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ORIGINAL PAPER

Polydopamine-based molecularly imprinting polymers on magnetic nanoparticles for recognition and enrichment of ochratoxins prior to their determination by HPLC

Meihua Hu[1,2] · Pengcheng Huang[1] · Lili Suo[2] · Fangying Wu[1]

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Abstract

A polydopamine-based molecularly imprinted polymer was deposited on the surface of magnetite (ferroferric oxide) nanoparticles (Fe_3O_4@PDA MIPs) and is shown to be an efficient and fairly specific sorbent for the extraction of various ochratoxins. The MIPs were characterized by IR spectroscopy and transmission electron microscopy. The adsorption capacities, evaluated through the *langmuir* adsorption isotherm model, are 1.8, 0.23 and 0.17 $mg \cdot g^{-1}$ for ochratoxin A, ochratoxin B and ochratoxin C, respectively. Parameters such as the amount of magnetic MIPs, pH value, time for ultrasonication, elution solvent and volume were optimized. Following desorption from the MIP with acetonitrile, the ochratoxins were quantified by HPLC with fluorometric detection. Under optimal experimental conditions, the calibration plots are linear in the range of 0.01–1.0 $ng \cdot mL^{-1}$ of OTA, 0.02–2.0 $ng \cdot mL^{-1}$ of OTB, and 0.002–0.2 $ng \cdot mL^{-1}$ of OTC. The LODs are between 1.8 and 18 $pg \cdot mL^{-1}$, and the recoveries from spiked samples are 71.0% - 88.5%, with RSDs of 2.3–3.8% in case of rice and wine samples. The MIPs can be re-used for at least 7 times.

Keywords Rice · Wine · Separation · Fe_3O_4 · Template · Langmuir adsorption isotherm · Toxin

Introduction

Ochratoxins (OTs) are a group of chemically related mycotoxins that can be present in food [1]. Ochratoxin A (OTA), ochratoxin B (OTB) and ochratoxin C (OTC) are the main ochratoxins among the seven analogues [2] (Scheme S1). Considering their nephrotoxic, teratogenic and immunotoxic effects to human health [3], OTA was classified as a possible carcinogenic compound (Group 2B) for human by the International Agency of Research on Cancer (IARC) [4]. Some countries and organizations have set limitations of OTA for foods, the European Union stipulated the maximum limits as 5 and 3 $\mu g \cdot kg^{-1}$ for raw cereal and processed cereal products, respectively [5], China and Australia marked 5 $\mu g \cdot kg^{-1}$ as the maximum limit for cereal [2, 6]. OTB and OTC were also detected in foods [7], and they additionally become attention focus due to the potential toxicity [2], especially for OTC, which can convert to OTA through oral and intravenous administration [8]. However, the maximum amounts of OTB and OTC have not been limited by any country or organization.

High performance liquid chromatography (HPLC) with fluorometric detection is the main approach to detect OTs in foods [9], often along with a clean-up step, such as solid phase extraction (SPE) [10] or immunoaffinity column (IAC) [7]. Although these pre-concentrations technologies offered advantages like high sensitivity and selectivity, the practical limitations were remained owing to high operation cost, or complicated operating process. Therefore, proposing a robust and rapid pre-treatment way for complex food samples was necessary.

Molecularly imprinted polymers (MIPs) possess predetermined recognition ability, high stability, and a wide range application for analytes [11]. MIPs have been

