

Magnetic solid-phase extraction of pesticides in environmental water samples using Fe₃O₄@SiO₂@C18 nanoparticles coupled to GC-MS determination

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Abstract

A rapid magnetic solid-phase extraction (MSPE) method coupled to Gas Chromatography-Mass Spectrometry (GC-MS) was developed for the simultaneous extraction of ten pesticides belonging to various categories (insecticides, herbicides and fungicides) in environmental water samples. The magnetic Fe₃O₄@SiO₂@C18 nanoparticles were synthesized by coprecipitation of Fe²⁺ and Fe³⁺ ions, at alkaline conditions, under hydrothermal treatment and used as adsorbents of MSPE.

The proposed method is optimized by means of experimental design and response surface methodology. Several parameters influencing MSPE efficiency were investigated. The most important were the amount of the sorbent and the extraction time. Under optimal conditions, the MSPE-GC-MS method presented fast simple separation and analysis, and excellent linearity in the range of 6.4–5000.0 ng/L, with coefficients of determination (R²) higher than 0.9901 for all compounds. Moreover, the performance of the MSPE method was compared to a conventional SPE and the MSPE method was comparable.

Finally, the optimized method was applied in a case-control study carried out in Rivers Aliakmonas, Loudias and Axios (Macedonia Region-North Greece). The most frequently detected compounds were atrazine, methylparathion, chlorpyrifos and irgarol.

The magnetic Fe₃O₄@SiO₂@C18 composites based MSPE method proved promising for convenient and efficient determination of pesticides in environmental water samples.

Keywords: Experimental Design, GC-MS, magnetic solid-phase extraction, natural waters, pesticides

1. Introduction

The occurrence of pesticides and their conversion products in aquatic system is one of the major environmental problems worldwide. These residues may cause long-term adverse effects to the aquatic environment, and even harm human life. Therefore, it is extremely essential to develop convenient, sensitive and rapid methods for their determination (Ccanccapa A., *et al.*).

Sample pretreatment procedures are crucial for the whole analysis process, which aim at enriching targeted analytes

and eliminating matrix effect. Magnetic solid-phase extraction (MSPE), has drawn extensive attention in sample preparation in recent years (Ma J *et al.*), (Synaridou M. *et al.*). Is a new mode of SPE based on the adoption of magnetic nanoparticles (MNPs) as sorbents, at micro- or nano-scale and shows great advantages in separation science. The powdery magnetic adsorbent can be reversibly agglomerated and re-dispersed in solution or suspensions by the application and removal of an appropriate magnetic field, thus realizing the phase separation conveniently.

2. Materials and Methods

Analytical standards were purchased by Fisher Scientific (Leicestershire, UK), purity >98.4%. Stock standard solutions were prepared at a concentration of 5-100 µg/L in methanol and were stored at -20°C. All solvents used were of pesticide residue analysis grade and purchased from Labscan (Dublin, Ireland). OasisTM HLB cartridges (divinylbenzene/N-vinylpyrrolidone copolymer, 200 mg, 6 cm³) were purchased from Waters (Mildford, MA, USA).

Preliminary experiments were initially performed in order to evaluate the MSPD extraction efficiency using different solvents (n-Hexane, Methanol and Ethyl-acetate). Results obtained have shown that Ethyl-acetate displayed the highest extraction efficiency. The influence of the ionic strength was also investigated in the range of (0-5% (w/v)). In all cases enrichments factors were slightly decreased with increasing ionic strength.

For the selection and assessment of the other main factors affecting the extraction a Box-Behnken design (BBD) was applied. A total of 15 runs were carried out according to the BBD and low, middle and high levels of the coded values were designated for the variables. Finally, optimal extraction conditions were obtained using the desirability function of the STATISICA 7.0 software. The optimal conditions to extract pesticides with the aid of MSPE are 55mg of Fe₃O₄@SiO₂@C18 as sorbent, extraction time 7 min and elution time 5 min. Under optimal conditions, the model predicted maximum total extraction profitability of 0.9789.

Isolation of target analytes from natural water samples were performed off-line, using the proposed MSPE method. Before the MSPE procedure, 55 mg of the sorbent ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C18}$) were placed into 50 mL beaker, previously activated with methanol (2 mL). Afterwards, 10 ml of water sample was added into the beaker. The mixture was vortexed for 1 min and then sonicated for 7 min. Subsequently, an ordinary magnet was placed at the bottom of the vial to harvest the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C18}$ NPs and the supernatant was discarded. The pesticides were desorbed with 2*1.5 mL of ethyl acetate by ultrasonication (5 min) and the desorption solution was separated from the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C18}$ NPs by the magnet and collected in a vial. The extracts were evaporated to dryness under a gentle stream of N_2 and reconstituted into 100 μL of hexane. The final sample was filtered directly into an analysis vial using 0.45 μm PVDF syringe filter and injected to a Gas Chromatography coupled with Mass Spectrometry (GC-MS).

3. Results and discussion

The optimum conditions were implemented to verify the applicability of the proposed method for the quantitative determination of target analytes. Quality parameters including, the linear range, the accuracy R (%), the limits of detection (LODs), and limits of quantification (LOQs) the intra-day precision RSD_r (%), inter-day precision RSD_R (%), were investigated. Linearity in the range of 6.4–5000.0 ng/L, with coefficients of determination (R^2) higher than 0.9901 for all compounds. Average

recoveries of target analytes are found to be in the range of 60-98,7%. High sensitivity with limits of detection ranging from 6,4-240 ng/L, were achieved, as well as good precision with relative standard deviations of 1.6-14.5% (intra-day).

Through an extensive sampling in the Rivers Axios, Loudias and Aliakmonas, located in Macedonia Region in the North Greece, the presence of 10 currently used pesticides in water was assessed. Fifteen water samples stations were established, and 43 samples were collected. Four pesticides had detection frequencies greater than 10% in Aliakmonas River, the longest river in Greece. The most frequently detected were two herbicides atrazine and irgarol and two insecticides methyl-parathion and chlorpyrifos. Three pesticides (ethoxyquine, chlorothalonil and chlorpyrifos-methyl) were not detected in any sample.

4. Conclusions

Functionalized MNPs were synthesized to serve as solid-phase extraction sorbents for simultaneous enrichment and detection of pesticides in natural waters with the aid of GC-MS. The developed method has been demonstrated to be simple, sensitive, cost-effective and potentially applicable for the determination of pesticides. Considering that these nanoparticles are easy-to prepare, cost effectiveness and easy of separation and dispersion, this method is promising for the screening of the selected compounds in natural waters.

References

- Ccancapa A., Masia A., Navarro-Ortega A., and Picó Y., (2016), Pesticides in the Ebro River basin: Occurrence and risk assessment, *Environmental Pollution*, **211**, 414-424.
- Ma J., Wu G., Li S., Tan W., Wang X. and Li J., (2018), Magnetic solid-phase extraction of heterocyclic pesticides in environmental water samples using metal-organic frameworks coupled to high performance liquid chromatography determination, *Journal of Chromatography A*, **1553**, 57-66.
- Synaridou M., Sakkas V., Stalikas C. and Albanis T., (2014), Evaluation of magnetic nanoparticles to serve as solid-phase extraction sorbents for the determination of endocrine disruptors in milk samples by gas chromatography mass spectrometry, *Journal of Chromatography A*, **1348**, 71-79.