Magnetic Solid Phase Extraction using Magnetic Mesoporous Silica for Preconcentration of Organophosphorus Pesticides

Nur Husna Zainal Abidin, Wan Nazihah Wan Ibrahim, Nor Suhaila Mohamad Hanapi

Abstract: *The present study describes the synthesis, characterization and application of two mesoporous silica material based coated magnetic nanoparticles namely Fe_3O_4-SBA-15 and Fe_3O_4-MCM-41 for the simultaneous preconcentration of three selected organophosphorus pesticides (OPPs) namely chlorpyrifos, diazinon and parathion methyl from water samples. The resultant sorbent material was physicochemically and morphologically characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and N_2 adsorption analysis. OPPs pesticides extraction efficiency of two sorbents were evaluated through magnetic solid phase extraction (MSPE) using high performance liquid chromatography with ultraviolet detector (HPLC/UV). The main parameters affecting the sorbent efficiency namely extraction time and desorption solvent were optimized. Comparatively, Fe_3O_4-SBA-15 achieved excellent percent recovery (97.5%) compared to the Fe_3O_4-MCM-41 (87.1%) under optimum condition respectively. The result appealed that the Fe_3O_4-SBA-15 composite was efficient sorbent with good capability for the preconcentration of selected OPPs from water samples.*

Keywords : Mesoporous silica materials, magnetic nanoparticles, organophosphorus pesticides and magnetic solid phase extraction

I. INTRODUCTION

Organophosphorus pesticides (OPPs), including chlorpyrifos, diazinon and parathion methyl, have been widely used in modern agriculture. Some are highly toxic to human and environment. Due to their extensive usages in agriculture or insect in public spaces, OPPs and their metabolites leached into our environment which exist in water sources and other environmental sources [1],[2]. Although in general the concentration is low, at an escalated level, if not prevented, they might impose great global risk of health [3], [4]. Hence, it is indispensable to develop simple and sensitive pre concentration steps which are capable of detecting their trace residue concentrations in environmental samples. Various pre-treatment methods have been used for the separation OPPs in various matrices including solid phase extraction (SPE) [5], solid phase microextraction (SPME) [6], dispersive solid phase extraction (DSPE) [7] and micro-solid phase extraction (µ-SPE) [8].

From the time when the examination on the technology in 1999 by Šafaříková and Šafařík [9], magnetic solid phase extraction (MSPE) has acquired extensive acknowledgement. Magnetic solid-phase extraction (MSPE) is an innovative green analytical technique that employs a magnetic material as a sorbent to separate targeted compounds suspended or dissolved in a liquid mixture from other interferences. The prime benefits of this technique over its conventional predecessors are its simplicity, smaller consumption of organic solvent and shorter analysis time [10]. Normally, the MSPE sorbent will be prepared by combining two types of different materials; an organic sorbent with high adsorption capacity and an inorganic material with superparamagnetic properties such as ferroferric oxide (Fe_3O_4) [11]. Fe_3O_4 is commonly used in the preparation of magnetic sorbent as it is inexpensive, biocompatible and easy to synthesize. Owing to the magnetic properties, magnetic sorbent can be easily separated from an aqueous phase using a magnetic field.

Among the popular organic sorbents are silica based mesoporous materials, denoted as MCM-41 and SBA-15 have gained significant attention because of their inertness, large surface area, high porosity, chemical and thermal stability as well as flexible modifiable surface [12]. MCM-41 and SBA-15 is categorized as the p6mm space with the 2D hexagonal arrangement of parallel oriented [12]. In general, major difference between MCM-41 is that SBA-15 exhibits by larger mesopores, thicker silica walls (3.1 to 6.4 nm) which provide high hydrothermal stability [13]. However, both of the mesoporous silica is notoriously difficult to be separated from solution. This problem has been alleviated by the hybridization of mesoporous silica materials with magnetic nanoparticles. Thus, the present work has been undertaken with the aim of studying the performance of two newly synthesized sorbents, namely Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 as sorbent to extract organophosphorus pesticides (OPPs) from water samples respectively.

