



Analytical Methods

Preparation, evaluation and application of diazinon imprinted polymers as the sorbent in molecularly imprinted solid-phase extraction and liquid chromatography analysis in cucumber and aqueous samples



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ABSTRACT

A series of diazinon imprinted polymers (MIPs) were prepared and evaluated in the binding study in comparison with a non-imprinted polymer (NIP). The optimised MIP was evaluated as a sorbent, for extraction and preconcentration of diazinon from aqueous media and cucumber tissue. The HPLC-UV method was calibrated, in the range of 0.025–10 mg/kg. The results indicated that the optimised MIP had an excellent affinity for diazinon. The molecularly imprinted solid-phase extraction (MISPE) procedure was optimised with a recovery of 77–98%, in aqueous solution, and a recovery of 82–110%, in cucumber. The intra-day variation and inter-day variation values were less than 8.26% and 9.7%, respectively. Our data showed that, the MIP enabled the extraction of trace amounts of diazinon successfully from aqueous solution and cucumber, demonstrating the potential of MISPE for rapid, sensitive and cost-effective sample analysis.

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1. Introduction

Molecular imprinting is a method for synthesising specific recognition sites in polymeric matrices (Hadizadeh, Zakerian, & Mohajeri, 2013). In this process the functional monomers are used to interact with a template molecule in a pre-polymerization solution and a cross-linker monomer is applied to fix the spatial arrangement during polymerisation. After washing and removing the template molecule, the imprinted cavities are able to recognize the template and its similar analogues (Hadizadeh, Zakerian, et al., 2013). Molecularly imprinted polymers (MIPs) are cheap, robust materials with a high mechanical and chemical stability, reusable with different applications (Schirmer & Meisel, 2008). The MIPs could be applied as the sorbent in solid-phase extraction (Hadizadeh, Hassanpour Moghadam, & Mohajeri, 2013; Sahebna-sagh, Karimi, & Mohajeri, 2013), as the stationary phase in liquid

chromatography (Sun, Qiao, & Liu, 2006), as the carrier in drug delivery systems (Malaekheh-Nikouei, Ghaeni, Motamedshariaty, & Mohajeri, 2012; Malaekheh-Nikouei, Vahabzadeh, & Mohajeri, 2013) and as the recognition agents in biosensors (Alizadeh, Zare, Ganjali, Norouzi, & Tavana, 2009). Molecularly imprinted solid-phase extraction (MISPE) is a technique which is commonly used for sample preconcentration and clean-up before analysis (Moller, Nilsson, & Crescenzi, 2001; Schirmer & Meisel, 2008; Sun, Schussler, Sengl, Niessner, & Knopp, 2008). The MISPE is a convenient, high speed and selective method in comparison with alternative extraction methods. Furthermore, MISPE can coupled with analytical procedures (Schirmer & Meisel, 2008). Therefore, the MIPs are widely used in development of selective sorbents for extraction and determination of trace analytes.

Organophosphate pesticides (OPs) are used widely in agriculture, public health and domestic fields for controlling insects (Razavi, Hosseinzadeh, Abnous, Sadat Motamedahariaty, & Imenshahidi, 2013). Diazinon (O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate) is an anti-cholinesterase organophosphate pesticide, which is commonly used against insects in agriculture and also for controlling silverfish, cockroaches, and ants in residential and commercial buildings (Prince, Fan, Skoczinski, & Bushway, 2001). Diazinon functions as an acetylcholinesterase

Abbreviations: AIBN, 2,2'-azo-bis-iso-butyronitrile; B_{max} , maximum binding sites; EGDMA, ethylene glycol dimethacrylate; K_D , dissociation constant; MAA, methacrylic acid; MISPE, molecularly imprinted solid-phase extraction; NIP, non-imprinted polymer; ACN, acetonitrile.

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(AChE) inhibitor. The inhibition of this enzyme causes an abnormal accumulation of acetylcholine in the synaptic cleft at muscarinic, nicotinic, and central sites results in the toxic effects such as headache, dizziness, convulsions, delirium, and depression (Liang, Balcer, Solomon, Messe, & Galetta, 2003). Also, other toxic effects of diazinon on hepatocytes, spleen, thymus, blood cells, lymph nodes, and heart have been reported in human and animals (Razavi et al., 2013). Several analytical methods have been developed for detection and measurement of anti-AChE OPs (Aprea, Colosio, Mammone, Minoia, & Maroni, 2002). Most of them need time-consuming procedure, sophisticated and expensive equipments with skilled operators. The maximum residue limit (MRL) of diazinon in cucumber, set by WHO, is 0.5 mg/kg (0.5 ppm) (Kabir, Rahman, Ahmed, Prodhon, & Akon, 2008). Diazinon is usually determined by GC methods (GC-MS, GC-ECD, GC-FPD, etc.) in cucumber and other fruits (Bagheri, Es'haghi, & Mesbahi, 2012; Garrido Frenich, Martínez Vidal, Fernández Moreno, & Romero-González, 2009; Srivastava, Trivedi, Srivastava, Lohani, & Srivastava, 2011; Zhao et al., 2011). The extraction and preconcentration procedures are usually performed in above mentioned methods before analysis to increase sensitivity. The quantification limit set in these studies is around 0.001–0.01 mg/kg (0.001–0.01 ppm); which is significantly less than the MRL of diazinon in fruits (Bagheri, Es'haghi, Es'haghi, & Mesbahi, 2012; Garrido Frenich et al., 2009; Srivastava et al., 2011; Zhao et al., 2011). Obviously, the sensitivity of HPLC-UV method, for analysis of OPs, is much lower than that of GC methods. But the lower cost and more availability of HPLC methods are the important advantageous. The quantification limit of diazinon assay by HPLC-UV in different fruit juice or agriculture products was 0.05–0.54 mg/kg (0.05–0.54 ppm) (Gebreegzi, Foster, & Khan, 2000; Seebunrueng, Santaladchaiyakit, Soisungnoen, & Srijaranai, 2011). Preconcentration procedures are also necessary in HPLC methods. Thus, new approaches such as solid-phase extraction (SPE), supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), and solid phase microextraction (SPME) have been of particular interest (Heidari, Shahtaheri, Alimohammadi, & Rahimi-Froshani, 2009; Shahtaheri, Abdollahi, Golbabaie, Rahimi-Froushani, & Ghamari, 2008; Shahtaheri, Ibrahim, Golbabaie, Hosseini, & Fouladi Dehghi, 2007; Shahtaheri, Mesdaghinia, & Stevenson, 2005). Recently, because of stability, low cost and ease of preparation, molecular imprinting has become an interesting research field to prepare an specific sorbent (MIP) for SPE of compounds in environmental and occupational samples (Haupt, 2003). In addition, the MIPs can be also used as a sorbent for the analogues of the main template or other structurally similar molecules (Wang et al., 2011). It is of great interest to develop a new MISPE that uses diazinon as a template for the extraction of this toxin from aqueous media and cucumber tissue. The aim of the present study was development of an optimised MIP for diazinon, evaluation of its binding properties and development of MISPE for sample preparation, clean-up and preconcentration of toxin from aqueous media and cucumber tissue. In this study, we coupled MISPE with HPLC-UV assay as a rapid, easy, affordable and accessible method for determination of diazinon in cucumber. We tried to increase the sensitivity of the assay to an acceptable level by MISPE.