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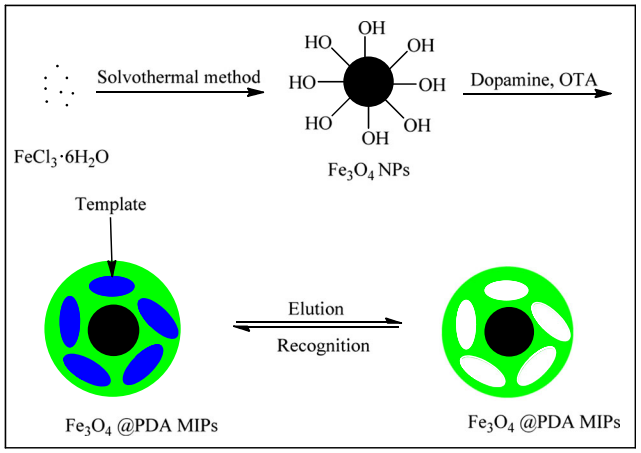
✉ Fangying Wu
fywu@ncu.edu.cn

[1] College of Chemistry, Nanchang University, Nanchang 330031, People's Republic of China

[2] Physical and Chemical Department, Nanchang Centre for Disease Control and Prevention, Nanchang 330038, People's Republic of China

successfully applied in the determination of OTA in wine [12, 13]. However, these MIPs have several limits such as poor accessibility, low affinity binding, high diffusion barrier and the uncompleted removal of template [14]. To overcome the problems above, nanomaterials with small size and high surface-to-volume ratio had been attempted to support the surface imprinting procedure, such as Fe_3O_4 [15], TiO_2 [16], and quantum dots [17]. Fe_3O_4 nanoparticles (Fe_3O_4 NPs) coated MIPs had gained considerable attention owing to the unique size and satisfied physical properties [18]. However, The common synthesis procedure of magnetic MIPs was complicated, which involved functional monomers, cross linkers, initiators and relative harsh conditions, such as oxygen free [19]. Therefore, enhancing the general synthesis procedure of magnetic MIPs was another requirement.

Dopamine was often used to synthesize the magnetic MIPs owing to the ability of self-polymerization in a weak alkaline solution [20, 21]. Herein, dopamine was covered on the surface of the Fe_3O_4 NPs as a adsorption temperate by self-polymerization to synthesize the magnetic MIPs in the Tris-HCl buffer (pH 8.5) (Scheme 1), the product was called Fe_3O_4@polydopamine molecularly imprinted polymers (Fe_3O_4@PDA MIPs). Fe_3O_4@PDA MIPs was able to recognize and enrich the presented OTs in the rice and wine samples through the specific position. Besides, the features and functions of Fe_3O_4@PDA MIPs, which contained MIPs amount, desorption condition and extraction efficiency, were investigated respectively.



Scheme 1 Schematic procedure of the preparation of OTA-imprinted magnetic MIPs

Experimental

Reagents and materials

The standard compounds contained OTA and OTB with the purities 98.14%, and 99.14%, respectively, purchased from Stanford Chemicals Company (Oregon, America, www.stanfordchem.com), OTC with the purity 98%, bought from Toronto Research Chemicals (Toronto, Canada, www.trc-canada.com), aflatoxin B_1 with the purity >99%, purchased from Pribolab Company (Singapore, www.pribolab.com), fumonisin B_1 and zearalenone with the concentration 50.5 $\mu g \cdot mL^{-1}$ and 102.2 $\mu g \cdot mL^{-1}$, purchased from Romer Company (Germany, www.romerlabs.com) and Sigma-Aldrich Company (Australia, www.sigmaaldrich.com), respectively. All chemical reagents for the synthesis of Fe_3O_4 NPs and Fe_3O_4@PDA MIPs were of analytical grade and used without any further purification. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ethylene glycol, anhydrous sodium acetate, hydrochloric acid, sodium hydroxide, dopamine hydrochloride bought from Sinopharm Chemical Reagent (Shanghai, China, www.sinoreagent.com). Methanol and acetonitrile were HPLC grades and purchased from Merck (Darmstadt, Germany, www.merck-chemicals.com).