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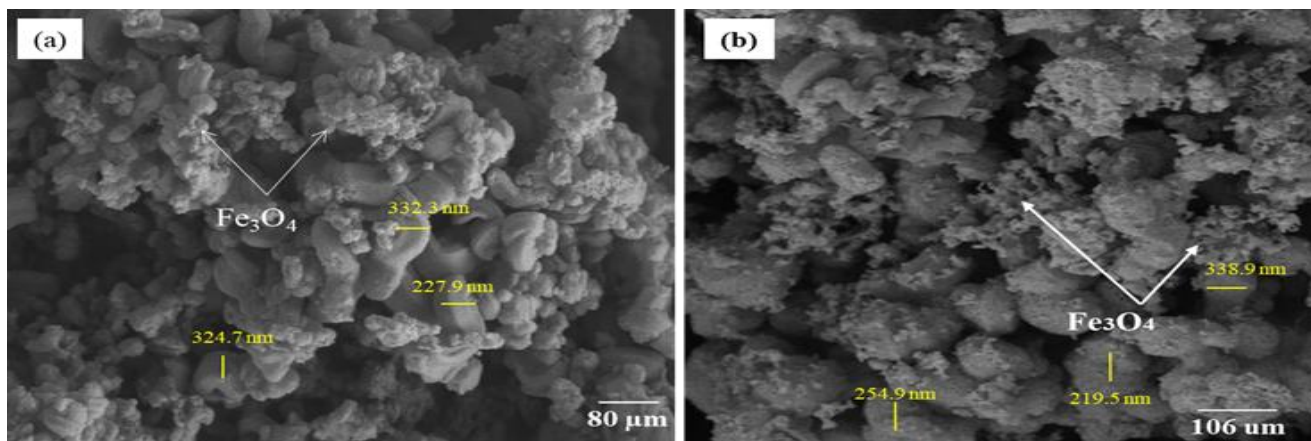
Fig. 1.FESEM Images for (a) Fe_3O_4-MCM-41 and (b) Fe_3O_4-SBA-15
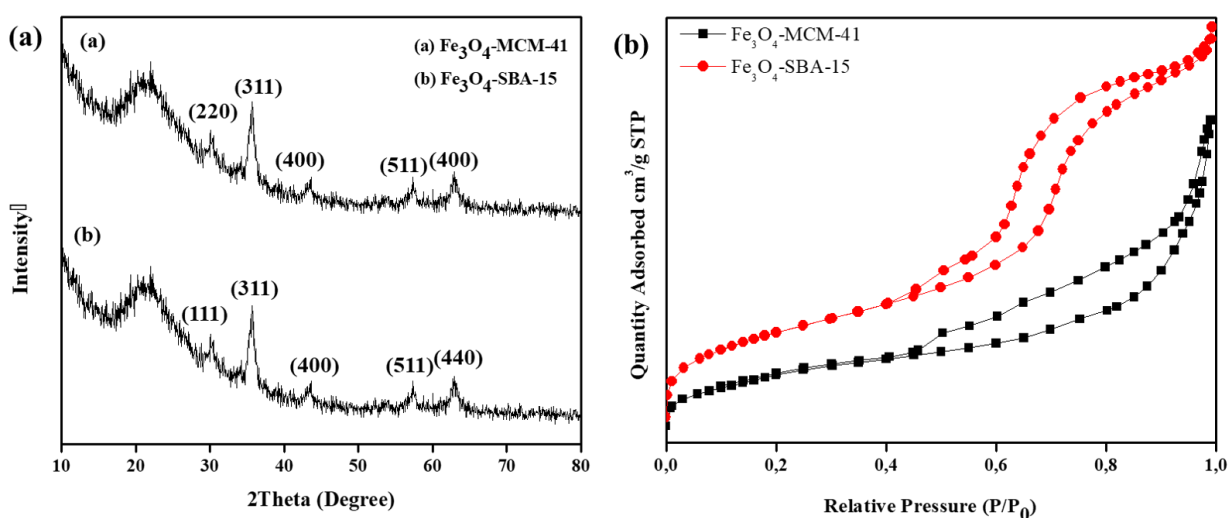
Fig. 2.(a) Wide angle XRD Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 and (b) N_2 adsorption-desorption isotherm

