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Preparation and evaluation of a novel molecularly imprinted polymer coating for selective extraction of indomethacin from biological samples by electrochemically controlled in-tube solid phase microextraction

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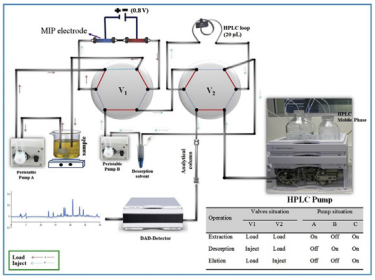
HIGHLIGHTS

- Molecularly imprinted polymer coated in-tube solid-phase microextraction was prepared.
- Electrochemically controlled in-tube solid-phase microextraction-HPLC was developed.
- Method was applied for selective extraction of indomethacin from biological samples.
- The effective parameters on the extraction efficiency of indomethacin were optimized.
- The method showed good linearity for indomethacin in the range of 0.1–200 μg L^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, an automated on-line electrochemically controlled in-tube solid-phase microextraction (EC-in-tube SPME) coupled with HPLC-UV was developed for the selective extraction and preconcentration of indomethacin as a model analyte in biological samples. Applying an electrical potential can improve the extraction efficiency and provide more convenient manipulation of different properties of the extraction system including selectivity, clean-up, rate, and efficiency. For more enhancement of the selectivity and applicability of this method, a novel molecularly imprinted polymer coated tube was prepared and applied for extraction of indomethacin. For this purpose, nanostructured copolymer coating consisting of polypyrrole doped with ethylene glycol dimethacrylate was prepared on the inner surface of a stainless-steel tube by electrochemical synthesis. The characteristics and application of the tubes were investigated. Electron microscopy provided a cross linked porous surface and the average thickness of the MIP coating was 45 μm. Compared with the non-imprinted polymer coated tubes, the special selectivity for indomethacin was discovered with the molecularly imprinted coated tube. Moreover, stable and reproducible responses were obtained without being considerably influenced by interferences commonly existing in biological samples. Under the optimal conditions, the limits of detection were in the range of 0.07–2.0 μg L^{-1} in different matrices. This method showed good linearity for indomethacin in the range of 0.1–200 μg L^{-1}, with coefficients of determination better than 0.996. The inter- and intra-assay precisions (RSD%, n = 3) were respectively in the range of 3.5–8.4% and 2.3

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–7.6% at three concentration levels of 7, 70 and 150 μg L^{-1}. The results showed that the proposed method can be successfully applied for selective analysis of indomethacin in biological samples.

1. Introduction

Determination of chemical compounds in various matrices, including environmental, food, and biological matrices is a serious problem in modern analytical chemistry. Since solid phase microextraction (SPME) was introduced by Arthur and Pawliszyn [1] in the early 1990s, it has been widely accepted and applied as a sample preparation technique. Compared with the conventional extraction techniques such as liquid–liquid extraction (LLE) and solid phase extraction (SPE), SPME integrates sampling, extraction, concentration, and injection into one single step, so it is inexpensive, simple, sensitive, time-efficient, and solvent-free [2,3].

Successful on-line combination of SPME to HPLC was accomplished using in-tube SPME that utilized an inner surface of a coated capillary [4–7]. In this method, the extraction principle of SPME is based on the partitioning of target compounds between stationary-phase or coating of the extraction tube and sample solutions. The extraction performance of in-tube SPME largely depends on the coating. Therefore, after this report, many commercial (such as a piece of GC capillary columns) and synthesized coated tubes were employed for in-tube SPME-HPLC [8–10]. However, these capillaries are limited to some applications due to their low applicability for polar and ionic species, poor stability, and easy swelling in organic solvents that may lead to capillary breakage and loss of coatings, all of which greatly affect the extraction performance and lifetime [11]. This has directed the scientists to synthesis of new coatings based on electrochemically coated stainless steel capillary (as an unbreakable capillary) [12]. However, in-tube SPME method showed poor selectivity and low extraction efficiency to ionic compounds. Recently, to overcome this difficulty, a new method based on combination of electrochemically controlled solid phase microextraction (EC-SPME) and in-tube SPME was developed for extraction of ionic components, namely electrochemically controlled in-tube SPME (EC-in-tube SPME) [13].

