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Molecularly imprinted polymer-coated hollow fiber membrane for the microextraction of triazines directly from environmental waters

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ABSTRACT

In this work, novel molecularly imprinted polymer-coated hollow fibers (MIP-HFs) have been prepared and evaluated for the development of a micro-solid phase extraction method for the analysis of triazines in aqueous samples using high performance liquid chromatography and UV detection. The proposed extraction method combines liquid-liquid microextraction and molecular imprinting technology. In brief, a thin film of toluene is immobilised in the pores of the obtained MIP-HF. Afterwards, the conditioned MIP-HF is immersed in the water sample. Under stirring for a certain time, the target analytes are liquid-liquid extracted from the sample to the immobilised toluene and then these diffuse to the specific binding sites of the MIP. The effect of various experimental parameters as time and stirring-rate and salting-out effect among others, were studied for the establishment of optimum rebinding conditions. Recoveries for seven triazines tested in 100 mL pure water samples spiked with 15 $\mu g\,L^{-1}$ of each triazine were within 0.8–6.9%, with a relative standard deviation (RSD) < 10% (n = 3). The detection limits (LODs) were within 0.05–0.1 $\mu g\,L^{-1}$, depending upon the triazine. The proposed methodology was successfully applied to extract the triazines from spiked tap and river water samples at $\mu g\,L^{-1}$ concentration level. The mircroextraction procedure with the developed MIP-HFs overcomes the typical low performance and lack of selective recognition of MIPs in aqueous media, allowing the determination of triazines in environmental waters at expected real concentration levels.

1. Introduction

In recent years, great developments in analytical instrumentation have been produced, allowing the determination of any compound in a great variety of samples. Typically, target analytes are determined by chromatographic techniques coupled to common detectors (e.g., UV, fluorescence) or, more recently, mass spectrometry (MS) or tandem MS. However, direct injections of crude sample extracts are not recommended since matrix components can interfere the detection and quantification of target analytes. At this regard, sample preparation is still considered the bottleneck of the whole analytical process and impacts nearly all the later steps in the analytical process [1].

Liquid-phase microextraction (LPME) has emerged as an alternative to the traditional liquid-liquid extraction (LLE) [2–4]. Initially, LPME systems were based on the extraction of analytes from aqueous samples into a small drop of organic solvents suspended from the tip of a microsyringe. In order to improve the stability and reliability of LPME, Pedersen-Bjergaard and Rasmussen introduced hollow-fiber-LPME (HF-LPME) in 1999 [5]. In HF-LPME, a low polarity organic solvent is immobilized as a thin supported liquid membrane (SLM) in the pores of a porous hollow fiber. The lumen of the hollow fiber is filled with a microliter volume of an acceptor solution and the whole assembly is placed in a sample solution for extraction of target analytes. The target analytes are extracted from the aqueous sample through the organic SLM and further into the acceptor solution inside the lumen of the hollow fiber. The small amount of organic solvent required makes HF-LPME an environmental friendly extraction technique. Another advantage is attributable to the sample-to-acceptor volume ratio, leading to a very high enrichment factor, making HF-LPME a very sensitive technique although with limited selectivity [6–12].

Molecularly imprinted polymers (MIPs) are synthetic materials with artificially generated selective recognition sites able to rebind a target molecule. MIPs are obtained by polymerizing functional and cross-linking monomers around a template molecule. Once polymerization has taken place, the template molecule is extracted and binding sites with shape, size and functionalities complemen-

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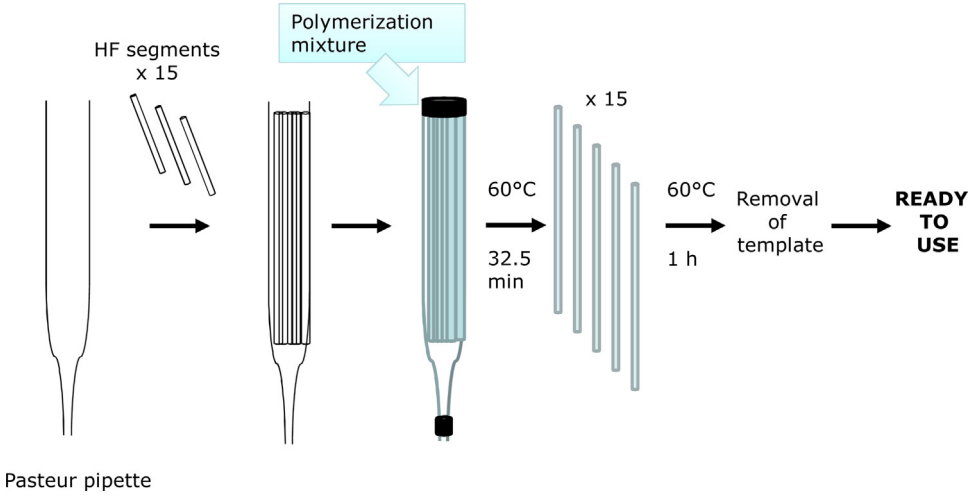

