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A polythiophene–silver nanocomposite for headspace needle trap extraction

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ABSTRACT

A nanocomposite consisting of polythiophene–silver was prepared and implemented as a desired sorbent for headspace needle trap extraction. Colloidal silver nanoparticles (Ag NPs) with narrow size distribution and high stability were synthesized in water–in–oil microemulsion. This simple procedure was adapted to prepare highly monodispersed Ag NPs, starting from an initial synthesis in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles. Polythiophene (PT) was synthesized by chemical oxidative polymerization in the presence of anhydrous ferric chloride while its polymeric structure was confirmed by Fourier transform infrared spectrometry (FTIR). Eventually, the prepared PT was dispersed in an AOT/*n*-decane solution containing Ag NPs for 1 h in which the NPs were adsorbed on the polymer surface. The dynamic light scattering (DLS) analysis of NPs solution revealed that the monodisperse Ag NPs have been synthesized successfully with the size distribution below 10 nm. Other instrumentations such as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and atomic absorption spectrometry (AAS) confirmed the fabrication of the PT–Ag nanocomposite. The applicability of the synthesized sorbent was examined by needle trap extraction of some polycyclic aromatic hydrocarbons (PAHs) in aqueous samples in conjunction with gas chromatography–mass spectrometry detection (GC–MS). Important parameters influencing the extraction process were optimized. The linearity for all analytes was in the concentration range of 0.01–10 ng mL^{-1}. The limits of detections were in the range of 0.002–0.01 ng mL^{-1}, using time–scheduled selected ion monitoring (SIM) mode while the RSD% values ($n = 3$) were all below 12%. The developed method was successfully applied to real water samples obtained from different rivers and Persian Gulf, while the relative recovery percentages were in the range of 85–103%.

1. Introduction

Nanoparticles (NPs), due to their unique properties, have become highly applicable in analytical chemistry [1,2]. The incorporation of NPs could progressively simplify the sample treatment step [3]. Metallic and metal–oxides NPs are, nowadays, the desired extraction probes for target analytes from environmental and biological samples [4,5]. Among the enormous variety of metal NPs (MNPs), silver (Ag) and gold (Au) NPs have attracted increasing interest and have been used as sorbent materials. This is due to their large specific surface area, high adsorption capacity, the ease of synthetic procedures, biocompatibility and low temperature modification [6,7].

During the last few years, many methods have been developed to prepare Ag NPs, while the microemulsion approach is mostly preferred. This method controls some particle properties including size, geometry, morphology and homogeneity [8,9]. The Ag NPs are prepared in the aprotic solvent containing the sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as the surfactant. Then the synthesized NPs could be extracted from micelles by adding a substrate that contains a thiol group or organic sulfide [10]. The strong affinity of Ag NPs to heteroatoms has been vastly investigated and shown that the adhesion of Ag NPs to S–terminated substrates is at least four times greater than the electrostatic interactions with N–terminated substrates [11]. A substrate with sulfur heteroatom is therefore desired [12]. The stabilization of the synthesized Ag NPs can be achieved by their immobilization on a solid substrate such as the polymeric surface [13]. On this regard, the synthesized nanocomposites have been extensively used in different sorbent–based microextraction techniques [14]. Conductive polymers (CPs) have been increasingly used as the substrate

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for the fixation of NPs. CPs are multifunctional materials with various properties such as their stability, simplicity of synthesis from an inexpensive monomer, and unique electrochemical properties [15,16]. Among the conducting polymers–based composites, polythiophene (PT)–metal or metal oxide nanocomposites are attracting growing interest because of their advanced properties [17–19]. As it is expected, the sulfide groups in the PT structure could strongly interact with Ag NPs. So, the dispersion of PT in an organic solution containing the Ag NPs could be a simple, fast and applicable method for the preparation of PT–Ag nanocomposite. The self-assembly of Ag NPs on a substrate can be used for constructing a "two–dimensional" nanocomposite. The nano metric domain of these composites increases the superficial area of the material, boosting the extraction efficiency and improving the extraction kinetics. The polymeric domain mostly enhances the hydrophobic and π-π interactions with the target analytes. This justifies that the PT–Ag nanocomposite would be expected to be an appropriate sorbent for isolation of polycyclic aromatic hydrocarbons (PAHs). PAHs are well known for being highly carcinogenic to humans and persistent in the environment. PAHs are lipophilic compounds with very low water solubility and therefore, their concentration in water is very low [20,21]. Consequently, monitoring trace level concentration of PAHs in surface water is quite important in environmental studies as well as tap water quality control. Annual average environmental quality standards (AA-EQS) values for individual PAHs range from 0.002 to 2.4 μg L^{-1} [22]. Capillary gas chromatography-mass spectrometric detection (GC–MS) [23], high performance liquid chromatography (HPLC)–MS [24] and HPLC–UV–DAD or fluorometric detection [25,26] are the most widely used methods in PAHs analysis. According to very low concentrations of PAHs in water, the pre-concentration process is crucial. The ideal sample preparation should be simple, automatic, miniaturized, rapid, safe to operators, environmental friendly and economic. In this regard, microextraction techniques, specially, needle–based extraction methods have been developed. Needle trap extraction devices have recently become popular as they have advantages of SPME and SPE. Additionally, in this approach, the quantity of extracting phase is much greater than SPME and other benefits such as robustness, easier handling during sampling and desorption, the susceptibility of automation and on–line coupling to GC instruments are associated with this methodology [27,28].