Standard solutions were prepared as follows: 2.0 mg of OTA, 2.5 mg of OTB and 0.5 mg of OTC were dissolved in acetonitrile and stored in a 1 mL flask, respectively, and then 2.0 $mg \cdot mL^{-1}$ OTA, 2.5 $mg \cdot mL^{-1}$ OTB and 0.5 $mg \cdot mL^{-1}$ OTC was gained. An intermediate standard solutions of OTs at the concentrations of 0.5 $\mu g \cdot mL^{-1}$ OTA, 1.0 $\mu g \cdot mL^{-1}$ OTB and 0.1 $\mu g \cdot mL^{-1}$ OTC were prepared in acetonitrile. And the working standard solutions of their desired concentrations were obtained in acetonitrile. All the standard solutions were stored at 4 °C in the refrigerator. Ultrapure water used from a Milli-Q water purifier (18.2 MΩ·cm) (Millipore, Molsheim, France, www.millipore.com) was used throughout the work.

Preparation of magnetic molecularly imprinted polymers

Fe_3O_4 NPs were synthesized according to our previous work [22]. The magnetic MIPs were prepared according to the document [23] with some modification. Briefly, Fe_3O_4 NPs (0.2 mg) were dissolved in Tris-HCl buffer (80 mL), and the solution was mechanically stirred for 1 h at room temperature until well-suspended. Afterwards, OTA (5 mL 1.6 $\mu g \cdot mL^{-1}$) was added to the solution, stirring for 2 h continually. Then dopamine hydrochloride (100 mg) was added and the reaction was continued for another 4 h at ambient temperature. The Fe_3O_4@PDA MIPs acquired were washed with ultrapure water and the solution of 3% (*v*/v) acetic acid and 20% (v/v) acetonitrile to extract the template molecules until OTA was not detected by HPLC. Finally, the Fe_3O_4@PDA MIPs were dried. For comparison, Fe_3O_4@polydopamine molecularly non-imprinted polymers (Fe_3O_4@PDA MNIPs) were prepared and washed using the same protocol but without OTA as the template molecule in the self-polymerization stage.

Preparation of real samples

In this study, rice and wine were purchased at local supermarkets (Nanchang, China) randomly. And three samples of each kind were taken. Each sample was replicated for five times. All the samples were extracted according to the procedure in GB 5009.96-2016 [24] (See the Electronic Supporting Material).

Extraction procedures

In this work, Fe_3O_4@PDA MIPs (15 mg) was added in 100 mL beaker with ultrapure water (50 mL) at OTs concentrations (0.01–1.0 ng·mL^{-1} OTA, 0.02–2.0 ng·mL^{-1} OTB and 0.002–0.2 ng·mL^{-1} OTC). The solution was adjusted at pH 3 through HCl (0.1 M). After performing the extraction by an ultrasonic water bath for 5 min at room temperature, the magnetic MIPs were separated through a commercial NdFeB magnet (10 × 5 × 4 cm) and the supernatant was decanted. Acetonitrile (1.0 mL) was used to desorb the target compounds from the magnetic MIPs. Acetonitrile solution above (0.5 mL) was mixed with 1% acetic acid solution (0.5 mL), which was the initial composition of the mobile phase during the chromatiographic separation, and then 10 μL of the solution was injected into HPLC for further analysis.

HPLC analysis

All of measurements of OTs were detected by UltiMate 3000 HPLC with Fluorescence Detector (FLD) (ThermoFisher, USA, www.thermofisher.com). The column of separation used was Eclipse Plus C18(150 mm × 4.6 mm, 3 μm) (Agilent; www.agilent.com) at 35 °C as the column temperature. The conditions of the gradient elution were carried out according to GB 5009.96-2016 [24] with a minor modification (See the Electronic Supporting Material).

Results and discussion

Preparation and characterization of magnetic molecularly imprinted polymers

The synthesis of magnetic MIPs which utilized OTA as the template molecule was depicted in Scheme 1. The magnetic MIPs films were formed on the surface of Fe_3O_4 NPs through the unique adhesive effect based on self-polymerization of dopamine. The template OTA was imprinted in the polymer layer through the non-covalent interactions of –NH_2 and –OH groups on PDA as well as the –COOH and –NH groups on OTA. Subsequently, the modified OTA templates were extracted in acidic solution, resulting homologous cavities for the recognition of target OTA, OTB and OTC.