According to the literature, the substantial increasing trend in application of the electrical field in solid based extraction techniques can be attributed to several reasons [14]. Modification of the conducting polymer properties by varying the conditions during the electropolymerization step can provide extraction of analytes with different sizes and charges. Moreover, electrically assisted solid based extraction techniques offer higher number of exchange sites in comparison with the conventional ones, which contain fixed number of exchange sites. This is because the properties of the material and thus the number of exchange sites can be externally controlled by electrochemically controlling the charge of the material [15,16]. Also, the use of polymer based fiber films in solid based extraction techniques can be extended to analysis of neutral electro-inactive analytes by taking the advantage of electrochemically controlled hydrophobic/hydrophilic 'switching' [17]. On the other hand, electrically assisted solid based extraction techniques can be used to extract ions and analytes that normally need to be derivatized prior to traditional solid based extractions [18,19]. In addition, there is no need for changes of the solvent to desorb the analytes in electrically assisted solid based extraction techniques because the extraction and desorption steps are performed merely by altering the potential of the conducting polymer coated electrode [20]. Finally, in comparison with the desorption techniques normally used in traditional solid based extractions, alteration of electrochemical potential of the polymer may lead to faster desorption of electrostatically held analytes [21]. In this method, similar to in-tube SPME, selection of a suitable adsorbent is necessary.

Molecularly-imprinted polymers (MIPs) are synthetic materials with artificially generated recognition sites being able to rebind a target molecule specifically in preference to other closely-related compounds. Formation of the MIPs typically involves copolymerization of a complex formed by the template and a functional monomer via either covalent or non-covalent interaction (hydrogen bond, ionic and/or hydrophobic interaction) with a cross-linking agent (leading to a highly cross-linked, three-dimensional network polymer) in the presence of a suitable porogenic solvent [22,23]. Some preparation methods of molecular imprinting polymers to onsider are chemical grafting, soft lithography technique [24], molecular self-assembled approach [25], and electropolymerization [24].

The electropolymerization method for synthesis of MIP coated fiber provides a simple and rapid technique to control the thickness of the MIP coating. In most cases, the creation of imprinted sites within this material is based on irreversible overoxidation occurring in polypyrrole (PPy) and recognition properties are attributable to introduction of oxygen containing groups such as carbonyl and carboxyl in the pyrrole units during the overoxidation process [26,27]. The selective interaction with imprinted conducting PPy is commonly based on hydrogen bonding between the hydrogen atom in the N–H group of the pyrrole units and some functionalities in the template structure (e.g., C=O group, imine nitrogen atom) [28,29]. However, PPy coatings have a relatively low adsorption capacity. Therefore, PPy-based SPME coatings have been often applied in EC-in-tube SPME to increase their capability for extraction of ionic analytes.

The PPy-based EC-SPME and EC-in-tube SPME techniques operated based on the electroactivity and reversible redox properties of PPy [12,13,30–32]. Moreover, a parameter that plays a significant role in increasing the selectivity of MIPs is the use of cross linkers, which leads to formation of a single hole in the highly cross-linked polymer and shell three-dimensional network polymer. The purpose of this work is to develop a novel MIP-coated SPME tube with good selectivity for the extraction of indomethacin. Therefore, by an electrochemical method, a novel MIP coating consisting of pyrrole as a functional monomer and ethylene glycol dimethacrylate (EGDMA) as a cross linker was coated inside a stainless-steel tube and used as the in-tube SPME for selective extraction of indomethacin as a model analyte in biological samples (urine, plasma, and blood). Then, the extraction capability and selectivity of the MIP-coated tubes were compared with the non-imprinted polymer (NIP) coated tubes. In addition, several factors affecting the performance of the MIP coated in-tube SPME were optimized. To the best of our knowledge, no investigation has been reported on synthesis of molecularly imprinted poly (pyrrole-EGDMA) polymer by electropolymerization in the literature. Finally, by design of suitable setup, the tube prepared was utilized for on-line electrochemically controlled in-tube SPME coupled with HPLC for selective determination of indomethacin in complex matrices.