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Synthesis and characterization of cross-linked molecularly imprinted polyacrylamide for the extraction/preconcentration of glyphosate and aminomethylphosphonic acid from water samples

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ABSTRACT

The present study describes the synthesis of molecularly imprinted polyacrylamide and its applications for the selective adsorption of glyphosate (GP) and its degradation product, aminomethylphosphonic acid (AMPA). The molecularly imprinted polymers (MIPs) were prepared by polymerization in a homogeneous medium, which is known as the "in bulk" method. The reagents used for the synthesis were acrylamide (AAm) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linking reagent, and azobisisobutyronitrile (AIBN) as the radical initiator. The selectivity of the MIPs was evaluated with non-imprinted polymers (NIPs) for each polymer synthesized without the template molecule. Polymer characterization was carried out by thermogravimetry (TG) analysis, Fourier-transform infrared spectroscopy (FT-IR), elemental analysis, and scanning electron microscopy (SEM). The experimental data on the adsorption kinetics were best explained by a pseudo-second-order kinetic model. The Langmuir–Freundlich nonlinear isotherm model for two adsorption sites had the best fit to the experimental data for glyphosate and AMPA. The maximum adsorption capacities were 3.37 and 4.74 mg g^{-1} for MIP–GP and MIP–AMPA, respectively. According to the relative selectivity (k') values, higher selectivities for the analytes were observed in aqueous medium for the MIPs than for the NIPs.

1. Introduction

Due to the high demand for agricultural products, the use of pesticides is intensifying. The use of glyphosate (N-(phosphonomethyl)glycine (GP) – a nonselective, post-emerging, synthetic organophosphorus molecule – as a herbicide stands out, and its presence is strictly related to human action [1,2]. This herbicide has been widely used in agriculture for controlling annual and perennial weeds, particularly in sugarcane plantations [3,4]. Glyphosate is rapidly degraded in the environment, and the main product of its degradation is aminomethylphosphonic acid (AMPA) [5,6]. Both glyphosate and AMPA exhibit characteristics that makes their determination difficult, such as high solubility in aqueous medium, low solubility in organic solvents, high polarity, low volatility, and the absence of chromophore groups that absorb in the visible region [7,8]. The chemical structure of glyphosate and AMPA are shown in Fig. 1.

Because of these properties of glyphosate and AMPA, derivatization reactions are necessary, and the specific derivatization utilized depends on the whether spectroscopic or chromatographic methods will be applied [9,10]. Prior to the derivatization step, the analytes must be properly extracted. Various methods have been developed to improve recovery [4–11]. Solid-phase extraction (SPE) has been shown to be effective, and in the majority of methods, extraction is performed by employing ion-exchange resins or modified silica (C_{18}) [12,13]. Although these solid phases exhibit high efficiency in retaining the glyphosate and AMPA analytes, they are non-selective materials for which elutions must be performed in acidic media because of their high polarities. Thus, eluate evaporation is very expensive, even when a rotary evaporator is employed, and the time demands for sample preparation can be too great. In this context, the use of molecularly imprinted polymers (MIPs) as the adsorbent material, which are selective for the analytes of interest in SPE, has received attention [14–16]. MIPs

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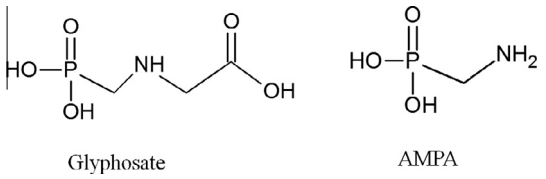

Fig. 1. Chemical structure of glyphosate and AMPA.

can be re-used several times without significant effects on their performance, and their synthesis is simple and inexpensive [17,18]. Despite the attractive properties of MIPs, the use of such polymer materials for SPE of glyphosate and AMPA is restricted, most likely because of their high solubility in water and low solubility in organic solvents. Adequate adoption of a porogenic solvent is key so that the polymer can display selective properties, especially in the aqueous matrix used for analysis. Among the few studies regarding the use of MIPs for glyphosate and AMPA, the development of a chemiluminescence sensor [15] and a method for extracting in tea samples with subsequent determination by chromatography–mass spectrometry (GC–MS) [19] are described.

In this study, the synthesis of a new MIP is introduced for the extraction/preconcentration of glyphosate and AMPA in water samples. Cross-linked polyacrylamide was chosen as an alternative, selective and inexpensive adsorbent material. The quantification of analytes was performed by high-performance liquid chromatography with a fluorescence detector and pre-column derivatization.