The infrared spectra characterization was performed by the Fourier Transform Infrared Spectrometer (FT-IR) (Bruker, Germany, www.bruker.com). Compared with the absorption bands in Fig. S1A, the Fig. S1B show that two new absorption bands at 1609 cm^{-1} and 1467 cm^{-1} emerged, which corresponded to the C=C stretching vibration in the aromatic rings [25], and the C–C stretching vibration from PDA [20], respectively. Fe_3O_4 NPs and Fe_3O_4@PDA MIPs were also characterized by a JEM-2100 Transmission Electron Microscope (TEM) (JEOL, Japan, www.jeol.cn). Their average diameters (inset of Fig. S1A and B) were 252 nm and 301 nm, respectively. This shows that Fe_3O_4 NPs were fully covered by PDA. Therefore, these results indicate that the PDA film was modified on the surface of Fe_3O_4 NPs. As shown in Fig. S2, Fe_3O_4@PDA MIPs have excellent dispersibility after ultrasonication and can rapidly be separated through an extra magnet, which suggested a satisfied magnet-controlled property.

Extraction condition optimization

It is significant to choose optimal extraction conditions that improve the absorption efficiency of OTs. The recovery was used as an absorption efficiency index in the whole procedure. Therefore, the following parameters were optimized: (a) sample pH value; (b) amount of sorbent; (c) ultrasonic time; (d) desorption conditions; (e) solution volume. Respective data and figures are given in Fig. S3, (See the Electronic Supporting Material). The following experimental conditions were found to give best results: (a) best sample pH value: 3.0; (b) optimal amount of sorbent: 15 mg; (c) ultrasonic time: 5 min; (d) desorption conditions: 1.0 mL acetonitrile; (e) solution volume: 50 mL.

Moreover, Fe_3O_4@PDA MNIPs were used to adsorb three OTs under the above optimized conditions. The recoveries were only 23.2%, 15.8%, and 37.6% for OTA, OTB, and OTC, respectively, which was possibly attributed to the non-covalent combination between target compounds and polydopamine through π-π and hydrogen bonds [21]. The standard chromatogram of OTs under the different materials was showed in Fig. 1. Comparing to the standard chromatogram produced by the pretreatment utilized direct injection (d), the retention time and the peak area of OTs pretreated by Fe_3O_4@PDA MIPs (c) are almost the same, however, three OTs pretreated by Fe_3O_4@PDA NMIPs (b) have much lower peak areas. This indicates the imprinted cavities of Fe_3O_4@PDA MI Ps were formed and exhibited the high affinity toward target compounds.

Reusability of Fe_3O_4@PDA MIPs

To test the reusability of Fe_3O_4@PDA MIPs, 10 mL of acetonitrile as the optimum desorption solvent were used to rinse

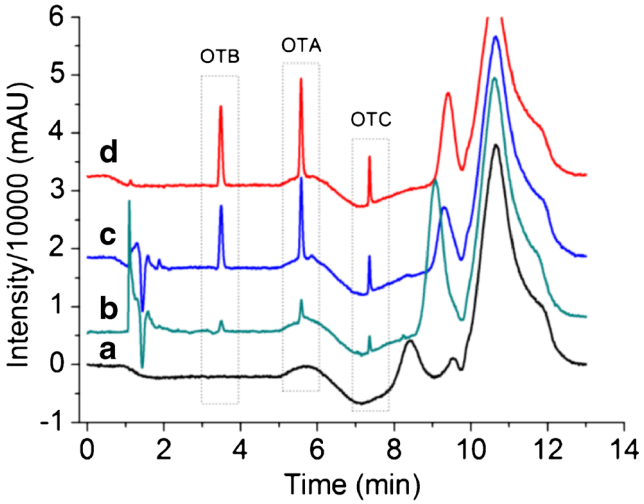


Fig. 1 The standard chromatogram of blank (**a**), after pretreatment by Fe_3O_4@PDA NMIPs (**b**), after pretreatment by Fe_3O_4@PDA MIPs (**c**) and by direct injection (**d**) with OTA and OTB 1.0 ng·mL^{-1}, OTC 0.2 ng·mL^{-1}

