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A NOVEL MOLECULARLY IMPRINTED MAGNETIC MATERIAL FOR THE ACCURATE DETERMINATION OF ZEARALENONE MICOTOXIN IN COMMERCIAL FLOUR SAMPLES BY HPLC-MS/MS

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Zearalenone (ZEN) belongs to the class of mycotoxins mainly produced by Fusarium fungi and generally occurs in cereal grains. ZEN shows oestrogenic activity and, due to its persistency in the food chain, it constitutes a risk to human and animal health thus requiring monitoring actions. For this reason, analytical methods for its accurate determination are required and pre-concentration and clean-up become fundamental aspects to take into account. Molecularly imprinted polymers (MIPs) are widely used as selective or specific materials for sample extraction and enrichment; some examples can be found about MIPs prepared for the extraction of ZEN from different matrices, mainly obtained by bulk polymerization. In this framework, a great improvement can be brought by employing MIP particles in the nanometre dimension range, which provide extensive contact with the sample, hopefully improving analyte recovery. The present work deals with the preparation of MIPs nanoparticles, designed for ZEN binding, and their application to ZEN extraction from different flour samples for the consequent analysis by liquid-chromatography coupled to mass spectrometry (LC-MS). The material was prepared by an innovative polymerization approach, which involves multiple steps: a controlled aggregation of magnetite particles; a coating and functionalization of the aggregates with tetraethylorthosilicate and vinyltriethoxysilane; finally, the formation of an external polymer shell, synthesized in the presence of a dummy template molecule, in order to obtain specific cavities for the interaction with ZEN. The dummy template molecule (quercetin) was selected for its structural similarity to the analyte of interest and was preferred to the use of the real template to avoid problems of contamination due to residual ZEN in the material. The dimension of the MIP nanoparticles was monitored during the entire synthesis, which led to a final average diameter of 900 nm. The corresponding non-imprinted polymer (NIP) was prepared as well, for selectivity comparison, and both materials were characterized by scan electron microscopy (SEM), showing a similar morphology. The thermodynamic and kinetic behaviours of both ZEN-MIP and NIP were investigated by means of static and dynamic adsorption tests, demonstrating a higher adsorption capacity of the imprinted nanoparticles and quick kinetics, with equilibrium reached after a 10 min contact. The ZEN-MIP material had 55-fold more affinity for ZEN than the NIP material, which supported its potential for ZEN pre-concentration from complex food matrices. Therefore, a simple protocol was

proposed for the pre-treatment of flour samples, slightly modifying a previous method developed in our laboratory [1]. After evaporating an acetone extract of the flour sample, the residue was reconstituted in a suitable solvent and put in contact with the MIP material for 30 min; afterwards, the MIP was washed, to remove interferents physically adsorbed onto the surface, and two elution steps were performed to recover ZEN. The samples were analysed by HPLC-triple quadrupole MS in multiple reaction monitoring, to enhance specificity and sensitivity. Excellent recovery (89±11 %) and matrix effect (101±2 %) were observed for the compound of interest, by testing three fortification levels on blank samples. The method detection and quantitation limits were 44 and 140 pg g^{-1} respectively, while repeatability was assessed by evaluating intra-day and inter-day relative standard deviations (7% and 10%, respectively). The proposed method was compared with a simple solid-liquid extraction and with a clean-up by classical solid phase extraction, showing a significant improvement in the observed matrix effect by using the MIP material. Finally, seven flour samples of different cereals were analysed, demonstrating the suitability of the method to ZEN accurate determination in complex matrices.

References

[1] La Barbera G., Capriotti A., Cavaliere C., Foglia P., Montone C., Chiozzi R., Laganà A., Toxins, 2017, 9, 147.