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Core-shell poly(dopamine) magnetic nanoparticles for the extraction of estrogenic mycotoxins from milk and yogurt prior to LC–MS analysis

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ABSTRACT

In this work, core-shell poly(dopamine) magnetic nanoparticles synthesized in our laboratory have been applied as dispersive solid-phase extraction (dSPE) sorbent for the extraction of a group of six mycotoxins of interest including zearalenone, α-zearalanol, β-zearalanol, α-zearalenol, β-zearalenol and zearalanone, from complex matrices such as milk (whole and skimmed cow milk and semi-skimmed goat milk) and yogurt (an unsweetened natural yogurt) prior to their LC–MS analysis. 17β-estradiol-D_5 was used as internal standard. The procedure includes a deproteinization step prior to the extraction procedure. Matrix-matched calibration and a recovery study were carried out in the selected matrices, providing good linearity, relative recovery values in the range 70–120% with RSDs lower than 16% and LODs between 0.21 and 4.77 μg/L for milk samples and between 0.29 and 4.54 μg/kg for yogurt samples.

1. Introduction

Mycotoxins are toxic secondary metabolites produced by different fungi species, which contaminate agricultural commodities either before harvest or under post-harvest conditions (Belhassen et al., 2015). One of the most relevant groups of mycotoxins found in food includes zearalenone (ZEN) and its derivatives α-zearalanol (α-ZAL), β-zearalanol (β-ZAL), α-zearalenol (α-ZEL), β-zearalenol (β-ZEL) and zearalanone (ZAN) which, contrary to other mycotoxins, are capable of binding to estrogenic receptors producing multiple endocrine disorders (Zinedine, Soriano, Moltó, & Mañes, 2007). These mycotoxins have an important estrogenic activity and their estrogenic potential changes from one compound to another. It has been demonstrated that β-ZEL shows a higher estrogenic activity than α-ZEL or ZEN (Marin, Ramos, Cano-Sancho, & Sanchis, 2013).

The intake of contaminated foodstuffs constitutes the main via of human exposure to such mycotoxins. In this sense, milk and dairy products play a very important role since they represent an important part of the diet of humans all over the world. Besides, this kind of compounds tend to accumulate in fatty tissues due to their lipophilic nature reaching the milk of animals quite easily (Socas-Rodríguez, Asensio-Ramos, Hernández-Borges, & Rodríguez-Delgado, 2013). Furthermore, it should be taken into account that the contamination of food of animal origin may take place through the intake of contaminated feed or by the intentional administration of these compounds; in particular, α-ZAL has been widely used as growth promoter (Flores-Flores, Lizarraga, López de Cerain, & González-Peñas, 2015). As a result, ZEN and its metabolites, including α-ZAL, were banned in the European Union (EU) in 1996 in order to protect the health of the consumers (European Community Council Directive, 1996), though maximum residue limits (MRLs) have not been established yet for any of them in milk.

Regarding the analysis of ZEN and its metabolites in milk and dairy products, few papers are available in the literature. Due to the complexity of milk and dairy products samples, a previous extraction step is necessary in order to preconcentrate the target analytes and remove interferences. Different extraction techniques have been applied to achieve this goal, principally SPE (Capriotti et al., 2015; Huang et al., 2014; Xia et al., 2009), though others like DLLME (D'Orazio, Asensio-Ramos, Hernández-Borges, Rodríguez-Delgado, & Fanali, 2015) or LLE (Tsiplakou, Anagnostopoulos, Liapis, Haroutounian, & Zervas, 2014) have also been used. Besides the above mentioned methods, some works can be found in which several techniques are used in order to improve the removal of the interferences. This is the case of the use of ultrasound assisted extraction (UAE) combined with a defatting and a SPE clean-up

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step (Chen et al., 2013) or LLE followed by a SPE used for clean-up (Sørensen & Elbæk, 2005). Finally, it is worthy to mention the work of Zhang et al. (Zhang et al., 2013) who decided not to include any extraction step and replace it for a dilution and sample filtering.