the MIPs to recover the template for twice before applying in the next. Fig. S5 indicates that the adsorption efficiencies for the three OTs had no significant decrease after at least seven consecutive adsorption-desorption cycles, and the recoveries were more than 86.8%, 82.6% and 80.2% for OTA, OTB and OTC, respectively. This manifested that Fe_3O_4@PDA MIPs have satisfied stability.

Adsorption isotherms

The binding properties of the Fe_3O_4@PDA MIPs for the three OTs were studied. In general, two models which the Langmuir for describing monolayer adsorption, and the Freundlich for assuming heterogeneous surface energy were applied to evaluate the adsorption property [26]. The isotherms data was then fitted to the Langmuir or Freundlich models to assess the adsorption capacity and the adsorption mechanisms of the adsorbent at a certain temperature. Equilibrium isotherm was determined by using batch studies with various initial concentrations of the three OTs (0.016–4 mg·L^{-1} for OTA, 0.032–0.16 mg·L^{-1} for OTB and 0.0032–0.4 mg·L^{-1} for OTC) at 25 °C under the optimal conditions.

The parameters of the Langmuir equation and Freundlich equation were calculated according to our previous report [3]. Table S1 shows that the correlation coefficients of OTA, OTB and OTC were 0.994, 0.995 and 0.997 from the Langmuir equation, respectively, which given better fitting than those provided by the Freundlich model ($R^2 = 0.986$, 0.929 and 0.938, respectively). This illustrates that the Langmuir isotherm model provided with more satisfied the experimental data, and the results suggest the mechanism that three OTs were adsorbed on the surface of Fe_3O_4 @PDA MIPs through the monolayer molecular adsorption. The maximum adsorption capacities were calculated by the Langmuir equation as 1.8 mg·g^{-1}, 0.23 mg·g^{-1} and 0.17 mg·g^{-1}, respectively, which were far outweighed to the limitation level of OTA (5 μg·kg^{-1}) in China.

Coexisting compounds studies

Aflatoxin B_1, fumonisin B_1 and zearalenone are common several mycotoxins presented in food samples. Thus, to evaluate the selectivity of the method, the interference of the three mycotoxins to the recoganition of Fe_3O_4@PDA MIPs was investigated. The presence of following amounts of foreign substances compared with the concentration of 1.0 ng·mL^{-1} OTA resulted in less than ±5%: 50 fold (50 ng·mL^{-1}) aflatoxin B_1 and fumonisin B_1, and 20 fold (20 ng·mL^{-1}) zearalenone. Additionally, three batches of each coexisting compound were performed under the same batch of magnetic MIPs. Fig. S6 show that the recoveries of OTs under each coexisting compound were more than 80% with RSDs which below 3.8%. Since the measured amounts of coexisting substances in real sample were lower than the tolerable concentrations, the extraction capacity of Fe_3O_4@PDA MIPs to the target was proved.

Analytical performance

Under the optimized conditions, the calibration curves were obtained in the range of 0.01–1.0 ng·mL^{-1} OTA, 0.02–2.0 ng·mL^{-1} OTB and 0.002–0.2 ng·mL^{-1} OTC for a sample volume of 50.0 mL with the calibration curves eq. Y = 37,812.9X + 5532.0, Y = 12,856.0X + 105.3 and Y = 56,021.5X + 91.2 (Y, the peak area and X, ng·mL^{-1} of the target), the correlation coefficient (R) were 0.9995, 0.9995 and 0.9996, respectively. The limits of detection (LODs) with three times of the S/N ratio were 1.8 pg·mL^{-1} for OTA, 18 pg·mL^{-1} for OTB and 3.2 pg·mL^{-1} for OTC. To verify the reproducibility of the method, three different batches magnetic MIPs were prepared according to the synthesized protocol strictly. The recoveries were measured under the optimized conditions. The results show that the recovery deviations of the three materials were less 5.0%. This illustrated an excellent reproducibility of the magnetic MIPs for extraction of OTs.

