofibers have been used due to their high aspect ratio (surface to volume ratio) and extraction efficiencies [11]. Among different fabrication methods, electrospinning is the simplest approach capable of synthesizing nanofibers with different compositions and shapes [12]. To extend this fascinating technique, various nanofibers with different secondary nanostructure have been fabricated [13,14]. Moreover, electrospinning have been developed for fabricating nanofibers with core–shell structures [15–18]. These structures in compared with the conventional fibers have gained higher attentions due to their high aspect ratios and flexibility in surface properties and specific mechanical functions such as hardness and tensional strength [19,20]. Based on the basic electrospinning setup, two syringes feed inter-separated and coaxial “inner fluid” and “outer fluid” to spinneret. Under application of high voltages, the electrospinning liquid is drawn out from spinneret and forms a “compound Taylor cone” with a core–shell structure. After coaxial jet, the core–shell structure will be built and maintain as the prepared fibers are collected on the counter electrode surface [21]. In order to achieve a suitable Taylor cone with a core–shell structure, a precise control and balanced injection

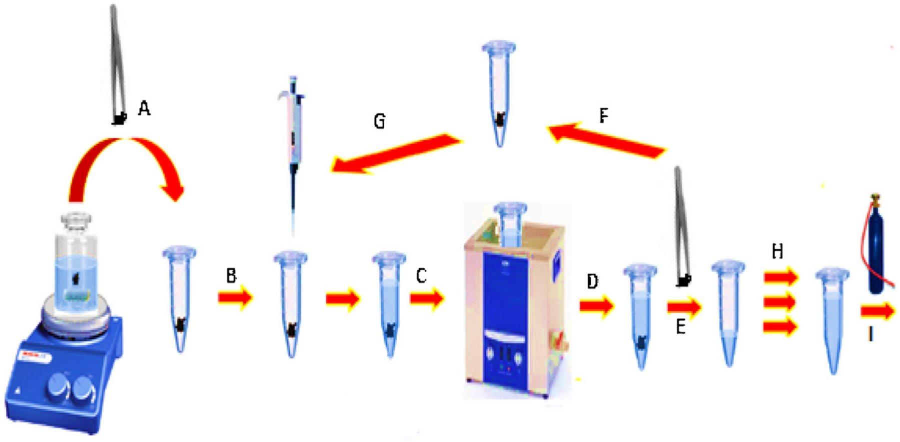

Fig. 2. Stages of immersed μ-SPE procedure; (A) sorbent withdrawal from sample and transfer into microtube, (B) addition of desorption solvent by micro-pipette, (C) desorption under sonication, (D) removal of microtube from ultrasonic bath, (E,F) sorbent withdrawal from microtube and transferring into another microtube for second desorption, (G) addition of desorption solvent, (H) transfer the contents of microtubes to just one microtube, (I) solvent evaporation using the nitrogen flow.