In recent years, nanomaterials have gained importance in diverse fields and also in Analytical Chemistry. In this sense, magnetic nanoparticles (m-NPs) have aroused great interest in extraction and preconcentration techniques, principally due to their capacity to be easily isolated from the matrix by an external magnet without retaining residual magnetization. Because of their particular physical and chemical properties (among other good features), both iron oxides (magnetite, Fe_3O_4, and maghemite, γ-Fe_2O_3) have been the m-NPs most widely used in dispersive SPE (dSPE) as well as other applications (Martín, González Orive, et al., 2014; Martín, Salazar, et al., 2014; Shi et al., 2014). This nanomaterial has to be coated with an inorganic or organic layer to increase its stability, protecting it against oxidation and avoiding the formation of agglomerates. In that way, by using specific coatings it is also possible to carry out a further functionalization of their surface, which may be used to establish successful interactions with the target analytes without losing the magnetic properties. In this sense, dopamine (DA) has attracted wide interest due to its self-polymerization capacity in aqueous phase under weak alkaline conditions, allowing the formation of a surface-adhesive film onto a diversity of organic and inorganic materials (Lee, Dellatore, Miller, & Messersmith, 2007). To the best of our knowledge, poly(DA) (pDA) NPs, also designated as NPs@pDA, have only been applied in magnetic SPE (m-SPE) in very few occasions (Ma et al., 2013; McCullum, Tchounwou, Ding, Liao, & Liu, 2014; Shi et al., 2014; Socas-Rodríguez, Hernández-Borges, Salazar, Martín, & Rodríguez-Delgado, 2015; Wang et al., 2013). That is why there is still the need of demonstrating the full potential of these new materials for the extraction of a wide variety of analytes, specially, from complex food matrices. In particular, they have been successfully applied to the determination of four aflatoxins from red wine (McCullum et al., 2014), berberine from a Chinese medical plant (*Cortex Phellodendri*) (Shi et al., 2014), six polycyclic aromatic hydrocarbons from environmental water samples (Wang et al., 2013) and seven antibiotics, three perfluorinated compounds and benzo(a)pyrene from lake and tap water (Ma et al., 2013). Finally, a previous work developed by our group also applied for the first time laboratory-made core-shell Fe_3O_4@pDA m-NPs as sorbents for the m-μSPE of a group of twelve compounds with estrogenic activity from water samples (Socas-Rodríguez et al., 2015). The synthetic procedure demonstrated to be very easy, simple and with a very low cost.

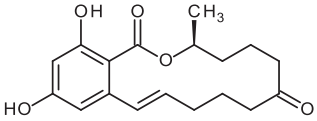
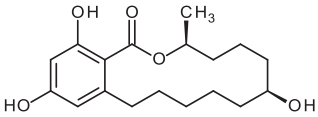
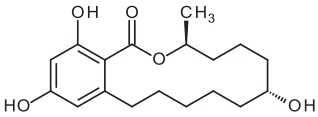
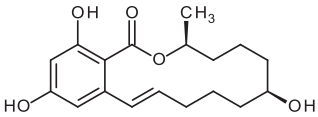
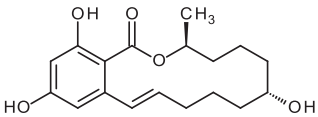
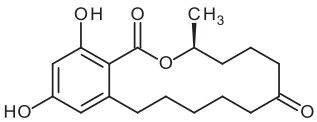
Taking into account the above, the aim of this work was to prepare core-shell Fe_3O_4@pDA m-NPs and to explore their possible application as sorbent for the m-μSPE of a group of six mycotoxins, including ZEN and its metabolites α-ZAL, β-ZAL, α-ZEL, β-ZEL and ZAN from complex food matrices, such as milk (a whole and skimmed cow milk and a semi-skimmed goat milk) and yogurt (an unsweetened natural yogurt). To the best of our knowledge, this is the first time that the performance of Fe_3O_4@pDA-m-μdSPE is applied for the extraction of estrogenic mycotoxins from milk and dairy products. Furthermore, this work constitutes one of the very few articles in the literature dealing with the analysis of this group of mycotoxins in dairy products.

2. Experimental

2.1. Chemicals and materials

Mycotoxin analytical standards of ZEN (CAS 17924-92-4), β-ZAL (CAS 42422-68-4), α-ZAL (CAS 26538-44-3), β-ZEL (CAS 71030-11-0), α-ZEL (CAS 36455-72-8), and ZAN (CAS 5975-78-0) from Sigma-

Table 1
Chemical structure and some properties of the studied mycotoxins.

Analyte	Structure	Molecular formula	M (g/mol)	Solubility in water (g/L, 25°C)	Vapor pressure (mmHg)	Log K_{OW}	Melting point (°C)	pK_a
Zearalenone (ZEN)		$C_{18}H_{22}O_5$	318.4	$9.6{\cdot}10^{-1}$ (pH 1–5)	$5.21{\cdot}10^{-15}$	2.765 ± 1.193	162–165	7.58 ± 0.40
β-Zearalanol (β-ZAL)		$C_{18}H_{26}O_5$	322.4	$5.5{\cdot}10^{-1}$ (pH 1–6)	$4.16{\cdot}10^{-14}$	4.648 ± 0.508	152–158	8.08 ± 0.60
α-Zearalanol (α-ZAL)		$C_{18}H_{26}O_5$	322.4	$5.5{\cdot}10^{-1}$ (pH 1–6)	$4.16{\cdot}10^{-14}$	4.648 ± 0.508	180–182	8.08 ± 0.60
β-Zearalenol (β-ZEL)		$C_{18}H_{24}O_5$	320.4	1.9 (pH 1–5)	$3.40{\cdot}10^{-15}$	3.184 ± 1.175	173–174	7.61 ± 0.60
α-Zearalenol (α-ZEL)		$C_{18}H_{24}O_5$	320.4	1.9 (pH 1–5)	$3.40{\cdot}10^{-15}$	3.184 ± 1.175	169–170	7.61 ± 0.60
Zearalanone (ZAN)		$C_{18}H_{24}O_5$	320.4	$2.6{\cdot}10^{-1}$ (pH 1–6)	$6.65{\cdot}10^{-14}$	4.284 ± 0.548	190–195	7.83 ± 0.40

Data taken from (SciFinder® database).