Analysis of real samples

In order to evaluate the accuracy and practicability of the method, three different levels of OTs were added in real samples of rice and wine with five parallels tests for the recoveries. Table S2 presents the recoveries, the OTA, OTB and OTC in the rice and wine were 70.0–90.0%, in addition, the RSDs were 2.3–3.8% for real samples. However, for coffee sample,

Table 1 Comparison of the different analytical methods for the determination of OTs in food

Detection method	Sample	Sample treatment	Recovery (%)	LOD ($\mu g \cdot kg^{-1}$)			Ref.
				OTA	OTB	OTC	
LRET	Beer	LLE	94–119%	0.027			[27]
Electrochemical sensor	Cereal	IAC	96–113.1%	0.002			[28]
Electrochemical sensor	Red wine	AuPtNPs	94.4–109%	0.000075			[29]
Fluorescence assay	Beer, wine	SWCNHs	92–115.9%	1.6			[30]
LC-Orbitrap	Dairy products	LLE, Cleanup (salt) and SPE	86.6–113.7%	0.009	0.01		[31]
LC-MS/MS	Milk	LLE and Cleanup (salt)	86.4–88.1%	0.2	0.05		[32]
LC-MS/MS	Wheat	LLE	88.0–104.0%	0.3	0.5		[33]
ELISA	Millet and maize	LLE	84.3–111.7%	0.005	0.001	0.001	[2]
HPLC	Rice and wine	LLE and Cleanup (MIPs)	71.0–88.5%	0.0018	0.018	0.0032	This work

LRET luminescence resonance energy transfer, *LLE* liquid liquid extraction, *IAC* immunoaffinity column, *AuPtNPs* platinum-enclosed gold cores, *SWCNHs* single-walled carbon nanohorns, *LOD* limit of detection

the recoveries of OTs (no more than 40%) were low due to matrix effects. This illustrated that the method exhibited a favourable accuracy and excellent precision for the determinations of OTs in rice and wine samples.

Many pre-treatment and analytical methods have been used to enrich and detect OTs in food samples. Compared with these reported methods, the magnetic MIPs as a sample pre-treatment technology owned many cavities to recognize OTs effectively. Simultaneously, the magnetic MIPs were reused for many times (more than 7 cycles). Although the recoveries were lower than other methods, the magnetic MIPs can recognize and enrich three OTs with the LODs of 1.8–18 $pg \cdot mL^{-1}$. The comparison results were given in Table 1. This indicated that Fe_3O_4@PDA MIPs was an ideal extraction technique in the pre-treatment of OTs in rice and wine.

Conclusions

A pre-concentration technology based on Fe_3O_4@PDA MIPs for the extraction of OTs was established for food samples. The magnetic MIPs possessed both of magnetic nanoparticles and MIPs properties. In comparison with the traditional pre-concentration ways, this strategy possessed small amounts of Fe_3O_4@PDA MIPs, high separation rate and good adsorption capacity for the targets. In addition, Fe_3O_4@PDA MIPs were easy to regenerate at least 7 cycles without the obvious decrease of recovery after washing procedures. Hence, the Fe_3O_4@PDA MIPs were applied with HPLC as a sensor to separate and detect the OTs in rice and wine samples. Future work will be done to purify the matrix from coffee sample and further improve the specificity for the magnetic MIPs.

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Compliance with ethical standards The authors declare that they have no competing interests.

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