II. EXPERIMENTAL

A. Chemical and Reagents

Merck in Darmstadt, Germany was the supplier for Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate $FeCl_3.6H_2O$, potassium dihydrogen phosphate (KH_2PO_4), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), analytical grade acetonitrile, methanol, acetone and n-hexane. For the synthesis of MCM-41 and SBA-15 material, tetraethyl orthosilicate (TEOS), Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P-123, MW= 5800 g/mol), cetyltrimethylammonium bromide (CTABr) and Ludox colloidal (30%), hydrochloric acid (HCl, 37%) and ammonium hydroxide (NH_4OH, 25 %) were obtained from Sigma Aldrich. Pesticide standard of chlorpyrifos, diazinon

and parathion methyl prepared in methanol were purchased from Sigma Aldrich (purity assay in range of 98-101 %). Stock standard solution (1000 mg/L) of each pesticide was prepared in methanol, then a 100 mg/L intermediary standard mixture stock was achieved. The working stock solutions were also formulated on a daily basis in ultrapure water and kept at 4 °C.

B. Instrumentation

Characterization of prepared sorbents were analyzed using field emission scanning electron microscopy, FESEM (JEOL JEM-2300, Tokyo, Japan) and X-ray diffraction (XRD) analysis (Rigaku Miniflex II X-ray diffractometer with stationary X-ray source Cu Kα radiation, Japan). The specific surface area and averaged pore size were determined using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) (Belsorp-mini II, Japan). Chromatographic analyses were
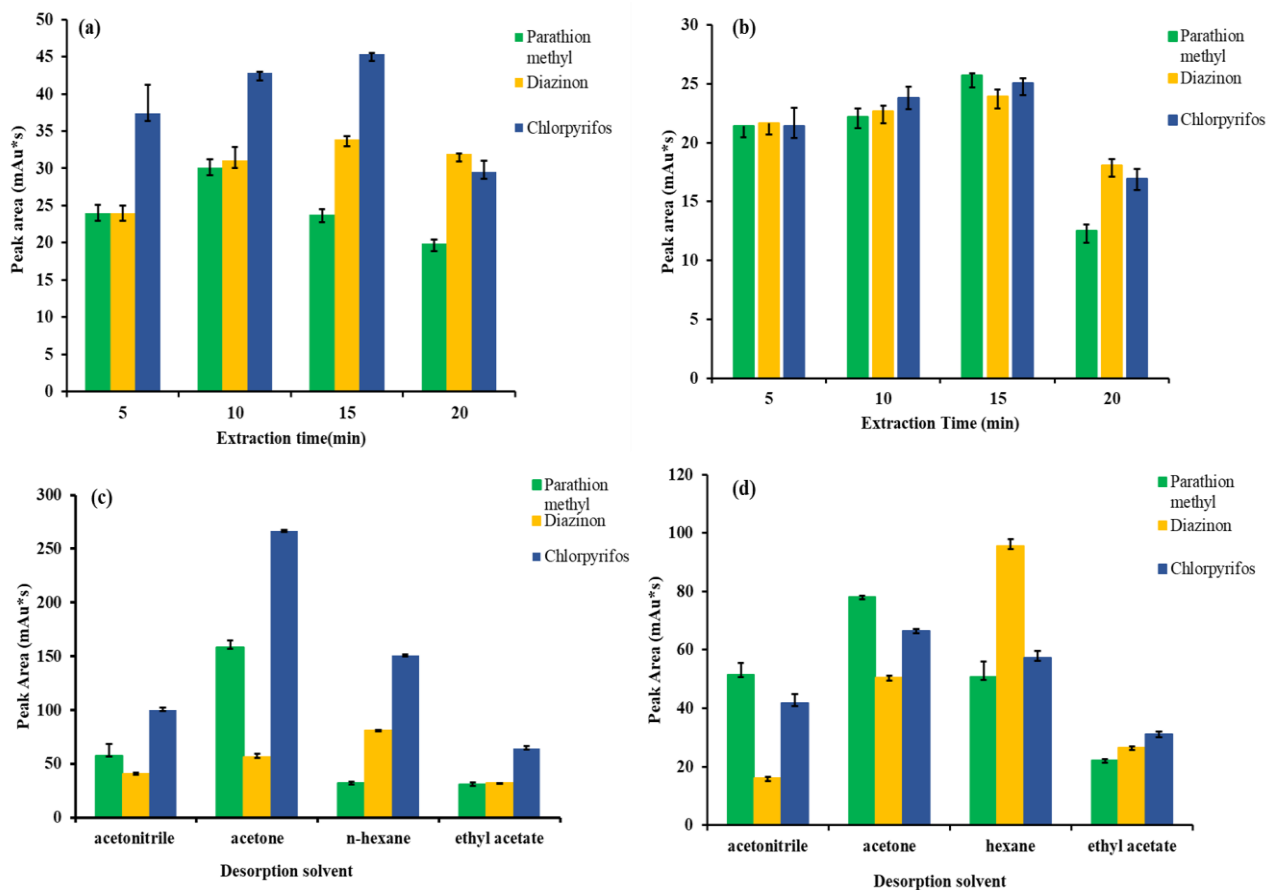
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Fig. 3.Effect of extraction time for (a) Fe_3O_4-MCM-41 and (b) Fe_3O_4-SBA-15 and effect of desorption solvent for (c) Fe_3O_4-MCM-41 and (d) Fe_3O_4-SBA-15

