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Molecularly imprinted polymers for the determination of organophosphorus pesticides in complex samples

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ABSTRACT

Organophosphorus compounds constitute an important class of pesticides whose the toxicity of which arises from the inhibition of the acetylcholinesterase enzyme. They exhibit a wide range of physico-chemical properties, thus rendering their determination in complex oil samples particularly difficult. To facilitate their analysis at the trace level in various samples (environmental waters, soils, vegetables…), molecularly imprinted polymers (MIPs) that are synthetic polymers possessing specific cavities designed for a target molecule have been prepared. Often called synthetic antibodies, MIPs can replace antibodies in different application fields. Indeed, as immunosorbents, MIPs can be used as selective sorbents for the solid phase extraction of target analytes from complex matrices or as recognition elements in sensors. Their synthesis, characterization and use as selective sorbent for the selective recognition of organophosphorus pesticides have been already largely described and are summarized in this review.

1. Introduction

The increasing use of pesticides for agricultural purposes cause serious risks to the human and animal health. Organophosphorus pesticides (OPPs) are among the most used pesticides. As mentioned in a recent review related to their analysis in fruit and vegetables, they are found mutagenic, carcinogenic, cytotoxic, genotoxic, teratogenic and immunotoxic [1]. Their determination, at very low concentration levels in environmental samples and foodstuff, constitutes a real analytical challenge. Indeed, OPPs exhibit a wide range of physico-chemical properties thus explaining the possibility to analyze some of them either by gas chromatography (GC) for the most volatile compounds or by liquid chromatography (LC) for the most polar ones. For their analysis through GC, different types of detectors have been used including some specific detectors such as flame photometric detector (GC-FPD) or nitrogen phosphorus detector (NPD) and mass spectrometers for their identification capabilities [1,2]. These recent years, OPPs analysis through LC have been carried out in association with mass spectrometry (LC-MS) with regard to its higher sensitivity and identification capabilities, as compared to UV detection [1–3]. However, despite the advances in the development of such highly sensitive analytical instruments including high resolution mass spectrometry that can be associated with different ionization sources, a pre-treatment is usually necessary in order to extract and isolate the analytes of interest from complex samples before their determination [2].

The analysis of pesticide residues, including OPPs in environmental samples (waters, soils, sediments…), foodstuffs and biological fluids has been often reviewed, showing that numerous extraction methods have been developed for the treatment of solid and liquid samples those last ten years. Some of these reviews have focused on the development of various methods for the treatment of a given type of samples such as water samples [4], foodstuffs [5,6], such as fruits and vegetables [7], fatty vegetable matrices [8], foods of animal origin [9], olive and olive oil [10], baby-food [11] and honey using various techniques [12]. Others have reported the potential of a method or a group of close methods for the treatment of various types of samples such as solid-phase based extraction method for food and environmental samples [13], stir bar sorptive extraction (SBSE) for fruits and vegetables [14], single drop liquid extraction (SDLE) for waters and fruit juices [15] or liquid-phase micro-extraction for water samples including SDLE and dispersive liquid-liquid extraction [16], matrix solid phase dispersion (MSPD) for foodstuffs such as vegetables [17] or food from animal origin [17,18].

Despite the use of these efficient extraction and clean-up methods, matrix components are unavoidably present in final extracts thus

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causing a risk of matrix effect during GC or LC determination [19,20]. The effects caused by these matrix components can be reduced by improving the chromatographic resolution as can be achieved using multidimensional chromatography or by improving the selectivity during the sample treatment.

Selectivity, during sample pretreatment, can be obtained by using sorbent able to retain compounds by a molecular recognition mechanism. For this, it comes therefore possible to use immunoaffinity supports (i.e. immunosorbents, ISs) based on the use of specific antibodies that target a molecule of interest. The high selectivity and affinity of the antigen-antibody interactions allows a selective clean-up to being reached with high enrichment factors as already demonstrated for numerous pesticides in complex samples [21] including OPPs from water samples [22]. Other selective supports, called oligo-sorbents, have been recently proposed using aptamers immobilized onto a solid support. Aptamers are oligonucleotides with a specific sequence able to bind a given molecule with the same affinity as antibodies. Aptamers were recently successfully applied to the selective extraction of different target analytes from biological fluids and food samples [23,24]. A DNA sequence was previously described for the recognition of OPPs but not applied yet to their extraction from real samples [25]. Once the sequence is available, developing an oligosorbent is less expensive than an IS. However, despite their high potential, a limited number of sequences is, to date, available. This molecular recognition mechanism can also be exploited using molecularly imprinted polymers (MIPs) that are synthetic polymeric materials possessing specific cavities designed for a template molecule. MIPs are often called synthetic antibodies in comparison with IS. They offer some advantages including easy, cheap and rapid preparation and high thermal and chemical stability [26]. The use of MIPs as selective sorbents for solid-phase extraction (SPE) is recent. It was initially proposed by Sellergren et al. in 1994 for extracting pentamidine present at low concentration in urine [27]. Since this first application, numerous MIPs were developed for the selective extraction of target analytes from complex samples [28–31]. Because of their high selectivity, they have been also already successfully used in several other fields such as sensors [32–34], bioassays [35,36] and enantiomeric separation [37].

