UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF MESOPOROUS MCM-41 AND SBA-15 SILICA FOR DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES IN FRUIT SAMPLES BY USING DISPERSIVE AND MAGNETIC SOLID PHASE EXTRACTIONS

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

Widespread use of organophosphorus pesticides in fruits leads to residue accumulation and bioaccumulation. Traces amounts of organophosphorus pesticides (OPPs) in fruits have made their analyses difficult, hence sample pre-concentration is crucial. This study investigated four types of mesoporous silica sorbents namely MCM-41, Fe_3O_4-MCM-41, SBA-15 and Fe_3O_4-SBA-15 for the microextraction of OPPs from fruit matrices prior to high performance liquid chromatography ultraviolet detection (HPLC/UV) analysis. Mesoporous silica MCM-41 and SBA-15 were successfully synthesized and characterized using fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption analysis and vibrating sample magnetometer (VSM). MCM-41 and SBA-15 were employed as sorbents in the dispersive solid phase extraction (DSPE) of three OPPs including chlorpyrifos, diazinon and parathion methyl. Under optimized conditions the proposed SBA-15/DSPE method provides good linearity ($r^2 \geq 0.9922$) with good limit of detection (LODs) for analyte in fruit samples in the range (0.03-0.09 mg/L). Meanwhile, MCM-41/DSPE also showed good linearity ($r^2 \geq 0.9912$) with good LODs (0.04-0.10 mg/L). The DSPE proved a successful extraction technique with high relative recoveries in the range of 80.7% to 96.0% and 73.0% to 112.4% for the SBA-15 and MCM-41, respectively. The use of SBA-15 and MCM-41 magnetized with iron oxide (Fe_3O_4) in the magnetic solid phase extraction (MSPE) were investigated. The developed method (Fe_3O_4-SBA-15/MSPE and Fe_3O_4-MCM-41/MSPE) were applied for the extraction of three selected OPPs (chlorpyrifos, diazinon and parathion methyl) in grape and strawberry spiked samples prior to HPLC-UV analysis. Both sorbents combined the advantages of high adsorption capacity of mesoporous silica and the capability of magnetite particles for easy isolation from the samples. Under optimized conditions, the results of Fe_3O_4-SBA-15/MSPE method provided good linearity ($r^2 \geq 0.9942$) with excellent relative recoveries (89.2 – 118.9%) and low LODs (0.03-0.08 mg/L), while Fe_3O_4-MCM-41/MSPE demonstrated good linearity ($r^2 \geq 0.9935$) with excellent limits of detection (LODs) (0.04 - 0.09 mg/L) and good relative recoveries of (83.5-120.0%). This method proved to be rapid and efficient for simultaneous analysis of OPPs in fruit spiked samples. The overall results proved that the proposed methods provide alternative approaches in sample preparation through different microextraction methods to solve analytical problems.

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