performed using Agilent 1200 LC (Agilent Technologies, CA, USA), consisted with quaternary pump and Diode Array Detector (HPLC/UV). The separation of OPPs was conducted on a ZORBAX Eclipse C18 (2.1 x 100 mm, 5 µm particle size) using mobile phase a mixture of acetonitrile and 1 mM phosphate buffer (pH 4.5) in the ratio of 60: 40 v/v at a constant flow rate of 0.2 mL/min.

C. Synthesis of Magnetic Sorbents

The formulation of Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 composite were prepared by adding 1 mmol $FeCl_2.4H_2O$ and 2 mmol $FeCl_3$ to 0.5 g of MCM-41 mixed with 100 mL doubled distilled water. The resultant liquid was added dropwise with 10 mL of aqueous ammonium hydroxide solution and continuously stirred for 1 hour. Finally, the obtained products were centrifuged with doubled distilled water until pH become neutral and dried in a vacuum desiccator at room temperature [14]

D. Magnetic Solid Phase Extraction Procedure

In the MSPE procedure, 50 mg of magnetic sorbents (Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15) was added to a 10 mL of ultrapure water, spiked with 1 mg/L of targeted analytes. Next, the mixture was subjected to orbital shaker for 15 minutes (min) to allow adsorption of analytes onto the sorbent surface. The sorbent was then isolated form the aqueous phase by an external magnetic field and the supernatant was decanted.

The adsorbed analytes were eluted from magnetic sorbent with 500 µl of desorption solvent by ultrasonication. The desorption solvent was then evaporated under N_2 stream, reconstituted with 100 µl of a selected diluent, and filtered through 0.45 µm nylon syringe filter. Finally, 2 µl of aliquot was injected into the HPLC/UV system for analysis.

