

Magnetic solid-phase extraction based on palmitate coated magnetite nanoparticles for the analysis of PAHs in soil leachates

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Polycyclic aromatic hydrocarbons (PAHs) are toxic substances that are resistant to degradation and have been included in the European Union list of priority pollutants [1]. Soil is an important reservoir of these contaminants but, due to their hydrophobic nature and low water solubility, a measurement of their total remaining amount in soil is a poor indicator of its potential environmental impact.

Solid-phase extraction (SPE) is the methodology most commonly used in the analysis of pollutants in aqueous samples; nevertheless, this is a time consuming and laborious technique for large sample volumes. Magnetic SPE (mSPE) methods using magnetic nanoparticles (MNPs) have been recently applied to the separation and pre-concentration of pollutants in environmental matrices, mainly in water samples. In recent years, nanoparticles of magnetite (Fe_3O_4) subjected to different surface modifications (using surfactants, polymeric coating, biosorption thin-film, etc.) were assayed as new mSPE adsorbents.

In this work, mSPE using palmitate (PA) coated magnetite NPs coupled with gas chromatography-tandem mass spectrometry (GC-MS/MS), was developed for the extraction of 16 PAHs from soil leachates. Finally, the developed methodology was applied to evaluate the PAHs leached from soils with different physico-chemical characteristics.

Experimental

GC-MS/MS analysis was performed with an Agilent 7890A gas chromatograph equipped with a multimode inlet (MMI) and coupled to an Agilent Model 7000 triple quadrupole mass spectrometer Model 7000. The MMI was operated in solvent vent mode with a liner packed with glass wool. The optimized chromatographic program consisted on three MS/MS transitions, one quantifier and two qualifier transitions, for most of the target compounds. Analytes were confirmed by their retention time and the identification of target and qualifier transitions. The quantification of the studied compounds was based on their relative response factor to seven calibration standards in the range from 2 to 80 ng mL⁻¹. Each calibration level was spiked with 50 ng mL⁻¹ of labelled internal standards.

Soil Extraction. Extraction and clean-up of PAHs from soil were carried out by ultrasound assisted extraction (UAE) following a procedure previous developed by our group for the analysis of these compounds in soil [2].

Soil leachates were obtained by placing 5 g of soil in centrifuge tubes together with 50 mL of ultrahigh-quality water. Samples were rotated during 24 h using an overhead shaker Heidolph at ambient temperature. Then, the tubes were centrifuged at 4500 rpm for 30 min and supernatants were collected and filtered through glass fibre filters, 2.1 cm diameter and 2.7 µm pore size, placed at the end of 20 mL glass columns.

Preparation and characterization of the MNPs. PA coated MNPs were obtained following the procedure described by Ballesteros and Rubio [3]. The morphology and particle size of the coated MNPs were examined by transmission electron microscopy (TEM) in a JEOL JEM 2100. Element analysis was performed with a LECO CHNS-932 microanalyser. The spectroscopic study was conducted on a Jasco FTIR-460 Plus spectrophotometer.

mSPE procedure. A 50 mL volume of soil leachate, 2.5% of acetone and 200 mg of PA-coated MNPs were mixed in a 100 mL conical flask closed with a glass cap. The flasks were stirred for 45 min using a Vibromatic Rocking at a vibration frequency of 370 oscillations min⁻¹. Then, the MNPs were isolated by

placing the magnet on the wall of the flask and discarding the soil leachate. The MNPs were then extracted twice with 2 mL of ethyl acetate and the combined extracts were concentrated to 1 mL. Finally, the labelled standard solution was added and the extract was injected into the GC-MS/MS system for analysis.

For recovery studies, soil leachates were spiked with the appropriate working solutions in methanol, the fortified samples were extracted by mSPE following the procedure described above.

Results and discussion

Surface modification of the Fe_3O_4 NPs with PA was confirmed by TEM, element analysis and Fourier transform infrared spectroscopy. The effect of several parameters on the extraction efficiency of 16 PAHs from soil leachates was evaluated. Firstly, the type of agitation, sample volume (50 and 100 mL), extractive solvents of the PAHs from the MNPs (acetonitrile and ethyl acetate) were evaluated, followed by the evaluation of the effects of different parameters that could affect the performance of the extraction, such as the extraction time (15, 30 and 45 min), salt addition (0, 0.1 M and 0.2 M KCl), percentage of organic solvent in the extract (from 0 to 10%) and the amount of NPs (100 and 200 mg). The optimal extractive procedure is described in the experimental section.

Efficiency of the nanoparticles for the extraction of PAHs from soil leachates was evaluated. Recoveries of these contaminants from soil leachates spiked at three different fortification levels, from 0.2 to 1 ng mL^{-1} , were low for the four PAHs with lower molecular weights and satisfactory for the rest (ranging from 68 to 120% for the others, with standard deviations < 9 %). The developed method provided a preconcentration factor of, at least, 50 times and the limits of detection ranged from 0.8 to 5.1 ng L^{-1} .

Finally, the developed method was successfully applied to soil leachates obtained from soils with different physico-chemical characteristics. The amount PAHs present in the leachates may be explained by the soil organic matter content together with other soil characteristics.

The present work demonstrates the applicability of the PA- Fe_3O_4 NPs for the determination of PAHs in soil leachates, which is of interest for mobility and bioavailability studies of these pollutants in soil. As far as we know, this is the first reported study on the application of MNPs to the analysis of contaminants in soil leachates.

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References

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