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Insight into the performance of molecularly imprinted poly(methacrylic acid) and polyvinylimidazole for extraction of imazethapyr in aqueous medium

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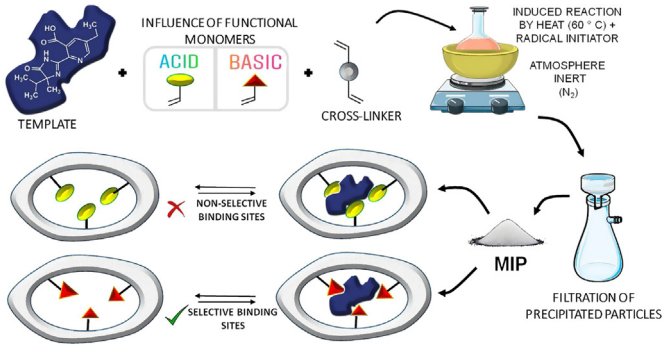
HIGHLIGHTS

- MIP-MAA (acid polymer) and MIP-VN (basic polymer) were prepared.
- MIP-VN sorbs selectively more imazethapyr than MIP-MAA.
- Imprinted sites played a more important role in selective and adsorptive features of polymers than textural data.
- Sorptive behavior of MIP-VN is better than commercial and synthetic adsorbents recently developed towards imazethapyr.

GRAPHICAL ABSTRACT



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ABSTRACT

The present paper describes the synthesis, characterization, and evaluation of two cross-linked molecularly imprinted poly(methacrylic acid) and polyvinylimidazole towards selective extraction of imazethapyr in aqueous medium. Characterization of materials was performed by FT-IR, TGA, SEM, TEM, elemental analysis and nitrogen adsorption/desorption measurements. Based on relative selectivity coefficients (k′), the molecularly imprinted polyvinylimidazole showed higher selectivity towards imazethapyr and some similar structurally compounds belonging to imidalizones families, imazapic and imazapyr, when compared with poly(methacrylic acid). The kinetics and isotherms of sorption as well as the thermodynamic parameters were then obtained by using the polyvinylimidazole. It was observed that the pseudo-first and second-order models provided the best fit for imazethapyr sorption. Regarding the sorption isotherm, the dual-site Langmuir–Freundlich model presented the best fit for the experimental data, thereby suggesting the existence of sorption sites with different affinities. The maximum sorption capacities obtained for the imprinted and non-imprinted polymers were found to be 27.1 and 24.4 mg g^{-1}, respectively. According to the obtained thermodynamic parameters, ΔG (0.96 kJ mol^{-1}), ΔH (−22.81 kJ mol^{-1}) and ΔS (−79.73 J mol^{-1} K^{-1}), it might be suggested that the sorption process is not too much favorable, exothermic and provides increase of order at the solid-solution interface. In this case, the low

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temperature is favorable for the sorption of imazethapyr, typical of physisorption, which match with low sorption activation energy (20.25 kJ mol^{-1}) determined from Arrhenius equation. The molecularly imprinted polyvinylimidazole exhibited higher sorption capacity when compared with previously reported commercial sorbents for imazethapyr.

1. Introduction

Imazethapyr belongs to a relatively new class of chemical compounds widely used in agriculture due to its wide range of crops such as rice, soybean, maize and oilseed rape. The phytotoxicity of imazethapyr and their similar structurally compounds, imazamethabenz, imazamox, imazapic and imazapyr belonging to imidazoline herbicides families depends upon the nature of the moiety attached to imidazoline ring [1]. In spite of not well known the toxicity mechanism in human beings, imazethapyr has been classified as a hazardous compound to the environment (Class III), according to Brazilian Health Regulatory Agency (ANVISA) [2]. Imazethapyr has also been considered a potential contaminant of surface and groundwater water according to the United States Environmental Protection Agency (US EPA) [3] due to its high leaching through soils, high solubility in water (1.4 g L^{-1}) and low absorption coefficient (log Kow = 1.49) [4–7]. Imazethapyr has been an environmental concern when used intensively due to contamination of non-target sites owing to changes in the structure of microbial community [8].

Owing to environmental monitoring concern, some countries have set regulatory limits for maximum levels of imazethapyr in food samples [9–11], whose allowable tolerances values are very similar to each other. For instance, according to ANVISA, the maximum levels of imazethapyr in rice, bean, and soybean are 0.05, 0.05 and 0.1 mg g^{-1}, respectively. US EPA [3] establishes the maximum levels as 0.10 mg g^{-1} for canola seed, soybean and vegetables, 1.2 mg g^{-1} for rice (bran), 0.10 mg g^{-1} for cattle meat byproducts and 0.10 mg g^{-1} for lettuce, while Health Canada's Pest Management Regulatory Agency (PMRA) set the maximum level in sunflower seeds as 0.1 mg g^{-1} [11]. On the other hand, for natural and potable water samples no quality standards or criteria have been established for this herbicide by the Brazilian governments, United States of America, European Community and Canadian [2,3,7,10,11].