Their synthesis, characterization and use as selective sorbent for the selective recognition of OPPs have been already largely described and mainly developed to be integrated in sensors or used in solid phase extraction. Fig. 1a illustrates the proportions of the application of MIPs for the determination of OPPs in these different fields. As shown by Fig. 1b, this field of research is very active since more than 70% of the papers have been published those last five years.

Therefore, this review focuses on the presentation of polymerization methods used to produce MIPs for OPPs, their characterization in pure media and their performance as SPE sorbents or as selective tools of sensors for the determination of OPPs in real samples.

2. Synthesis of MIPs

In the common approach, the synthesis of molecularly imprinted polymers (MIPs) involves first the solution complexation of a template molecule with functional monomers, through non-covalent bonds, followed by polymerization of these monomers around the template with the help of a cross-linker in the presence of an initiator. The choice of the chemical reagents making the MIP must be judicious in order to really create specific cavities designed for the template molecule. For these reasons, a monomer is chosen to develop strong interactions with the target analyte, i.e. an OPP or a structural analog acting as the template, in a porogen solvent. By the presence of a cross-linker, the polymerization takes place around the template. The template molecule is then removed, producing a polymer with binding sites complementary to the template in size, shape and position of the functional group. The conditions of synthesis of MIPs for OPPs (polymerization mode, reagents used), as reported in the literature, are summarized in Table 1.

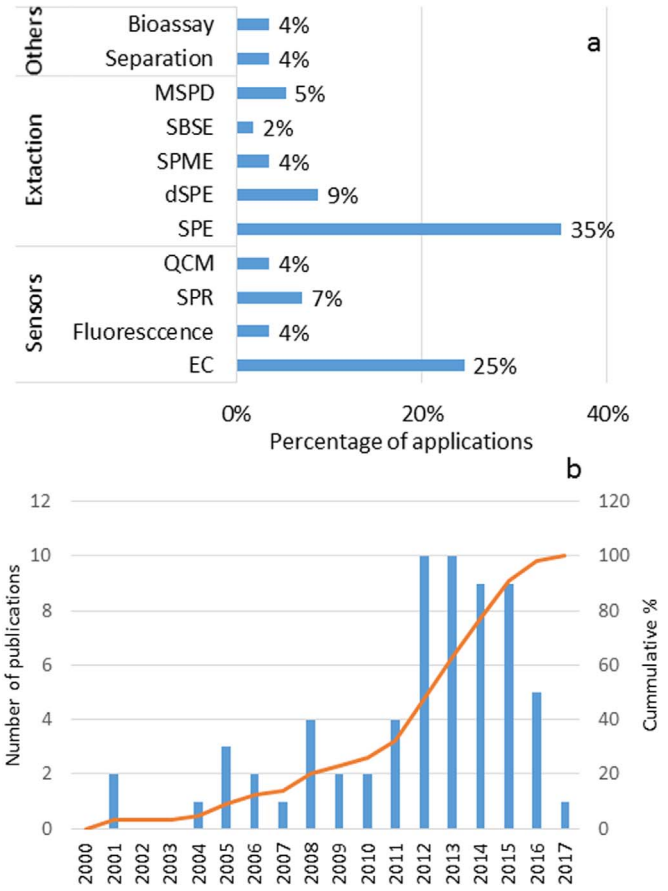

Fig. 1. Percentages of use of MIPs in the different fields such as sensors of different types e.g. piezoelectric (using quartz cristal microbalance (QCM) or surface plasmon resonance (SPR)), optical (i.e. fluorescence) or electrochemical (EC)), as extraction sorbent in conventional SPE, in dispersive mode applied to liquid samples (dSPE) or solid samples (matrix solid-phase dispersion, MSPD), in micro-solid-phase extraction (SPME), in stir-bar solid-phase extraction (SBSE) or as stationary phase for separation purposes or in bioassays (a) and cumulative percentages (red curve) of publications related to the development of MIPs for dedicated to OPPs (b) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

As shown in this table, MIPs were prepared by radical polymerization of organic acrylate of acrylic based monomers. In most of the cases, a conventional bulk polymerization is achieved and gives rise to a monolith that as to be ground and sieved to obtain particles that present an heterogeneous size distribution. This procedure is easy to achieve but it is time-consuming and its yields are less than < 50%, mainly explained by the loss of MIP, as fine particles removed during a sedimentation step. In order to obtain more regular and homogeneous beads or microspheres, MIPs can also be prepared by precipitation polymerization that results from an increased amount of porogen or by more sophisticated methods such as suspension polymerization or multi-step swelling or surface-grafting. It was also proposed to develop MIPs by the hydrolysis and the condensation of organo-silanes around the template, thereby thus giving rise to a hybrid sol-gel material. This synthesis achieved in aqueous media presents the advantages to facilitate the dissolution of polar templates.

As shown by data reported in Table 1, more than 20 different OPPs were used as template molecule, the most frequently reported OPP templates being chlorpyriphos, parathion, parathion methyl, dimethoate and monocrotophos. The structure of the main studied OPPs and their log P values are reported in Supplementary material (S1).

The use of a structural analog has been proposed to prepare MIPs for other chemicals to decrease the cost of the material when the target molecule is expensive and/or toxic as it is can be the case for some toxins. It is also a way to circumvent the risk of residual template