Journal of Chromatography A, 1469 (2016) 1–7

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Molecularly imprinted polymer monolith containing magnetic nanoparticles for the stir-bar sorptive extraction of triazines from environmental soil samples

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ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form
21 September 2016
Accepted 22 September 2016
Available online 23 September 2016

Keywords:
Molecular imprinting
Monolith
Magnetic nanoparticles
Stir-bar sorptive extraction
Triazines
Soils

ABSTRACT

In this work, novel molecularly imprinted stir-bars based upon the entrapment of modified magnetic nanoparticles within an imprinted polymer monolith is developed for stir-bar sorptive extraction (SBSE). Firstly, magnetic nanoparticles were surface modified with oleic acid followed by encapsulation inside a silica network. Then, vinyl-groups were grafted onto the particles surface for the subsequent copolymerization with the imprinting polymerization mixture using a glass vial insert as a mold. As a result, the obtained imprinted monolith presented magnetic properties allowing its use as magnetic stir-bar. Variables affecting both polymer morphology (i.e., amount of magnetic nanoparticles, polymerization time) and binding-elution conditions of target analytes (i.e., solvents, time) was carefully optimized. Optimum imprinted stir-bars were evaluated for the SBSE of triazines in soil sample extracts. Recoveries, at 16 ng g^{-1} concentration level, ranged from 2.4 to 8.7% with relative standard deviations lower than 15% (n = 3). Although low recoveries were obtained, the high selectivity provided by the new molecularly imprinted stir-bars allowed reaching detection limits below 7.5 ng g^{-1} by liquid chromatography coupled to UV detection.

1. Introduction

Sample preparation is still nowadays considered a critical step in the whole analytical process. In spite of the huge development in analytical instrumentation, especially the development of chromatographic equipment coupled to tandem mass spectrometry, samples must be typically treated in order to remove potential interferents and to preconcentrate target analytes. Besides, sample treatment must provide a robust and reproducible method independent of variations in the sample matrix. New objectives have been set during last decade such as using smaller initial sample sizes, improvement of selectivity in extraction, to facilitate the automation, and to minimize the amount of glassware and organic solvents to be used [1]. Accordingly, traditional liquid-liquid extraction was displaced by solid-phase extraction, and new miniaturized techniques such as solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE), among others, were developed.

SPME represented a breakthrough in traditional sample preparation since its introduction by Arthur and Pawliszyn [2]. In SPME, a silica fiber coated with an appropriated sorbent is used to extract target analytes, later thermally desorbed at the injection port of a gas chromatograph or with a small volume of a suitable solvent. Since then, SPME is considered a robust and well-developed technique and it has been incorporated to analytical laboratories. In order to increase the typical low capacity of fibers used in SPME, SBSE was proposed as an alternative. SBSE is based on the partitioning of target analytes between the sample (mainly aqueous-based liquid samples) and a stationary phase-coated magnetic stir bar [3]. For years, only polydimethylsiloxane (PDMS)-coated magnetic stir bars were commercially available and only recently a PDMS/Ethylene glycol copolymer as coating phase was introduced in the market, thus restricting the range of applications to the extraction of hydrophobic compounds due to the apolar character of PDMS. At this regard, the development of new magnetic stir-bars coated with more polar and selective sorbents has been an active research area during last 15 years [4].

In recent years, molecularly imprinted polymers (MIPs) have proven to be useful materials in several areas of analytical chemistry [5–12]. MIPs are cross-linked synthetic polymers obtained by copolymerizing a monomer with a cross-linker in the presence of a template molecule. After polymerization, the template is removed from the porous network by washing, leaving cavities in the

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http://dx.doi.org/10.1016/j.chroma.2016.09.051
0021-9673/

polymeric matrix that are complementary in size, shape, and chemical functionality to the template. Thus, the imprinted polymer is able to rebind selectively the analyte (the template) under certain experimental conditions. The inherent selectivity associated with MIPs has made them optimum sorbents to be used in the enrichment and clean-up of target analytes from complex samples [13]. Accordingly, the combination of molecular imprinting and SBSE would ideally provide a powerful analytical tool with the characteristics of both technologies, simplicity, flexibility, and selectivity.

In this regard, Zhu and colleagues developed magnetic stir-bars coated with a MIP consisting of a film formed from a formic acid solution of nylon-6 polymer, imprinted with monocrotophos to extract successfully and selectively several organophosphorus pesticides from dichloromethane solution for the analysis of environmental soil samples [14]. Besides, the MIP-coated magnetic stir bars showed not only the expected high selectivity, but also rapid equilibrium adsorption thanks to the porous nature of the imprinted polymer obtained combined with a proper thickness of the coated polymer film (~160–180 μm). More recently, the use of MIP-coated magnetic stir bars prepared by chemical bonding of the MIP to the stir-bar through silylation of the substrate surface and then multiple co-polymerization reaction, for the molecularly imprinted stir-bar sorptive extraction (MI-SBSE) of β2-agonists [15], triazole fungicides [16], sulfa drugs[17] and thiabendazole [18] in different samples has been proposed. All these developed methods require the coating of a MIP on the surface of a glass magnetic stir bar. Such procedure involves several tedious steps including cleaning, etching to provide a rough surface, washing steps, NaOH treatment to increase the amount of available silanol groups and finally silanization for allowing linkage of MIP to the surface. Besides, the treated glass magnet stir-bar must be immersed in the polymerization mixture in vertical position which is rather tricky making difficult the obtainment of MIP magnetic stir bars with proper size and shape.

