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Original Research Article

Fabrication of polypyrrole-silver nanocomposite for hollow fiber solid phase microextraction followed by HPLC/UV analysis for determination of parabens in water and beverages samples

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ABSTRACT

In the present study, a nanocomposite of polypyrrole-silver nanoparticles was made as a new sorbent of hollow fiber solid-phase microextraction method and it was utilized for the preconcentration and determination of trace amounts of parabens in water, fruit juice, and beer samples. Polypyrrole was synthesized by chemical oxidative polymerization on the wall surface of a hollow fiber. Then a green method was employed for the synthesis of silver nanoparticles on the polypyrrole. This coating showed impressive mechanical and chemical stability. Hollow fiber as solid phase microextraction fiber is conformable with complex matrices and exhibits high clean up and selectivity without memory effect due to its porosity. A number of significant factors were optimized. The limit of detection, under the optimal conditions, for all of the parabens was in 0.01 μg L^{-1}. The method exhibited good linearity in the range of 0.05–200 μg L^{-1}, with limit of quantification of 0.05 μg L^{-1}, coefficients of determination better than 0.9990 and extraction recoveries of 25.0–28.0%. The intra- and inter-assay precisions (RSD%, n = 3) were in the range of 2.4–3.1 % and 3.4–4.2%, respectively. The relative recovery values for the spiked samples were in the acceptable range of 90.4–104.0%.

1. Introduction

Parabens (family of alkyl esters of *p*-hydroxybenzoic acid) are widely utilized as preservatives in cosmetics, toiletries, pharmaceutical and personal care products (PCP) (e.g. solar lotions, hair gels, shampoos, creams and toothpastes), beverages, and foodstuffs. It is because of their broad-spectrum antimicrobial properties, efficacy, non-volatility, low cost, good stability, lack of distinguishable odor, taste, discoloration or hardening effect, and effectiveness over a broad pH range (Asiabi et al., 2015; Brausch and Rand, 2011; Darbre and Harvey, 2008) that they are popular. Methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), etc. are among the highly used parabens. The antimicrobial activity of parabens rises with the length of the alkyl side chain from methyl to butyl, yet their solubility in water declines simultaneously. A mixture of parabens is often used instead of a single exploit of paraben to reach high antimicrobial activity. The use of parabens in costumer products has recently given rise to concerns about their possible side-effects on human health (Alshana et al., 2015; Chen et al., 2018). Additionally, as a result of using them in personal care products, parabens are incessantly released into the environment through urban wastewater. To the aim of monitoring them, therefore, the development of simple, fast and precise analytical methods for the determination of parabens is highly needed. For the extraction of these compounds, a variety of methods have been used so far, including solid-phase microextraction (SPME) (Casado-Carmona et al., 2016; Souza et al., 2016), hollow-fiber based- liquid phase-microextraction (HFLPME) (Díaz-Álvarez et al., 2013; Esrafili et al., 2014), and dispersive liquid liquid phase-microextraction (DLLME) (Farajzadeh et al., 2010; Jain et al., 2013).

SPME has introduced as a powerful extraction technique because of its simplicity, economical utility, great efficiency, and solvent-free property (Amanzadeh et al., 2015). In SPME, a suitable coating is used to extract the analytes. A great number of efforts have thus been made for sorbent development (Aziz-Zanjani and Mehdinia, 2014). Generally, conventional SPME coatings have problems such as fragility, low thermal and chemical stability, memory effect, limited coating lifetime, being damaged at extreme pH levels, incompatibility with complicated matrices and low selectivity for the target analytes. As a result, to the aim of dealing with these problems, hollow fiber solid-phase microextraction (HF-SPME) was introduced by Es'haghi et al. (Es'haghi et al., 2010) as an alternative miniaturized sample preparation. This approach has many advantages: it is economical, simple and highly porous.

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Additionally, it benefits from wide surface area, high extraction recovery, high clean up and selectivity potential. In HF-SPME, the sorbent is placed into the pores of polypropylene hollow fibers, which is able to conform to complex matrices.

Conductive polymer (CP) has recently been utilized successfully as a functional coating (Bagheri et al., 2013; Mehrani et al., 2018). Conductive polymers, with a highly π-conjugated polymeric chain, have attracted a lot of attention because of their high electrical conductivity similar to that of metals, thermal stability, multifunctionality, unique electrochemical properties, economical utility, ease of synthesis, and treatment (Heeger, 2001). Among CPs, polypyrrole (PPY) is one of the most frequently studied conducting polymers due to its facile polymerization, thermal stability, stability in air, and environmental properties. PPY coating has different intermolecular interactions such as π–π, dipole–dipole, hydrophobic, and hydrogen bonding, in addition to exchange among the polymers and the analytes. These various interactions help PPY extract certain kinds of compounds from different matrices. PPY is durable and suitable for the extraction of polar compounds. However, it has a small specific surface area and a small extraction capacity (Zhao et al., 2013). To ameliorate the performance and increase the surface area of PPY, some functional materials and composite coatings, such as nanoparticles, are made ready (Feng et al., 2011; Schirmer et al., 2016).

Nanoparticles (NPs) have recently attracted attentions around the world for their intrinsic size-dependent physical, chemical, and biological properties compared to their macro scaled counterparts (de Dios and Díaz-García, 2010). Metallic NPs are suitable for the extraction of target analytes from environmental and biological samples. Among the various metal NPs, silver NPs are more popular as sorbents because of their high reactivity, large surface to volume ratio, high adsorption capacity and the ease of the synthetic procedure (Kaur and Gupta, 2009; Liang et al., 2005).

