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Molecularly imprinted polymer-based materials as thin films on silica supports for efficient adsorption of Patulin

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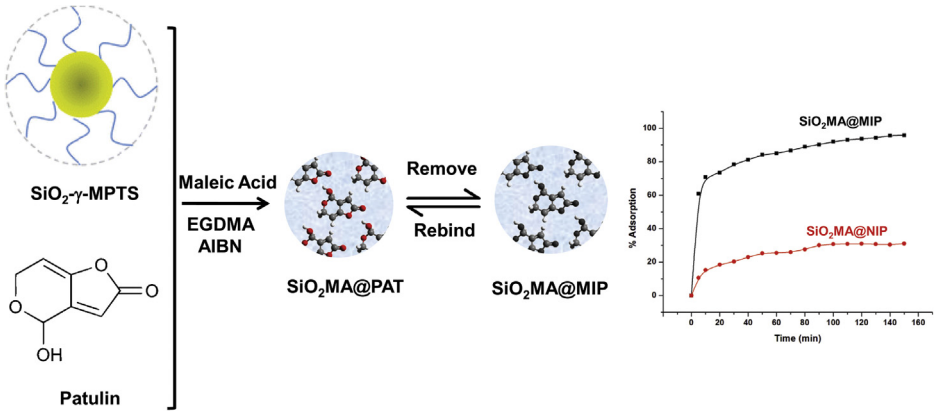
HIGHLIGHTS

- Development of MIP using modified Stöber silica as support for separation of Patulin.
- Evaluation of MIP and NIP adsorption behaviors towards Patulin.
- Fast uptake of Patulin by the imprinted adsorbent material.
- Best adsorption capacity with excellent recognition ability of SiO_2MA@MIP.

GRAPHICAL ABSTRACT



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ABSTRACT

A molecularly imprinted polymer material (MIP) was developedas thin films of polymer attached on the surface of a solid support. Such materials were made of Stöber silica particles chemically modified with methacryloyl groups, to which poly(methacrylic acid) or copolymers of methacrylic and maleic acids were grafted during their radical polymerization. The polymerization was carried out in the presence of the Patulin mycotoxin and the resulting materials were used as a matrix for separation of Patulin. The syntheses of the MIPs and the corresponding non-imprinted materials (NIP) were characterized by means of FT-IR, ^{13}C NMR and elemental analysis. The uptake capacity of Patulin by the MIPs was 1.55 mmol g^{-1}, four times higher than the corresponding NIP. The adsorption of Patulin on the MIP reached a steady state in only 20 min whereas full adsorption on the NIP took 120 min under the same conditions. The adsorption followed pseudo-second order kinetics. The adsorption isotherm was of a Freundlich type. Such MIPs could be employed as an efficient adsorbent for the removal of Patulin from complex media.

1. Introduction

Patulin (PAT) is a mycotoxin commonly found as a contaminant in many moldy fruits, vegetables, cereals and other foods. However, the major sources of contamination are apples products and apple

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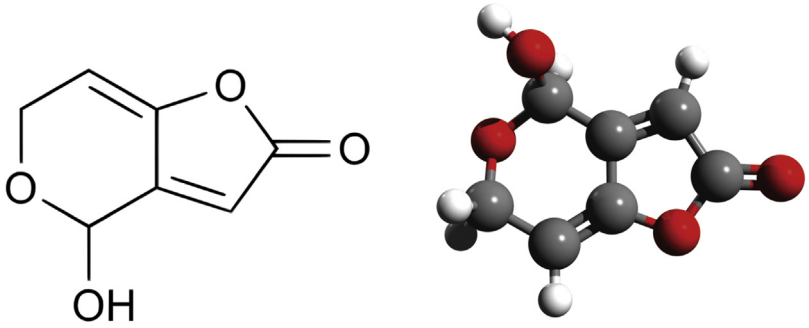

Scheme 1. Structure of Patulin.

juice [1–4] (Scheme 1). This mycotoxin is a toxic secondary metabolite produced by a number of species genus, *Penicillium expansum* that considered as the main source of Patulin in food [5]. So, Patulin can be used as an indicator of the quality of processed apple products [6]. PAT is known to be mutagenic, teratogenic, neurotoxic and possessesimmunotoxic genotoxic and gastrointestinal effects [7]. It also has adverse effects on the developing fetus [8]. The maximum acceptable levels of Patulin in apple based products set by the European Committee are 50 $\mu g\,kg^{-1}$ for fruit juices, 25 $\mu g\,kg^{-1}$ for nectars and fermented apple beverages, and 10 $\mu g\,kg^{-1}$ for solid apple products [9,10].