III. RESULTS AND DISCUSSION

A. Characterization

The synthesized sorbents (Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15) were characterized under field emission scanning electron microscopy (FESEM) in order to understand the surface morphology and the distribution of the magnetite particles on the surface of the sorbent. As shown in Fig. 1(a), MCM-41 is presented as a loosely agglomerated particles with rod like shape that was uniformly coated with Fe_3O_4 nanoparticles which, as can be seen, tends to agglomerate [15]. Similarly, with regards to Fig. 1(b), the bare spherical-like Fe_3O_4 nanoparticles are also agglomerated and dispersed onto the exterior surface of SBA-15 [16]. The size estimations from both micrographs showed that most particles have diameters (>250 nm). Besides, some particles could be seen in partially aggregated due to the existence of magnetic interaction between particles [14].

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After dispersing with Fe_3O_4 particles, it reveals that the surface does not significantly alter the mesoporous structure and did not direct to a physical change.

The XRD patterns of for both magnetic composites are displayed in Fig. 2(a). The less pronounced broad diffraction peaks in the range of 2θ at 20° to 30° that are the characteristics from the amorphous silica template. Meanwhile, several peaks with Miller indices of 220, 311, 400, 511 and 440 reflection respectively, which are indexed to the spinel structure pure stoichiometric Fe_3O_4 (JCPDS Card No. 19–0629) [14].

In line with the examination of the textural properties of magnetic composite (Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15), the N_2 adsorption-desorption isotherm was performed as represented in Fig. 2(b). The N_2 adsorption-desorption isotherms exhibit typical type IV physisorption curves with a well distinguished H1 hysteresis loop with a rapid increase in nitrogen uptake $p/p_0 = (0.4-1.0)$, which were associated to the characteristics of mesopores with uniform pore size. The surface area of synthesized sorbents was found Fe_3O_4-SBA-15 (471.93 m^2/g) and Fe_3O_4-MCM-41 (293 m^2/g). Even though the surface area of magnetic composite is reduced, it afforded an efficient substrate with a suitable surface area for interaction with the OPPs compounds.

B. Optimization

1) The Consequence of Extraction time

Extraction time is a key factor that performs a vital role in the MSPE procedure. With the intention of investigating the impact of extraction time, the OPPs pesticides on both Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 were studied at four different shaking periods in the range of 5 to 20 min. As can be seen in Fig. 3(a) to (b), the peak area of analytes increased gradually from 5 to 15 min, whereas extending the shaking period to 20 min does not show any significant improvement probably due to desorption of the analyte from the adsorbent. Therefore, the equilibrium between the aqueous phases and the sorbents was reached at 15 min.

2) The Effect of Desorption Solvent

An equally significant factor of MSPE, desorption step is one of the key processes affecting the ultimate fate contaminants in solids. In general, the selection of desorption

Analysis was conducted using HPLC. Peak identification: (P) parathion methyl, (D) diazinon and (C) chlorpyrifos

solvent, polarity of solvents, solubility of analytes relies on its compatibility of analytical instrument should be considered. Hence, four organic solvents namely acetonitrile, acetone, ethyl acetate and hexane were performed to elute the adsorbed analyte form the magnetic sorbents. The experimental results demonstrate that the best response of OPPs analytes (Fig. 3(c)-(d)) was obtained using acetone, respectively. These solvents were able to provide the highest response due to its highest desorption ability.

## C. The Application of Developed Method on Water Samples

In order to assess the applicability of the developed method, both Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 were used to isolate OPPs pesticides in real water sample. Prior to that, the water samples were spiked with OPPs standard solution with level 1 mg L^{-1}. Each sample was analyzed three times using the HPLC/UV. The same process was applied to uspiked samples. Table I, shows that Fe_3O_4-SBA-15 has high percent recovery (89.3-97.5%) as compared to the Fe_3O_4-MCM-41 method (80.8-87.1%) respectively. Triplicate MSPE data gave a satisfactory relative standard deviation (RSD) of (1.8-4.3%) and (2.7-5.2%) for Fe_3O_4-SBA-15 and Fe_3O_4-MCM-41, respectively. Accordingly, Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 successfully adsorbed OPPs pesticides due to hydrogen bonding through the hydroxyl group on silanol surface and anionic sites of chlorpyrifos (Cl, O and S) [17]. The obtained HPLC chromatograms for water samples are illustrated in Fig. 4(a), 4(b) and 4(c).