Fig. 1. Scheme of polymerisation procedure for the preparation of MIP-HFs.

tary to the target analyte are established. Such properties made MIPs to be considered ideal materials in Analytical Chemistry [13]. Their use in SPE, so-called molecularly imprinted SPE (MI-SPE), is by far the most advanced technical application of MIPs [14–16]. Besides, recent years have seen a growing interest in the combination of MIPs with other sample-preparation techniques such as solid phase microextraction (SPME) [17–21] and stir bar sorptive extraction (SBSE) [22–24], which highlights the adaptability of MIPs to almost any extraction technique.

Hollow fiber membranes coated with functional polymers for the "so-called" polymer-coated hollow fiber microextraction of organochlorine pesticides (OCPs) was proposed by Lee's group [25–27]. The high porosity of the HFs used allowed the coating of a large amount of polymer leading to a high loading capacity compared to that provided by the typical fibers used in SPME. Besides, in order to improve the extraction selectivity, Liu et al. proposed the coating of a MIP to a hollow fiber for the extraction of diethylstilbestrol and two of its analogues in milk samples [28].

The present paper presents a novel molecularly imprinted polymer-coated hollow fiber (MIP-HFs) prepared according to a new preparation procedure. The applicability of the modified fibers to selectively extract triazines directly from environmental waters has been studied. To circumvent the problem associated with the low selectivity of MIPs in aqueous medium, the combination of molecularly imprinted polymer-coated hollow fiber microextraction (MIP-HFM) and LPME is proposed and the extraction procedure is fully optimised. Triazine herbicides are widely used in agriculture and can migrate into surface, ground and finally into drinking water, which is of public concern due to the negative effects they might have on the environment as well as on human health. In fact, simazine and atrazine, the most widely used triazines, are included in the list of priority substances to be controlled in the field of water policy within the European Union [29], making necessary the development of analytical methods for triazines monitoring.

2. Experimental

2.1. Chemicals and materials

Desethylatrazine (DEA), desisopropylatrazine (DIA), simazine (SIM), cyanazine (CYA), atrazine (ATR), propazine (PPZ), and terbutylazine (TER) were purchased from Sigma-Aldrich (Madrid, Spain). Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and 2,2′-azobis-2-methylbutyronitrile (AIMN) were purchased from Sigma-Aldrich (Madrid, Spain). HPLC grade water, acetonitrile (ACN), and methanol (MeOH) were purchased from Scharlab (Barcelona, Spain). EGDMA and MAA were freed from stabilizers by distillation under reduced pressure, and AIMN was recrystallised from methanol prior to use. All other chemicals were of analytical reagent grade and used as received.

The porous hollow fiber (HF) was a Q3/2 polypropylene hollow fiber (Membrana, Wupertal, Germany) with an internal diameter of 600 μm, a 200 μm of wall thickness and 0.2 μm pores.

2.2. Standard solutions

Stock standard solutions (1 g L^{-1}) were prepared in acetonitrile and stored at −20 °C in the dark. Fresh dilutions from the stock solution were prepared in the appropriate solvents at the required concentration levels.

2.3. Preparation of MIP-HF

A stock polymerisation solution was prepared containing template molecule (PPZ, 1.5 mmol), functional monomer (MAA, 6.0 mmol), cross-linker (EGDMA, 30 mmol), initiator (AIMN, 1.3 mmol), and porogen (toluene, 8.7 mL). Proper amounts of such stock polymerisation solution were taken for the preparation of MIP-HFs. HFs were cut in pieces of 6 cm length and carefully weighted. The ends of these segments were sealed by applying mechanical pressure. As schematically depicted in Fig. 1, a number of 15 segments of HF were located inside a glass Pasteur pipette which was filled with the polymerisation solution (~2 mL) sealing both ends with rubber pieces. The pipette containing the HFs immersed in the polymerisation mixture was placed into a temperature controllable incubator (S160D model) purchased from Stuart (Barloworld Scientific, Staffordshire, UK) with the temperature set to 60 °C. The polymerisation reaction took place during a determined time, after which the so-called MIP-HFs were removed from the reaction mixture, separated each other and placed into an empty 15 mL vial. The vial was closed and introduced in the incubator at 60 ºC for further 60 min. Finally, MIP-HFs were immersed in a methanol:acetic acid (1:1, v/v) solution for 2 h, under vigorous stirring in order to remove the template. Non-imprinted polymeric materials (NIP-HF) were also prepared as described above but without the addition of template.