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Zinc oxide/polypyrrole nanocomposite as a novel solid phase microextraction coating for extraction of aliphatic hydrocarbons from water and soil samples

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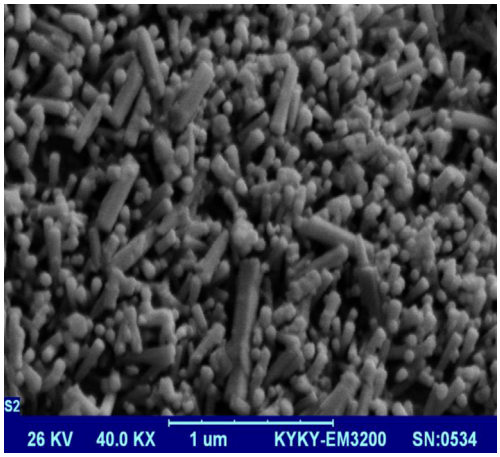
HIGHLIGHTS

- ZnO/polypyrrole (ZNO/PPY) nanocomposite coating was fabricated on stainless steel.
- Nanocomposite coating morphology was evaluated using scanning electron microscopy.
- It was applied for HS-SPME of aliphatic hydrocarbons in water and soil samples.
- Separation and determination of the hydrocarbons were performed by GC-FID.
- The method is suitable for routine analysis of *n*-alkanes in various environmental samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, ZnO/PPy nanocomposite coating was fabricated on stainless steel and evaluated as a novel headspace solid phase microextraction (HS-SPME) fiber coating for extraction of ultra-trace amounts of environmental pollutants; namely, aliphatic hydrocarbons in water and soil samples. The ZnO/PPy nanocomposite were prepared by a two-step process including the electrochemical deposition of PPy on the surface of stainless steel in the first step, and the synthesis of ZnO nanorods by hydrothermal process in the pores of PPy matrix in the second step. Porous structure together with ZnO nanorods with the average diameter of 70 nm were observed on the surface by using scanning electron microscopy (SEM). The effective parameters on HS-SPME of hydrocarbons (i.e., extraction temperature, extraction time, desorption temperature, desorption time, salt concentration, and stirring rate) were investigated and optimized by one-variable-at-a-time method. Under optimized conditions (extraction temperature, $65 \pm 1\,^{\circ}C$; extraction time, 15 min; desorption temperature, 250 °C; desorption time, 3 min; salt concentration, 10% w/v; and stirring rate, 1200 rpm), the limits of detection (LODs) were found in the range of 0.08–0.5 $\mu g\,L^{-1}$, whereas the repeatability and fiber-to-fiber reproducibility were in the range 5.4–7.6% and 8.6–10.4%, respectively. Also, the accuracies obtained for the spiked *n*-alkanes were in the range of 85–108%; indicating the absence of matrix effects in the proposed HS-SPME method. The results obtained in this work suggest that ZnO/PPy can be promising coating materials for future applications of

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SPME and related sample preparation techniques.

1. Introduction

Worldwide growth of the petroleum industry and marketing of petroleum products have resulted in environmental pollution by oil spills including leakages from tanks or tanker trucks and dumping of waste petroleum products. Aliphatic hydrocarbons as one type of petroleum pollutants are widely disseminated in the environment, with sources that can be natural or anthropogenic [1]. High levels of hydrocarbons represent a serious threat to the ecosystem functioning and human health via food chain and water resources [2]. Thus, design and development of reliable, fast, sensitive, and affordable analytical methods for determination of these pollutants in environmental samples is of great importance and commonly attracts the attention of scientific researchers.

Solid phase microextraction (SPME), developed by Pawliszyn and Arthur [3], is a rapid, simple, and solventless analytical sample preparation method [4]. In SPME technique, property of the coating is the most important key to enhance the extraction efficiency. A variety of commercial SPME coatings are available; however, they usually have drawbacks of low thermal and chemical stability besides the high cost and poor reusability. Thus, over the past decades, fiber fabrication methods with regard to the coating materials, and coating procedures have been the focus of many research projects. Recently, attention on application of nanomaterials as a sorbent phase in SPME has experienced impressive growth in terms of number of papers published in the literature [5–7].

