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Synthesis and characterization of magnetic-molecularly imprinted polymers for the HPLC-UV analysis of ametryn

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ABSTRACT

Magnetic molecularly imprinted polymer (mag-MIP) were developed for the analysis of ametryn (4-*N*-ethyl-6-methylsulfanyl-2-*N*-propan-2-yl-1,3,5-triazine-2,4-diamine), a popular triazine herbicide. Iron oxide (Fe_3O_4) nanoparticles were synthetized, and then modified with tetraethoxysilane (TEOS) and 3-mercaptopropyl-trimethoxysilane (MPS). Then MIPs' polymerimerization occurred in the nanoparticles' surface, using ethylene-glycol-dimethacrylate (EGDMA) as the building monomer, 2,2′-azobis(2-methylpropionitrile) (AIBN) as the radical initiator, and 2-vinylpyridine as the functional monomer. The functional monomer was previously chosen by computational simulation. The mag-MIPs' adsorption behavior well-fitted a Langmuir model (q_m of 8.6 mg g^{-1}, K_L of 5.2 L mg^{-1}) and pseudo first order kinetics (k_1 of 2.5×10^{-4} s^{-1}). The developed analytical methodology, using high-performance liquid chromatography with UV detection (HPLC-UV), showed suitable selectivity and had a limit of detection (LOD) and quantification (LOQ) of 25 and 82 nmol L^{-1}, respectively.

1. Introduction

Ametryn is a herbicide in the relevant group of triazines [1], it is particularly used to control weeds in various crops like sugar cane or corn, among others [2,3]. Its water solubility is about 185 mg L^{-1}, Log K_{ow} of 3, Log K_{oc} of 2.5, and its contamination levels range up to 0.13 and 0.35 μg L^{-1} in surface water and ground water respectively [1,4]. In general, legislation considers levels above 0.5 μg L^{-1} in water intended to human consumption to be unsafe [1]. Even though the use of pesticides has many decades, the development of analytical methods for their determination still remains a hot topic in analytical chemistry [5–7].

Since ametryn is so widely used, it is of huge relevance its swift determination in environmental samples, but of course, also in food samples. Some analytical methods can be found in literature making use of a wide range of techniques like liquid chromatography with mass spectrometric detection (LC-MS) [3,8], gas chromatography with mass spectrometric detection (GC–MS) [9,10], anodic stripping voltammetry [11], surface-enhanced Raman spectroscopy [12], surface plasmon resonance (SPR) [13], ion mobility spectrometry [14] or micellar electrokinetic capillary chromatography [15]. However these methods are usually associated with sample preparation techniques, crucial to remove matrix effects and even to obtain enriched extracts of trace analytes [16]. Some of the sample preparation techniques that have been applied include microwave-assisted solvent extraction [11], solid-phase microextraction (SPME) [9,10,14], liquid-liquid extraction [17] or solid-phase extraction [8].

Molecularly imprinted polymers (MIPs) are an interesting sample preparation tool in environmental research for the separation and analysis of organic contaminants from wastewater due to their minute size, greater surface area and selectivity towards the target molecules [10,13,18–23]. MIPs recently evolved to magnetic MIPs (mag-MIPs), these particles improve the separation and opened a new window for analyzing compounds in complex sample matrices [24]. Among other advantages, these hybrid materials offer enhanced selectivity, durability, and the possibility of reuse [25–29]. Recent reviews detail the wige range of possibilities using these interesting materials [30–32]. In this work, mag-MIPs for ametryn were developed and characterized aiming its application within an analytical methodology.

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2. Materials and methods

2.1. Chemicals and samples

All chemicals were of analytical grade and were used as received without further purification. Ultrapure water (resistivity not lower than 18.2 MΩ cm at 298 K) from a Direct-Q 3UV water purification system (Millipore) was used in all experiments. Ametryn, iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), 2-vinylpyridine, 3-mercaptopropyltrimethoxysilane (MPS), ethyleneglycol-dimethacrylate (EGDMA) and 2,2′-azobis(2-methylpropionitrile) (AIBN), atrazine, ciprofloxacin and folic acid were purchased from Sigma-Aldrich. Ammonium hydroxide, sodium hydroxide and hydrochloric acid were purchased from Synth-Brazil. Tetraethoxysilane (TEOS) was obtained from Acros Organics.

Food samples were purchased in local supermarkets.

2.2. Molecular modeling

Computer simulation was used to calculate the association-free energies interaction, in vacuo, between ametryn and several functional monomers commonly employed for MIP synthesis. The molecular mechanics studies were performed using the softwares HyperChem v. 8.0.5, OpenEye software package and VIDA v. 3.0.0 and the multiple minimum hypersurfaces with MOPAC program. Further details can be found in literature [33].

2.3. Mag-MIPs' synthesis

The synthesis of the Mag-MIPs is schematized in Fig. 1. The nanoparticles were prepared by dissolving $FeCl_3{\cdot}6H_2O$ (4.72 g) and $FeCl_2{\cdot}4H_2O$ (1.72 g) in 80 mL of water with vigorously stirring under nitrogen environment. Ammonium hydroxide (10 mL, 28% in water) was added to the system drop by drop and the reaction was kept at 80 °C for about 30 min. The black precipitate (the nanoparticles of Fe_3O_4) was removed using a magnet, then some unreacted chemicals were washed away using water and dried under vacuum. The particles of Fe_3O_4 were further modified by dispersing 300 mg in 40 mL of ethanol and 4 mL of water by ultra-sonication for 15 min. Then 5 mL of ammonium hydroxide and 2 mL of TEOS were added to the mixture and left to completely react for 12 h at 25 °C. The materials were then separated using a magnet, and were washed with water and dried in vacuum (completing step I of Fig. 1).

