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Electrochemically controlled in-tube solid phase microextraction

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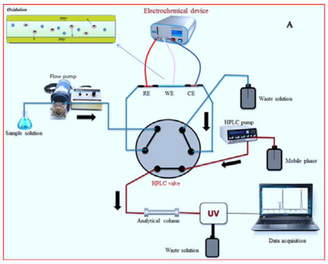
HIGHLIGHTS

- Pyrrole was elctropolymerized on the inner surface of a stainless steel tube.
- We report new in-tube SPME approach named electrochemically controlled in-tube SPME.
- After the completion of EC in-tube SPME–HPLC setup, the PPy-coated tube was used as working electrode.
- This approach, which combined electrochemistry and in-tube SPME, decreased the total analysis time and increased the sensitivity.
- Extraction ability of the tube in presence and in absence of applied electrical potential was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a new in-tube solid phase microextraction approach named electrochemically controlled in-tube solid phase microextraction (EC in-tube SPME). This approach, which combined electrochemistry and in-tube SPME, led to decrease in total analysis time and increase in sensitivity. At first, pyrrole was elctropolymerized on the inner surface of a stainless steel tube. Then, the polypyrrole (PPy)-coated in-tube SPME was coupled on-line to liquid chromatography (HPLC) to achieve automated in-tube SPME–HPLC analysis. After the completion of EC-in-tube SPME–HPLC setup, the PPy-coated tube was used as working electrode for uptake of diclofenac as target analyte. Extraction ability of the tube in presence and in absence of applied electrical field was investigated. It was found that, under the same extraction conditions, the extraction efficiency could be greatly enhanced by using the constant potential. Important factors are also optimized. The detection limit (S/N = 3) and precision were 0.1 $\mu g\,L^{-1}$ and 4.4%, respectively.

1. Introduction

Solid phase microextraction can overcome the problems of traditional methods by eliminating the use of organic solvents and by integrating sample extraction, concentration, and introduction into a single step [1]. This method is more rapid and less expensive than the traditional methods, and it can be easily automated [2,3]. In-tube SPME is a version of SPME which can be easily coupled on-line with HPLC for the analysis of less volatile and thermally labile compounds [4]. The capillaries with different lengths and diameters have been used [5–8]. In-tube SPME setups can be categorized as flow through extraction setups and as draw/eject extraction setups. These in-tube SPME methods using flow through and draw/eject extraction setups have been applied to the analysis

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of various samples [9–12]. However, one of the main difficulties limiting the wide application of in-tube SPME is the absence of a suitable stationary phase. Perhaps the best solution is to develop polar and ion-exchange coatings for direct extraction of the target species from sample matrices. Among different types of sorbents used for the extraction of analytes, conducting polymers, particularly PPy and its derivatives, have attracted a great attention due to their multifunctional properties (e.g., hydrophobicity, acid–base character, π–π interaction, polar functional groups, ion-exchange property, hydrogen bonding, and electroactivity) [13]. Pyrrole can be polymerized with oxidation reactions by either an electrochemical or a chemical method [14–16]. In several works, chemical polymerization of polypyrrole on the inner surface of capillary has been reported [1,2,17–20]. Limitations encountered with this method include: (1) due to less interactions between PPy and capillary, adhesion of PPy to capillary is not strong and this affect the mechanical stability of polymer, (2) the electrical conductivity of PPy produced by chemical method is often low and although development of electrical conductive PPy by chemical polymerization are reported [5], but these PPy were not used in SPME (or in-tube SPME), (3) the number of dopants in chemical polymerization method are very limited, (4) physical properties of the synthesized polymer cannot easily be controlled. Electrochemical synthesis is more convenient, because the polymer is directly electrodeposited on the surface of metals from an aqueous solution containing pyrrole and electrolyte. It has been shown that improved mechanical and thermal properties can be achieved for PPy coatings incorporated with sulfonated aromatic counter ions [21]. Also PPy layers doped with dopant anions like dodecylsulfate and dodecylbenzenesulfonate gave layers with short range order, whereas small BF_4^- or ClO_4^- anions produced amorphous porous layers, with rough surface morphology [22].