Because of its susceptibility to leach to groundwater from the soil, some studies have detected imazethapyr in water samples at very low levels (sub-mg L^{-1} level) [12–14]. Moreover, due to restricted information regarding pesticides residues in animal origin food, some recent reports have devoted efforts on the development of straightforward and simple methods for quality control [15]. Imazethapyr determination has been frequently carried out by very well developed and advanced analytical instrumentation such as liquid chromatography (LC) and gas chromatography (GC) by using MS/MS or diode array (DAD) as detectors [12,16,17]. However, due to the high complexity of water and food samples associated with the low levels of analyte, sample preparation methods based on enrichment and sample clean-up before instrument determination are still considered as a bottleneck and required for a reliable analysis.

Sample preparation methods towards herbicides analysis have been mostly performed by solid-phase extraction (SPE), which presents some advantages such as high enrichment factor, easy mechanization, and low organic solvents consumption [18]. Currently, the most common sorbents employed for extraction of imazethapyr are divinylbenzene materials, (LiChrolut EN and ENVI-Chrom P) [19], graphitized carbon [14], C18 (StrataTM C18), polymeric sorbent functionalized with N-Vinylpyrrolidone (StrataTM-X), polymeric sorbent functionalized with N-Vinylpyrrolidone and divinylbenzene (Oasis-HLB) [17] and poly (methyloctylsiloxane) (PMOS) immobilized onto silica [16]. The main limitations of these materials mainly those commercially available are attributed to the low selectivity, reusability, and repeatability in recovery studies [17,20,21]. In this sense, researchers in the field of separation science have been increasingly focused on the synthesis of sorbent materials with outstanding properties i.e. high sorption capacity, selectivity, low-cost, easier regeneration, storage endurance, and simplicity in the synthesis [22].

In this perspective, molecularly imprinted polymers (MIP) which explore supramolecular approaches during polymer synthesis by creation selective binding sites in the presence of template molecule have been widely used as highly selective materials in extraction procedures [23]. Many researchers have reported the synthesis of MIP for various classes of herbicides, such as triazine [24], sulfonylurea [25], chloroacetamide [26] among others.

Although MIP technology has been matured in the understanding the complementary concept for biological recognition based on lock-and-key mechanism, there still exist some difficulties in preparing MIP to large organic compounds containing acidic and basic binding sites, which might hinder the creation of selective binding sites [27,28]. A brief survey of literature demonstrates that very few attempts have been made for the synthesis of MIP towards extraction of imidazolinones herbicides. Such a finding might be most likely attributed to their amphoteric properties, which undergo effects on ionization of the different ionizable functional groups, as well as by the relatively large size of these molecules. To the best of our knowledge, the only study dedicated to the synthesis of MIP towards imidazolinone extraction was reported by Chen and coworkers [29], who developed an imazethapyr molecularly imprinted polymer-based solid-phase microextraction coating using one-step in situ polymerization method.

Notwithstanding, one should note that the choice of functional monomer, which will drive the formation of selective cavities is one of the most important parameters for obtaining highly imprinted polymers, mainly for larger molecules that present acidic and basic groups in their structure, such as imazethapyr [30]. In the current study, methacrylic acid and 1-vinylimidazole were chosen as acid and basic monomers, respectively, because the first one might establish hydrogen bonding with nitrogen and hydrogen atoms from template molecule, while the basic monomer might establish hydrogen bonding as well as acid-base reaction with carboxylic acid from template.

According to aforementioned and bearing in mind the influence of functional monomers in the formation of monomer-template complexes, the main objective of the present study deals with the complete investigation on the performance of acid molecularly imprinted poly (methacrylic acid) and basic polyvinylimidazole for the extraction of imazethapyr in aqueous medium. For this task, characterization of the polymers was performed by using Fourier Transform-Infrared (FT-IR), Elemental Analysis (CHN), nitrogen adsorption/desorption measurements, Thermogravimetric Analysis (TGA), Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM). A set of kinetic, isothermal, thermodynamic and selectivity experiments were performed to compare the selective and sorptive performance of imprinted polymers with regard blank polymer, as well as to get an insight into sorption mechanism with more details.

2. Experimental

2.1. Reagents

All reagents used in the experiments were of analytical grade. Imazethapyr (IMT), imazapyr (IMP), imazapic (IMZ), diuron (DIU), hexazinone (HEX), ametrine (AME), tebuthiuron (TBT) were purchased