Due to the low acceptable limits of Patulin in food products, sensitive analytical methods are required for the detection of traces of Patulin in samples. Also, analytical methods should be selective due to the complexity of the food samples which can contain interfering substances. Several analytical methods are commonly used for the detection of PAT in various apple based products like thin layer chromatography (TLC), high-performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS) [11]. HPLC with UV detection is the most widely used method and has been validated as an AOAC International official method [12].

Therefore, the pretreatment of the sample for HPLC analysis is necessary and crucial. Recently solid phase extraction have been used as alternative clean-up method substituting the traditional liquid-liquid extraction which is time consuming and uses organic solvents. The most common SPE for routine determination of Patulin are based on C18 or C8 modified silica as solid phase but these phases exhibit a poor selectivity for the separation of Patulin from complex matrices [13,14]. An attractive alternative method is presented, by using high selective molecularly imprinted polymers (MIPs) for the cleanup and pre-concentration of Patulin [15].

MIPs are synthetic macromolecular materials that contain shape-specific molecular recognition cavities coming from the imprint of the template molecule [16]. The created specific recognition sites are suitable for selective extraction of specific materials from complex matrices [17]. The MIPs generally produced by polymerization starting from functional monomers and high amounts of cross-linking agents in a porogen solvent in presence of target molecule,yielding a polymeric matrix where the target molecule is embedded. The subsequent removal of target species results in the formation of recognition sites, where the shape of the target is imprinted and the functional groups are favorably oriented for optimum interactions with the target molecule of interest. Most of MIPs are usually produced by bulk polymerization or precipitation polymerization. However, MIPs produced using such approach contain recognition sites deeply buried inside the polymer material, which limits the extraction or rebinding of the template. Obviously, surface imprinted MIPs are expected to improve accessibility to the recognition sites generated at the surface of the material, due to reduced mass transfer resistance to template. An expected benefit is an increase of the binding kinetics. So, surface grafting to the surface of solid supports has been proposed as a new surface imprinting technology for the synthesis of molecularly imprinted polymer with a better accessibility to the specific binding sites. Hence, imprinted polymer matrices produced at the surface of polystyrene beads were used as support for the development of chromatographic separation of proteins [18]. Molecularly imprinted layer-coated silica nanoparticles for bisphenol A (BPA) were also synthesized by molecular imprinting technique on silica nanoparticles [19]. A new molecularly imprinted polymer has been prepared on silica beads using the radical "grafting from" polymerization method for selective extraction of Patulin [20]. In this approach, the azo initiator was attached to the surface of silica to ensure the initiation of the photografting polymerization from the surface. 3-Aminopropyltriethoxysilane (APTS) was previously attached at the surface of silica to act as grafting agent for the immobilization of azo initiator at the surface of silica. The authors have noticed the lower binding affinity of the produced MIP which they attribute to the low grafting yield of the APTS on the surface of silica serving as anchor sites for the immobilization of azo initiator. To circumvent this problem, we have adopted an approach allowing the formation of silica containing polymerizable functions. This was achieved via sol-gel process by condensation of two kinds of precursors, tetraethoxysilane (TEOS) to generate silica and γ-methacryloxypropyltrimethoxysilane (γ-MPTS) bringing polymerizable functions. The polycondensation of these two precursors leads to the formation of silica containing surface polymerizable groups serving for the formation of MIP polymeric matrix. Two MIPs were prepared differing by the type of functional monomer interacting with Patulin. Adsorption studies of Patulin were carried out in order to assess the selective adsorption properties of the materials and the mechanism of adsorption.

2. Materials and methods

2.1. Materials

Patulin standard (≥98%, PAT), was provided by A.G. Scientific (San Diego, CA), dissolved in water/acetonitrile 90:10 and stored at 4 °C. The molecular structure is shown in Scheme 1. All solvents (acetonitrile, methanol, ethyl acetate) of HPLC grade were purchased from Fisher Scientific (Fisher chemicals HPLC, France). All reagents (acetic acid, acid and sodium carbonate) were obtained from Sigma-Aldrich (France). γ-Methacryloxypropyltrimethoxysilane (γ-MPTS) (molar mass 248.35 $g\,mol^{-1}$, purity 98%) and tetraethyl orthosilicate (TEOS, 98%) were purchased from Sigma-Aldrich. The stabilizer Polysorbate 20 was purchased from Aldrich under the trade name Tween®20. 2,2-Azobisisobutyronitrile (AIBN), methacrylic acid (MAA), maleic acid (MA), ethylene glycoldimethacrylate (EGDMA) was purchased