These $Fe_3O_4@SiO_2$ particles were subsequently altered with MPS. The 250 mg of the $Fe_3O_4@SiO_2$ were added to 50 mL of toluene (anhydrous) containing 5 mL of MPS and the mixture was left under dry nitrogen atmosphere for 12 h (completing step II of Fig. 1).

Meanwhile, an association of ametryn (0.2 mmol) with the functional monomer 2-vinylpyridine (0.8 mmol) was added into ethanol (30 mL) with agitation in a water bath at 25 °C for about 12 h. 200 mg of the produced $Fe_3O_4@SiO_2$-MPS were added into this system and subject to agitation for about 3 h. Then, 0.05 mmol of AIBN (the radical initiator) and 4.0 mmol of EGDMA (the building monomer, also known as cross-linking mediator) were added and sonicated in a water bath for 5 min. The mixture was purged using nitrogen gas during 5 min and the mixture was left to react at 60 °C in a nitrogen atmosphere for 24 h (completing step III of Fig. 1).

Subsequently the material was washed out by Soxhlet using acetic acid and methanol (1:9, v/v) during 48 h, changing the eluent every 8 h (step α in Fig. 1). The used eluent was analyzed by HPLC-UV and, when no analyte was detected, that meant that a thoroughly wash of the template was achieved. The obtained material was dried at 40 °C under vacuum, by this way completing the mag-MIPs synthesis. The magnetic non-imprinted polymers (mag-NIPs) were fabricated in a similar manner under the same conditions however without any analyte [34,35].

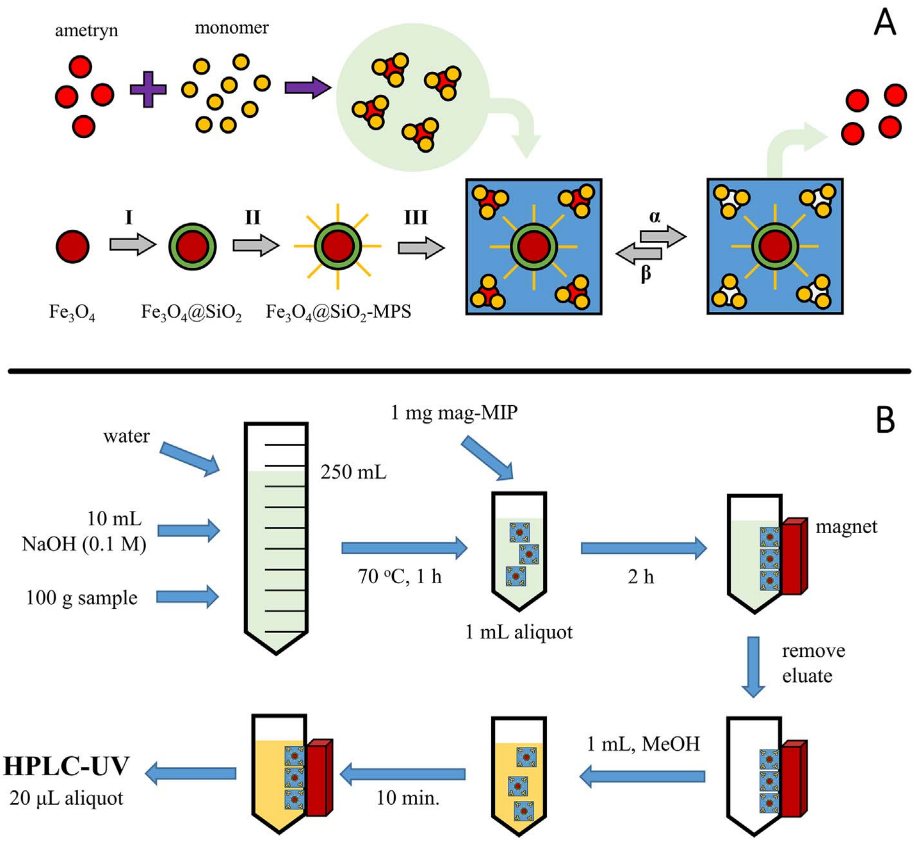

Fig. 1. A) Schematic representation of the mag-MIPs' synthesis. I – Modification of the Fe_3O_4 with TEOS, ca. 12 h in NH_4OH, forming $Fe_3O_4@SiO_2$; II – Modification of the $Fe_3O_4@SiO_2$ with MPS, for about 12 h in toluene, forming $Fe_3O_4@SiO_2$-MPS; III – Reaction between the $Fe_3O_4@SiO_2$-MPS particles and the product of the supramolecular reaction of the analyte (ametryn) and the functional monomer (2-vinylpyridine) in an environment with AIBN and EGDMA, for about 24 h at 60 °C; α – eluting, i.e. losing the analyte creating the imprinted spots; β – rebinding, the oppose process of eluting, filling the imprinted holes with the analyte. B) Schematic representation of the experimental procedure.