2. Experimental

2.1. Chemicals and materials

Diazinon, methacrylic acid (MAA), and ethylene glycol dimethacrylate (EGDMA) were obtained from Sigma–Aldrich (Milwaukee, USA). 2,2'-Azobis-iso-butyronitrile (AIBN) was purchased from Acros (Geel, Belgium). All solvents used [acetonitrile (ACN), chloroform, methanol, acetone, acetic acid and dichloromethane] were of HPLC grade.

2.2. Synthesis of polymers

Diazinon as the template and MAA (2.5 mmol) as the functional monomer, were dissolved in chloroform (5 mL) and kept at 4 °C for 1 h. The tube was placed in a shaker at 100 rpm for 1 h at room temperature. EGDMA (12.5 mmol) and AIBN (10 mg) were then added as the cross-linker and initiator, respectively. Different amounts of diazinon (0.833, 0.500, 0.416, 0.312 and 0.250 mmol) were applied to obtain diazinon/MAA molar ratios of 1/3, 1/5, 1/6, 1/8 and 1/10 in preparation of MIP₁, MIP₂, MIP₃, MIP₄ and MIP₅, respectively. After sonication for 5 min the mixture was sparged, in an ice bath, with oxygen-free nitrogen for 5 min and heated at 60 °C for 24 h to complete polymerisation. The resultant rigid polymer monoliths were powdered and sieved through 200 and 400 mesh stainless steel sieves (particle size between 38 to 75 µm). After washing the polymer particles with a methanol-ACN (7:3, v/v) mixture (4 × 25 mL) and finally with methanol (5 × 25 mL), the mixture was centrifuged at 3000 rpm for 10 min and the supernatant was analysed by HPLC. The washing step was continued until no diazinon or other chemicals were detected in supernatant. Non-imprinted polymer (NIP) was prepared under the same condition described above but in the absence of diazinon.

2.3. Batch adsorption procedure

The binding properties of polymers were examined by batch adsorption experiments. Dry polymer (10 mg) was added to 1.5 mL methanol-water (pH = 10) (75:25, v/v) with diazinon and was shaken for 24 h at room temperature. After centrifugation of the solution (3000 rpm for 10 min) the concentration of diazinon in supernatant was analysed by HPLC. The amount of bound diazinon was measured from the initial and final concentrations in solution after equilibrium. Each experiment was repeated four times and mean ± SEM (standard error of mean) was reported. The imprinting factor (IF) was obtained from Eq. (1) (Hadizadeh, Zakerian, et al., 2013):

$$\left\{ IF = \frac{K_{MIP}}{K_{NIP}} \right\} \quad (1)$$

where K value was the partition coefficient for MIP or NIP and calculated in (Hadizadeh, Zakerian, et al., 2013):

$$\left\{ K = \frac{\text{Bound Diazinon/g polymer}}{[\text{Free}]} \right\} \quad (2)$$

where [Free], was the final concentration of free unbound diazinon in the solution and bound diazinon was the amount of diazinon bound to per gram dry polymer after equilibrium. A Scatchard plot was drawn (Eq. 3) when the diazinon concentration was varied in the solution (Hadizadeh, Zakerian, et al., 2013):

$$\left\{ \frac{\text{Bound}}{[\text{Free}]} = -\frac{\text{Bound}}{K_D} + \frac{B_{\max}}{K_D} \right\} \quad (3)$$

The [Bound] value was the amount of diazinon bound to polymer after equilibrium; [Free] was the final diazinon concentration at equilibrium; B_{\max} was the maximum binding sites and K_D represented the dissociation constant. The values of K_D and B_{\max} could be obtained from the slope and intercept of the line drawn in a plot of Bound/Free vs. Bound.

2.4. Optimisation of MISPE protocol

150 mg of polymer (MIP₅ or NIP), was suspended and packed into an empty polypropylene SPE cartridge. The column was regenerated with 3 mL methanol-acetic acid (90:10 v/v), 10 mL dichloromethane and 5 mL ACN and then conditioned with 5 mL methanol

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