A great number of methods, including chemical reduction and thermal decomposition (Shin et al., 2004; Sun and Xia, 2002; Yang et al., 2007), have been implemented for the synthesis of Ag nanoparticles. The size, morphology, stability and properties of the Ag nanoparticles are highly affected by experimental conditions, the kinetics of interaction of metal ions with reducing agents and the adsorption processes of stabilizing agents with metal nanoparticles (Yin et al., 2002). Therefore, the synthesis method is a significant step to control the morphology of Ag NPs. Among the several methods of synthesis, chemical reduction is the most frequently applied method for the preparation of silver nanoparticles (Tao et al., 2006).

The present study applies modified Tollens process as a green synthesis approach for the preparation of silver nanoparticles. This is based on the reduction of silver complexes with ammonia by glucose (Sharma et al., 2009). The Tollens synthesis method generates Ag NPs with a controlled size in a one-step process by controlling ammonia concentration. The mean particle size declines by decreasing NH_3 concentration (Kvítek et al., 2005).

The synthesis of PPY-Ag NPs nanocomposite with high chemical and mechanical stability inside the pores of polypropylene hollow fiber as a novel sorbent was the main purpose of this study. To the best of our knowledge, there is no report about the green synthesis of a nanostructured PPY-Ag NPs composite coating as the extracting phase in HF-SPME. The effect of different parameters on the extraction efficiency of the analytes were investigated and optimized.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade. Standards of methyl paraben (MP), ethyl paraben (EP), and propyl paraben (PP) were obtained from Sigma–Aldrich (St. Louis, MO, USA). The stock solutions of the parabens (1000 mg L^{-1}) were prepared by dissolving 10 mg of the compounds in 10 mL of methanol. A mixed standard solution of parabens was prepared by adding an appropriate amount of each stock standard solution to a 25 mL volumetric flask and diluting it to the mark by methanol. All standard solutions were stored at 4 °C and protected from light. HPLC-grade methanol and acetonitrile were purchased from Caledon (Georgetown, Ontario, Canada). Pyrrole and silver nitrate were obtained from Aldrich (Milwaukee, WI, USA). The oxidant, ferric chloride ($FeCl_3{\cdot}6H_2O$) (Aldrich) was used to produce anhydrous salt. Ultra-pure water was produced on a Youngling ultrapure water purification system model Aqua Max TM-ultra (Seoul, South Korea). Other chemicals applied were of the analytical reagent grade or of the highest purity available. Plastic and glassware used for the experiments were previously washed with acetone and rinsed carefully with ultra-pure water. The Accurel Q3/2 polypropylene hollow fiber membrane (600 μm i.d., 200-μm wall thickness, and 0.2 μm pore size) was supplied by Membrana (Wuppertal, Germany).

2.2. Apparatus

Chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Chem inert HPLC valve from Valco (Houston, TX, USA) with a 20 μL sample loop and equipped with a Varian 9050 UV–Vis detector. Chromatographic data were recorded and analyzed using Chromana software (version 3.6.4). The separations were carried out on an ODS-3 column (250 mm × 4.0 mm, with a 5 μm particle size) from MZ-Analysentechnik (Mainz, Germany). A mixture of ultra-pure water and acetonitrile (55:45) at a flow rate of 1.0 mL min^{-1} was applied as the mobile phase and the analytes were detected at 254 nm. The particle size and morphology of the synthesized NPs were determined by a scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China).

FT-IR spectra (4000–400 cm^{-1}) were recorded on a Thermo Scientific Nicolet IR100 (Madison, WI, USA) Fourier-transform infrared (FT-IR) spectrometer using the KBr disk method with a sample/KBr ratio of 1:100 by mass.

2.3. SPME hollow fiber preparation

The polypropylene hollow fibers (3 cm) were cleaned with acetone to remove impurities and were dried in air. The fibers were placed into the solution consisting of 2 mL pyrrole. Then the anhydrous $FeCl_3$ (0.055 mol in 18 mL water) was added drop-wise and polymerization was carried out for 1 h at room temperature under stirring. The PPY on fiber was dried in an oven at 80 °C for 20 min. Afterward, Ag NPs were prepared by the modified Tollens method using water as an environmental friendly solvent and glucose as a green reducing agent on the surface of PPY film (Kvítek et al., 2005). According to this procedure, $[Ag(NH_3)_2]^+$ complex cation is formed in the presence of a sufficient ammonia concentration and, then, Ag^+ ions are reduced to Ag° by glucose. The fibers were placed into the Ag NPs solution for 1 h until silver NPs were adsorbed on PPY surface. Fig. 1 shows schematic preparation of PPY-Ag NPs composite inside the pores of hollow fiber. Scanning electron microscopy was applied to investigate the surface characteristics of Ag NPs.

2.4. Extraction procedure

The prepared PPY-Ag NPs hollow fiber was placed in 30.0 mL of the aqueous solution containing an appropriate concentration of parabens (the pH was adjusted to 9.0 using 1 mol L^{-1} NaOH solution) and the solution was stirred by a magnetic stirring bar at 500 rpm for 35 min. After the completion of the extraction, the fiber was removed from the vial and placed into a 1.5 mL glass vial containing an organic solvent (acetonitrile) for the desorption of the target analytes from the fiber by sonication for 5 min. Then, the volume of the desorption solvent was