Keeping these comments in mind, a completely different and much more simple and easy approach for the preparation of magnetic imprinted stir-bars is proposed. It is based on the direct synthesis of molecularly imprinted polymeric monoliths containing magnetic nanoparticles (NPs) by bulk polymerization. The system propazine:methacrylic acid:ethylene glycol dimethacrylate/magnetite nanoparticles has been used as a model for the preparation of the magnetic imprinted monoliths. The optimization of variables affecting both polymer morphology (i.e., amount of magnetic nanoparticles, polymerization time) and binding-elution conditions of target analytes (i.e., solvents, time) will be described in detail. Also, the performance of the new magnetic imprinted stir-bars for the MI-SBSE of triazines from soil samples will be assessed.

2. Experimental

2.1. Reagents

Desethylatrazine (DEA), desisopropylatrazine (DIA), simazine (SIM), cyanazine (CYA), atrazine (ATR), propazine (PPZ), and terbutylazine (TER) were purchased from Sigma-Aldrich (Madrid, Spain). Stock standard solutions (1 g L^{-1}) were prepared in acetonitrile and stored at −22 °C. Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 2, 2′-azo-bis-isobutyronitrile (AIBN), tetraethyl orthosilicate (TEOS), 3-methacryloyloxypropyltrimethoxysilane (MPS), iron (II,III) oxide nano-powder (Fe_3O_4, magnetite) with particle size <50 nm, oleic acid (OA) and 2-propanol were purchased from Sigma-Aldrich. HPLC-grade toluene, acetonitrile (ACN), and methanol (MeOH) were purchased from Scharlab (Barcelona, Spain). MAA was freed from stabilizers by distillation under reduced pressure and by passing through a short column packed with neutral alumina from Sigma-Aldrich. AIBN was recrystallized from MeOH prior to use and all other chemicals were used as received. Water was obtained from a Milli-Q purification system from Millipore (Madrid, Spain). Ammonia (25%) and acetic acid (HOAc) were purchased from Panreac (Barcelona, Spain).

2.2. Instruments and materials

HPLC 2 mL glass vials were purchased from Symta (Madrid, Spain) and 0.5 mL glass inserts were provided by Thermo Scientific (Waltham, MA). Soil sample extracts were prepared in an ultrasonic water bath (290 W, 50/60 Hz) purchased from R. Spinar (Barcelona, Spain) and collected with a Visiprep vacuum manifold from Supelco (Madrid, Spain). Glass columns (10 cm × 2 cm i.d.) were obtained from Scharlab (Barcelona, Spain) and suitable polyethylene frits were purchased from Supelco (Bellefonte, USA). External magnetic field was produced by a neodymium super magnet of 50 kg supplied by AimanGZ (Madrid, Spain).

2.3. HPLC analysis

Chromatographic analysis were carried out by an Agilent Technologies 1200 series HPLC instrument equipped with a quaternary high-pressure pump, a vacuum degasser, an autosampler, and a diode-array detector (Wilmintong, DE). Analytes were separated in a KROMASIL 100 C18 3 μm (150 mm × 4.6 mm i.d.) column with an Atlantis T3 3 μm (3.9 mm × 20 mm) guard cartridge. The injection volume was 100 μL, the flow-rate was 1 mL min^{-1} and analytes were monitored at 220 nm. The gradient elution was programmed to change from initial conditions of 20% ACN and 80% water to 54% ACN and 46% water in 21 min. Subsequently, solvents reached initial conditions in 1 min keeping last conditions for 5 min for a total run analysis of 27 min.

2.4. Modification of magnetic nanoparticles

2.4.1. Modification of magnetic nanoparticles with oleic acid

About 200 mg of commercial iron (II, III) oxide nanoparticles (<50 nm) were weighed and dispersed in a flask containing 15 mL of pure water (Flask A). Another flask containing 15 mL of water and 0.09 mL of OA was sonicated for 15 min (Flask B). Then, flask A was introduced in an oven at 80 °C and the solution contained in Flask B was added in three steps of 5 mL each, keeping the final solution in the oven for 10 min. A final rinse of flask B with 5 mL of water was added to Flask A and kept in the oven for 25 min. Finally, treated NPs (Fe_3O_4@OA) were separated from the solution with the help of an external magnetic field and sequentially washed three times with 15 mL of water and three times with the same volume of MeOH.

2.4.2. Synthesis of Fe_3O_4@SiO_2 and Fe_3O_4@OA@SiO_2

About 300 mg of magnetic NPs, or Fe_3O_4@OA NPs, were dissolved in 50 mL of 2-propanol and 4 mL of Milli-Q water by sonication for 15 min. Then, 5 mL ammonium hydroxide and 2 mL TEOS were added sequentially, and the mixture was reacted for 17 h at room temperature under a continuous orbital stirring. Then, with the help of an external magnetic field, the modified particles (Fe_3O_4@SiO_2 or Fe_3O_4@OA@SiO_2) were separated and rinsed sequentially 6 × 15 mL water and 2 × 15 mL MeOH. The final products were dried at room temperature overnight.

2.4.3. Synthesis of vinyl-modified magnetic NPs

An amount of 200 mg of previously obtained magnetic NPs (Fe_3O_4@SiO_2 or Fe_3O_4@OA@SiO_2) were dispersed in 50 mL of MeOH under sonication for 10 min. Then, 3 mL of MPS were added