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Uptake and translocation monitoring of imidacloprid to chili and tomato plants by molecularly imprinting extraction - ion mobility spectrometry

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ABSTRACT

The degradation of imidacloprid in soil and its uptake and translocation to chili and tomato plants was evaluated, as a proof of concept, of the possibilities of the combination of molecularly imprinted polymers (MIPs) and ion mobility spectrometry (IMS) for a fast and sensitive bioprocesses monitoring tool. To do it, a method based on the selective extraction of imidacloprid from soil and plant materials was developed. In the selected conditions, the MIP-IMS procedure provided a recovery of imidacloprid in soil and plant samples from 102 to 114%, for spiked concentration levels from 0.2 to 2.0 $\mu g\,g^{-1}$. Precision of the methodology, expressed as the relative standard deviation (RSD) of a 100 and 1000 $\mu g\,L^{-1}$ imidacloprid standard solution was 11 and 6%, respectively, being the RSD for the analysis of a soil sample spiked at a concentration level of 1 $\mu g\,g^{-1}$ of 11% ($n = 4$). Limits of detection and quantification of 0.03 and 0.10 $\mu g\,g^{-1}$ in the solid sample were also obtained, respectively. Regarding imidacloprid degradation, this study evidenced that the process follows a first order kinetics with a half-life between 39 and 45 days in soil, being necessary a growing period of 33 days before pesticide detection in stems and leaves.

1. Introduction

Ion mobility spectrometry (IMS) is a gas-phase separation technique in which ions are separated in a milliseconds scale under a weak and homogenous electric field and atmospheric pressure. IMS has received little attention from the analytical chemistry community which had the perception of IMS as a niche instrument for the detection of explosives, illegal drugs and chemical warfare agents [1]. However, IMS has recently gained special attention in many diverse areas such as pharmaceutical [2], clinical [3], food [4], agriculture [5] and environmental sciences [6] among others [7] due to its unique advantages of speed, trace-level sensitivity and simplicity.

In spite of these good features, this technique has not been fully exploited for the monitoring of (bio)reactions [8]. Processes understanding is an essential requirement to assure quality and purity in the pharmaceutical, petrochemical, polymer and food industries, as well as to evaluate the nature and the extend of bioprocesses. However, the potential of IMS is reduced due to its limited selectivity for the analysis of complex samples such as environmental ones. IMS measurement of a complex samples produces a mixture of reagent and analyte product ions which could complicate the interpretation of IMS spectra and interfere in analyte determination. The use of a sample pretreatment step or mathematical data treatments is mandatory.

Uptake, translocation and degradation of pesticides in soils and plants are considered relatively important bioprocesses due to the possible formation of toxic substances that can be hazardous to human health. The numerous negative health effects that have been associated with chemical pesticides include, among other effects, dermatological, gastrointestinal, neurological, carcinogenic, respiratory, reproductive, and endocrine effects [9]. In this context, nowadays there is a considerable research interest in the monitoring and understanding of these bioprocesses [10]. Experiments, designed to measure plant uptake and translocation under controlled environmental conditions, provide insight and information enabling the development of mathematical plant uptake models [11]. However, soil and plants are highly complex samples to be directly analyzed by IMS without a previous sample treatment. In recent years, the selectivity provided by smart sample treatments based on the use of immunosorbents [12] and molecularly imprinted polymers (MIPs) [13] has improved the analysis of pesticide residues in fruits by IMS.

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Table 1
Precedents on the use of MIPs for selective imidacloprid extraction.

Template	Monomer	Cross-linker	Porogen	Initiator	Others	Reference
Imidacloprid	MAA	EDMA	Acetonitrile	AIBN	–	14
Imidacloprid	AA	EDMA	Acetonitrile	AIBN	Nano Fe_3O_4 particles	15
Imidacloprid	MAA	EDMA	Acetonitrile	AIBN	–	16
Thiacloprid	Methylpropenoic acid - phenylethylene	EDMA	Acetonitrile	AIBN	–	17

Methacrylic acid (MAA), acrylic acid (AA), ethylene glycol dimethacrylate (EDMA), 2,2′-Azobis(2-methylpropionitrile) (AIBN).

The main aim of this work has been the development of an IMS-based methodology for the uptake, translocation, and degradation monitoring of imidacloprid, extracted from soil and plants using a sample treatment based on MIPs. Several precedents of the development of MIPs for selective imidacloprid extraction have been published in the literature (see Table 1). As it can be seen, imidacloprid or thiacloprid have been used as template molecules, methacrylic acid (MAA), acrylic acid (AA), methylpropenoic acid or phenylethylene as functional monomers, ethylene glycol dimethacrylate (EDMA) as cross-linking agent, acetonitrile as porogenic solvent, and 2,2′-Azobis(2-methylpropionitrile) (AIBN) as initiator [14–17]. Kumar et al. [15] synthetized a magnetic MIP for the selective separation of imidacloprid from honey and vegetable samples using a non-covalent approach with functionalized nano Fe_3O_4 particles.