The aim of this study was to synthesize a PT–Ag nanocomposite and introduce it as a needle trap device (NTD) sorbent. The extraction capability of this sorbent was extended to the determination of PAHs, as model analytes. Also, the different parameters affecting the sorption capacity of the NT as well as desorption and transferring of the target compounds into the GC system were investigated.

2. Experimental

2.1. Reagents and standards

Thiophene was purchased from Merck (Darmstadt, Germany) and was purified by distillation under reduced pressure. Silver nitrate, *n*-decane, thionyl chloride, chloroform, acetone and methanol were supplied from Merck. Hydrazine hydrate and AOT were prepared from Aldrich (Mississauga, Canada). The standard mixture of PAHs (2000 μg mL^{-1} in benzene: dichloromethane, 50:50) containing naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene was purchased from Supleco (Bellefonte, PA, USA). The stock solutions of the above components at the concentration of 10 μg mL^{-1} were prepared weekly by diluting the purchased mixture with methanol and working solutions for optimization of the method were prepared daily at the concentration of 10 ng mL^{-1} by diluting the stock solution with ultra-pure water. All of the above solutions were prepared in silanized glass vials and stored at −4 °C.

The oxidant, ferric chloride ($FeCl_3{\cdot}6H_2O$) (Aldrich) was used to produce anhydrous salt. To prepare the anhydrous $FeCl_3$, the hydrated salt was treated with thionyl chloride [29].

2.2. Methodologies

To evaluate the PT–Ag nanocomposite some characterization surveys were considered. Initially, FTIR was utilized to certify the PT structure. The particle size and size distribution of Ag NPs was determined by DLS analysis. After preparing the nanocomposite, the content of Ag loading on PT surface was quantified by atomic absorption spectrometry. The thermal stability of nanocomposite was examined by thermogravimetry analysis (TGA), while its morphology was studied by SEM. The FTIR spectrum was recorded by an ABB Bomem MB100 (Quebec, Canada). A Varian (Australia) model AA-220 atomic absorption spectrometer was used to quantify the Ag content. The SEM images were obtained by a XL30 (Philips, Netherland). Thermal stability of synthesized nanocomposite was measured using a Metler, Star SW 10.00 TGA. A peristaltic pump (Ismatec, Switzerland) was used for aspirating the headspace into the needle. The temperature of extraction media was controlled with circulating water bath (RTE-8 NESLAB, USA).

Aqueous standards of PAHs were prepared by spiking an appropriate amount of the working standard to a final concentration of 10 ng mL^{-1} for all analytes. The general microextraction procedure was performed as follows: A 10 mL sample or standard solution was transferred into a 25-mL headspace glass vial and immediately sealed with a Teflon septum. All the solutions were prepared in silanized glass vials. Then it was placed in a water bath at 80 °C and the headspace was allowed to equilibrate with the sample for 5 min. The NTD was eventually inserted through the vial septum and placed in the headspace of the sample. A 23 G needle was also inserted into the sample solution to purge the circulating headspace into the sample. The NTD and the purging needle were connected to a peristaltic pump to aspirate the headspace sample through the NTD. The peristaltic pump speed was adjusted at a flow rate of 3 mL min^{-1}. After performing the extraction for 30 min, the device was immediately inserted into the GC injector port for thermal desorption of the trapped analytes. Desorption was conducted at 280 °C for 5 min. The NTD was conditioned in the injection port prior to each extraction. To evaluate the presence of Ag NPs on the sorbent efficiency, distinct needles with PT and PT–Ag (1–5% of Ag NPs) were packed. These needles were applied to the extraction of some selected PAHs including naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenan- threne, anthracene, fluoranthene and Pyrene from aqueous samples. Several parameters, associating with the improvement of the NTD extraction efficiency and reduction of the carry over, were considered to be optimized. The initial experimental condition consisted of an extraction time of 20 min at 60 °C with no added NaCl, sample flow rate of 4 mL min^{-1} with the desorption time of 5 min at 280 °C.

A Hewlett-Packard gas chromatograph model HP 6890 series (HP, Palo Alto, USA) equipped with a split–splitless injector in conjunction with a HP 5973 mass–selective detector system was used. The MS was operated in the EI mode (70 eV). The separation of analytes was carried out using a capillary column TRB-5MS (Teknokroma, Barcelona, Spain) with 0.25 μm film thickness (30 m, 0.25 mm i.d.). The carrier gas was helium (99.999%) at a flow rate of 1 mL min^{-1}. The gas chromatograph was operated in the splitless mode and the split valve was kept closed for 5 min. The GC column temperature was programmed at 40 °C for 4 min, increased