2. Experimental

2.1. Material and chemicals

All of the reagents were of analytical purity. All of the solutions were prepared with ultrapure water. The standards for glyphosate and AMPA were obtained from Sigma–Aldrich (Steinheim, Germany). For the synthesis of the imprinted polymer, the following reagents and solvents were used: acrylamide (AAm), ethylene glycol dimethacrylate (EGDMA), azobisisobutyronitrile (AIBN), chloroform, and methanol (HPLC degree), all obtained from Sigma–Aldrich (Steinheim, Germany). Acetonitrile (ACN) (HPLC degree) and dimethyl sulfoxide (DMSO) were provided by Tedia (Brazil). A 0.05 mol L^{-1} tetraborate buffer ($B_4Na_2O_7 10H_2O$) and fluorenylmethyloxycarbonyl chloride (FMOC-Cl) solution in a 1 g L^{-1} acetonitrile was used for the derivatization reaction of glyphosate and AMPA. A 0.03 mol L^{-1} potassium dihydrogen phosphate (KH_2PO_4) solution with a pH of 5.75 was used as the mobile phase. Both reagents were obtained from Sigma–Aldrich (Steinheim, Germany). The mobile phase prepared for the quantification by HPLC-FD was composed as follows: ACN (0.03 mol L^{-1}):KH_2PO_4 (pH 5.75) in water (45:55 v/v). The pH of the buffer solution was adjusted with an aqueous solution of KOH.

2.2. Instrumentation

The chromatography system consisted of a UFLC Prominence instrument equipped with a liquid chromatographer (model LC-20AT, module model CBM-20A) and a fluorescence detector (model RF-20AXS; Shimadzu, Japan). All of the separations were carried out in a C-18 (0.46 mm i.d. × 15 cm in length and a particle diameter of 5 μm, Phenomenex, United States) reversed-phase column with a cell flow rate of 0.5 mL min^{-1} under isocratic conditions at room temperature. The mobile-phase composition was ACN/0.03 mol L^{-1}:KH_2PO_4 (pH 5.75) in water (45:55 v/v). LC solution software was used to acquire and process the chromatography data. The RF-20AXS detector was used for the detection and quantification of both analytes with emission and excitation wavelengths of 260 and 310 nm, respectively. The infrared spectra were obtained with a Fourier-transform infrared spectrometer model FT-IR 8300 (Shimadzu, Kyoto, Japan) operating in the transmission mode between 4000 and 400 cm^{-1}. Polymer morphology was evaluated by scanning electron microscopy (SEM) using the scanning electron microscope (model JEOL – JSM 300-LV, Tokyo, Japan) with an acceleration voltage of 30 kV. Thermal analysis was carried out by a thermogravimetric analyzer (TA Instruments, model TGA 2950, California, USA), with the temperature varying from 30 to 900 °C and with a heating rate of 10 °C min^{-1}. The glyphosate and AMPA extraction using MIPs was carried out with the aid of a Manifolf system (Agilent, USA) with a capacity for 12 cartridges, coupled to a vacuum pump (Marconi, Brazil). Empty SPE Supelco (United States) cartridges were employed, and Supelco polyethylene frits were used to fill in with the polymers.

2.3. Preparation of the MIP–GP and MIP–AMPA

The "in bulk" polymerization procedure was chosen for the preparation of the MIPs. For the synthesis of MIP–GP, 100 mg of the glyphosate template was dissolved in 30.0 mL of a DMSO and chloroform (1:1 v/v) mixture in a 200 mL glass flask. The mixture was kept under agitation in an ultrasonic bath for 20 min to dissolve the template. Then, 2.5 g of AAm was added, and the mixture was manually agitated for 5 min. Next, 10.0 mL of the cross-linking reagent (EGDMA) and 300 mg of the radical initiator (AIBN) were added. The reaction mixture was kept under nitrogen atmosphere for 10 min. The flask was then sealed and preserved in an oil bath for 24 h at a controlled temperature of 60 °C [15]. Once the synthesis was completed, the reaction flask was broken, and the obtained polymers were dried at 50 °C in an oven dryer for 12 h. The polymer was then macerated with a mortar and pestle and sieved through a steel sieve to obtain particles ⩽106 μm. The extraction of the template from the polymer matrix (MIP) was carried out in two steps. The first step was a pre-extraction using the Soxhlet solid–liquid extraction system, in which 1.0 g of MIP–GP and 140 mL of MeOH:HAc (4:1 v/v) were refluxed for 24 h. The second step was the complete removal of glyphosate from the MIP. For this purpose, the polymer was placed in an empty SPE cartridge, intercalated with frits in the upper and bottom parts. Next, with the aid of the Manifold system, 15 elutions (10 mL each) of MeOH:HAc (4:1 v/v) were washed through the cartridge until the template was completely removed, as indicated by HPLC with a fluorescence detector.

For the synthesis of MIP–AMPA, 100 mg of the AMPA template was initially dissolved in 10 mL of ultrapure water using an ultrasonic bath for 30 min, and then, 20 mL of acetonitrile was added. Next, 3.5 g of monomer and 15.0 mL of EGDMA were added. The times used for the synthesis and washing process were equal to those used for the MIP–GP synthesis.

For comparison purposes, non-imprinted polymer (NIP) was prepared the same way as both MIPs but without the addition of template, glyphosate, or AMPA during the synthesis procedure.

2.4. Adsorption kinetics

The kinetics data on glyphosate and AMPA adsorption were obtained from the evaluation of different contact times between the adsorbent and adsorbate. For these experiments, 100 mg of MIP–GP was agitated with 25.0 mL of glyphosate solution at a concentration of 1.0 mg L^{-1} in glass flasks at room temperature for different time periods (5, 15, 30, 60, 90, 120, 150, 180, 210, 240, and 270 min) [20–22]. The tests were performed at a pH of 6.5 in 0.05 mol L^{-1} phosphate buffer solution. The suspensions