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] is a systemic insecticide which belongs to the neonicotinoids family. Imidacloprid is used for the control of various sucking pests in different crops such as rice, maize, sunflowers, rape, potatoes, and sugar beets [18]. Imidacloprid protects roots and shoots after seed germination and the whole plant is also protected during its growth because the systemic imidacloprid is carried by the sap into the various parts of the crop. However, it is expected that the level of imidacloprid decreases during the growth, and very low levels should be found at the time of flowering, thus reducing the adverse effects on non-target insects such as bees [19].

In summary, the determination of the uptake, translocation, and degradation of imidacloprid from soil and plants based on a MIP-IMS methodology has been proposed for the first time. Uptake, translocation and metabolic pathways of imidacloprid after different types of application (foliar, soil and seed treatment, stem injection, and painting application) have been studied on various plant species using chromatography approaches [20–23]. The use of a well-studied pesticide such as imidacloprid as model compound to study uptake and translocation would allow the critical comparison of results obtained by the developed MIP-IMS procedure instead chromatography approaches previously reported in the literature, mainly from a Green Analytical Chemistry point of view.

2. Experimental section

2.1. Material, reagents and samples characteristic

All solvents used in this study were HPLC grade or higher. Organic solvents and buffer constituents were obtained from Scharlab (Barcelona, Spain). MAA, EDMA and AIBN were provided by Sigma (Steinheim, Germany).

Imidacloprid standard, PESTANAL® grade, was also purchased from Sigma–Aldrich. The stock solution of imidacloprid ($1.0\,g\,L^{-1}$) was prepared in acetic acid (5% v/v) in methanol and stored in a freezer at −20 °C and found to be stable for one month. The working solutions required for calibration (0.1, 0.2, 0.4, 0.6, 0.8, and $1.0\,mg\,L^{-1}$) were prepared daily.

2.2. Synthesis of MIP materials

An imidacloprid-selective MIP was prepared by bulk polymerization, using the information of a previously published protocol [14] as starting point. Imidacloprid was used as template, MAA as monomer, EDMA as cross-linker, acetonitrile as porogen, and AIBN as initiator. The molar ratio of template/monomer/cross-linker ratio was 1:4:20. A non-imprinted polymer (NIP) was also prepared in the absence of template molecule in the polymerization mixture. The solution (placed in a vial) was sonicated for 5 min and purged with nitrogen for additional 10 min. The polymerization was carried out in a water bath at 60 °C for 24 h. After polymerization, the glass vial was broken, and the resultant polymer was crushed in an agate mortar, dried in an oven at 80 °C overnight, and sieved with a steel sieve with size ≤100 μm in order to obtain a homogeneous particle size.

The MIP particles were treated with 100 mL 5% (v/v) acetic acid in methanol in a Soxhlet extractor for 24 h to remove the template from polymer and were then rinsed with the same solution until no imidacloprid signal was obtained by IMS analysis. The resulting polymer was dried at 60 °C for 24 h. Soxhlet extraction was not performed on the NIP particles.

2.3. Characterization of MIP particles

SEM images of polymers were taken with a scanning electron microscope S-4100, Hitachi (Ibaraki, Japan), provided with a field emission gun, a back secondary electron detector and an EMIP 3.0 image data acquisition system (Rontec, Normanton, UK).

Surface area and pore size values were calculated by nitrogen adsorption–desorption isotherms at −196 °C recorded on a Micromeritics (Norcross, GA, USA) ASAP-2020 automated instrument. Samples were degassed at 80 °C and 10^{-6} Torr before analysis. The total pore volume was calculated by converting the amount of nitrogen adsorbed at a relative pressure of about 0.99 to the volume of liquid adsorbate. The surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method.

2.4. Growth of plants in imidacloprid contaminated soils

Slurry spiking mode was used to incorporate the imidacloprid in the soil to study the uptake and translocation of imidacloprid from soil to plants. Approximatively, 10 kg soil was obtained from an agricultural area close to Valencia (Spain), taken from 0 to 10 cm to the surface, and stored in a hermetic plastic container at room temperature to avoid cross-contamination. The soil was homogenized and the absence of imidacloprid was checked previous to its use. 65 mg imidacloprid was added to 1 L of acetone, then poured over 20 L of soil (6.5 kg) and mixed thoroughly. The solvent was then allowed to evaporate for 48 h. After air drying, the soil was mixed to ensure homogeneity prior to growing plants. The concentration of imidacloprid in soil was determined to be $10\,\mu g\,g^{-1}$.

Small tomato and chili seedlings (approximately 10 cm height and 15–20 g) were transplanted into individual 500 mL pots with 40 g of