The electrochemistry has been used in extraction, separation, and detection. In separation, Hasan et al. have reported electrochemically modulated liquid chromatography (EMLC) which is a unique union of electrochemistry and chromatography [23]. EMLC has been applied to a wide range of separations [24]. Furthermore, the electrochemistry has been widely used in extraction. Electrochemically controlled solid-phase microextraction (EC-SPME), which was first suggested by Pan et al. [25], combines SPME with electrochemistry. EC-SPME is similar to EMLC in that it can use conducting polymers, whose charge can be electrochemically controlled by oxidation or reduction, as the stationary phase. Therefore, EC-SPME has an advantage over regular SPME, because the neutral charge of commercially available SPME apparatus leads to poor analyte recoveries and low analyte partition coefficients for some analytes [26]. The EC-SPME approach has clear advantages for polar, aromatic and charged analyte species due to its multifunctional properties [27]. The mechanism of operation for conducting polymer-based electroextraction (anion extraction) is based on the electrochemical redox transitions of the conducting polymer. This redox switching of a polymer between conducting and nonconducting states causes the movement of dopant ions in and out of the film to balance the polymer charge. Anion extraction and desorption has occurred. EC-SPME has been successfully used in the extraction of anionic [28–31], cationic [32], neutral [33], and both cationic and anionic [34] analytes. For instance, Liljegren and Nyholm used PPy coated microarray electrodes for electrochemically controlled solid-phase microextraction and preconcentration on individually addressable gold microband electrodes. The performance of the polymer, which was prepared by electrochemical polymerization, was investigated using chloride as a model analyte employing different extraction times and analyte concentrations [31].

In previous report, we electrosynthesized molecularly imprinted PPy film on the surface of stainless steel wire as a selective sorbent for benzoate anion [28]. In current work, PPy film is elctropolymerized on the inner surface of stainless steel tube. Then, the PPy-coated tube is coupled on-line to HPLC to achieve automated in-tube SPME and HPLC analysis. After the completion of EC-in-tube SPME-HPLC setup, the PPy-coated tube acted as working electrode for uptake of diclofenac as target analyte. Extraction ability of the PPy-coated tube with and without applied electrical field was investigated. Important factors in the in-tube SPME efficiency are also discussed. The purpose of this work was to develop a simple and sensitive in-tube SPME technique using the PPy-coated tube and electric field. To the best of our knowledge, this is the first report of using constant electric potential in in-tube SPME-HPLC.

2. Experimental

2.1. Chemicals and materials

Sodium diclofenac and other materials were purchased from Merck (Darmstadt, Germany). All solvents were HPLC grade and were purchased from Sigma–Aldrich (Steinheium, Germany). Milli-Q water (Millipore, Billerica, MA, USA) was used to prepare the samples. Proper amount of sodium diclofenac was dissolved in methanol to obtain stock solution of the analyte with a concentration of 1 mg mL^{-1}. Working standard solutions were freshly prepared by diluting the standard solution of the analyte with ultra-pure water to the required concentration. Pyrrole was obtained from Merck (Darmstadt, Germany), distilled and kept under nitrogen in darkness at 4 °C before use. pH was adjusted with 0.1 M sodium hydroxide and hydrochloric acid solutions.

2.2. Electrosynthesis of PPy on the inner surface of tube

Before synthesis, the stainless steel tube (10 cm × 0.80 mm i.d.) was cleaned with a mixture of acetone and pure water (70:30, v/v). This solution was percolated through the tube for 10 min, and then the tube thoroughly rinsed with water, acetone and water, respectively. Solutions of 0.1 mol L^{-1} pyrrole and 0.2 mol L^{-1} $LiClO_4$ were filled into container, purged with N_2 gas for 2 min, and then used as mother solution for electrosynthesis of PPy in tube. A very thin copper wire (15 cm × 0.07 mm diameter) was placed into the tube. The tube and the wire serve as working and counter electrodes, respectively (Fig. 1). Insulating material was used to prevent electrical connection between these electrodes. By passing the solution through the tube and applying a constant current of 3 mA, electrochemical polymerization of pyrrole was carried out. In order to have a PPy-coated tube with good mechanical stability,

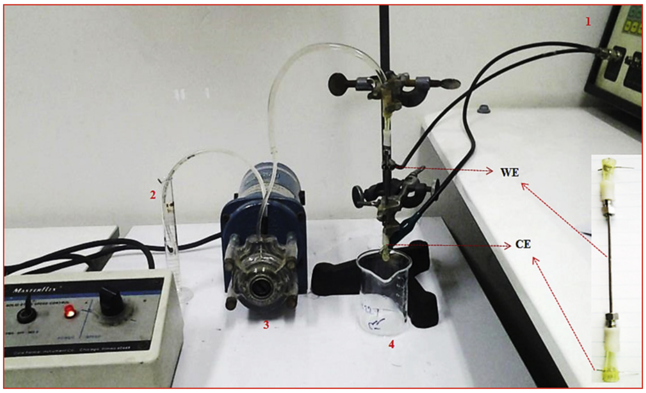

Fig. 1. Illustration of setup for electropolymerization of PPy into the tube: (1) power supply (electrochemical device), (2) polymerization solution, (3) flow pump, (4) waste solution. WE and CE are working and counter electrodes, respectively.