ZnO nanostructures can be easily prepared in various shapes and sizes using different chemical methods [8–11]. Due to good thermal stability, high specific surface area, and simple preparation procedure; it was reported that various types of ZnO nanostructures (e.g., one-dimensional ZnO nanomaterials, ZnO nanorods, and nanowires), can be used as a SPME active material in the sorbent phase for preconcentration and determination of a wide range of organic compounds [12–16]. However, the SPME fiber based on the fused silica support is easily broken and its service life is therefore limited. Also the extraction capacity of ZnO nanomaterials is debated and because of poor bonding of ZnO coating to the substrate, life time and reusability of ZnO coating is low and the coating peeling during SPME or GC injection procedures may be observed. Thus, it seems that improvement of the extraction capacity and bonding to the substrate are inevitable. ZnO/polymer nanocomposite coatings on metallic substrates are good alternatives to improve these drawbacks [17–19]. Nanocomposites have a lot of advantages in comparison with their conventional filler counterparts and base polymer. Suitable mechanical properties (e.g., strength, modulus, and dimensional stability), thermal stability and heat distortion temperature, chemical resistance, and large specific surface areas are some advantages of nanocomposites. Therefore, fabrication of ZnO nanostructures–appropriate polymer composite (inorganic–polymer composite), can remarkably improve both extraction capacity and adhesion of coating to the substrate. Polypyrrole is a conducting polymer with multifunctional properties (e.g., hydrophobicity, π–π interaction, polar functional groups, ion-exchange property, and hydrogen bonding) [20]. Besides all these advantages, PPy coatings are mechanically resistant with excellent adhesion to stainless steel (SS) substrate especially in electrochemical polymerization method. This makes the coatings suitable to be selected as the copolymer in composite structures.

The aim of the present work is to fabricate a novel SPME coating; ZnO/PPy nanocomposite, and evaluate its application for extraction and preconcentration of hydrocarbons in water and soil samples. To evaluate the new coating performance for extraction and preconcentration of hydrocarbons from water and soil samples in headspace solid phase microextraction, a series of experiments were performed.

2. Experimental

2.1. Chemicals and reagents

Pyrrole and standards of *n*-alkanes including tridecane (C_{13}), tetradecane (C_{14}), pentadecane (C_{15}), hexadecane (C_{16}), heptadecane (C_{17}), octadecane (C_{18}), nonadecane (C_{19}), icosane (C_{20}), docosane (C_{22}), and tricosane (C_{23}) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Also, all the organic solvents such as methanol and acetone were of HPLC-grade and obtained from Sigma–Aldrich (St. Louis, MO, USA). Zinc nitrate, urea, and sodium chloride were from Merck (Darmstadt Germany). Standard solutions of the hydrocarbons were prepared by appropriate dilution of the stock solution in hexane.

2.2. Apparatus

Gas chromatographic analyses were performed on an Agilent gas chromatograph system model 7890A (Palo Alto, CA, USA) equipped with a flame ionization detector (FID) and a split/splitless injector system. Chromatographic separation was done on Varian wall coated fused silica capillary column (30 m × 0.32 mm i.d., film thickness 0.25 μm). The injector was operated in the splitless mode and was maintained at 250 °C. Helium (purity 99.999%) was used as the carrier gas at the constant flow rate of 2.0 mL min^{-1}. The column oven was initially set at 50 °C, programmed to 90 °C at 25 °C min^{-1}, and then increased to 250 °C at 15 °C min^{-1}, at which the temperature was kept constant for 1 min. The FID detector temperature was set at 280 °C. A scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China) was used to evaluate the surface morphology of nanocomposite fiber coatings.

2.3. Preparation of ZnO/PPy nanocomposite film-coated SPME fiber

Fabrication of the ZnO/PPy nanocomposite SPME coating on the SS wire involved the following processes: (1) stainless steel wires with the length of 6.0 cm were used to fabricate the SPME fibers. Half (3.0 cm in length) of the stainless steel wire was washed sequentially with acetone, then methanol and finally gently with ultrapure water, and dried in the air. (2) The PPy film was directly electrodeposited on the surface of the SS wire from a 0.1 M electrolyte solution containing 0.1 M pyrrole monomer and 0.1 M oxalic acid by applying a constant potential of 0.8 V. Finally, the prepared PPy coating on SS wire (with 2 cm coating) was washed with deionized (DI) water and dried at 80 °C for 2 h. (3) The prepared PPy coating on SS wire was employed as the template for preparation of ZnO nanorods. 20 mL aqueous solution of equal amount zinc nitrate and urea (0.5 mol L^{-1}) was ultrasonically mixed in a glass bottle. Several PPy coated SS wires were inserted through a foam cap and a length 2.0 cm of SS wires was left at the end into the mixed solution for 60 s. (4) After that, the fiber was