Table I. Percentage recovery of OPPs from 10 mL water samples spiked with 1 mg/L each of chlorpyrifos, diazinon and parathion methyl

Sorbent	% Recovery (RSD%, n=3)		
	Chlorpyrifos	Diazinon	Parathion methyl
Fe_3O_4-MCM-41	80.8(4.6)	84.3(2.7)	87.1(5.2)
Fe_3O_4-SBA-15	97.5(1.8)	90.5(3.0)	89.3(4.3)
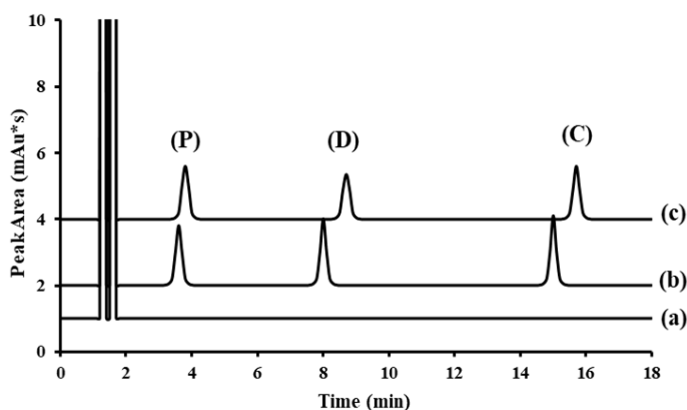
Fig. 4. Chromatogram obtained using MSPE sorbent from 10 mL of water samples for (a) blank (b) spiked OPPs (1 mg/L) for Fe_3O_4-MCM-41 (c) spiked OPPs for Fe_3O_4-SBA-15.
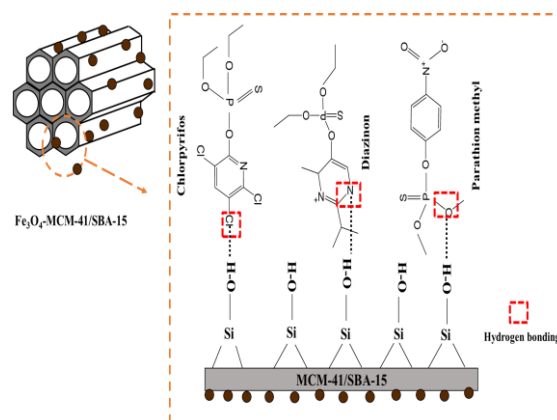
Fig. 5.Proposed adsorption mechanism for OPPs adsorption using Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15

D. Proposed Adsorption Interaction

The adsorption of the selected pesticides onto Fe_3O_4-MCM-41 and Fe_3O_4-SBA-15 surface is illustrated schematically in Fig. 5. The structure of sorbent possesses silanol group on mesoporous silica materials while the selected OPPs pesticides have different anionic sites (O, N, S and Cl). Hydrogen of hydroxy group on silanol surface shows binding abilities towards the anionic groups through strong hydrogen bonding [17]. Therefore, the selected OPPs are extracted from all synthesized sorbent through strong hydrogen bonding.

E. Assessment with Other Methods

A literature research on determination of OPPs pesticides in water samples was conducted to assess the proposed technique with some other previously reported methods. As tabulated in Table II, the developed MSPE method offers recovery to be highly comparable with solid phase extraction (SPE) [5], dispersive solid phase extraction (DSPE) [18]) and solid phase microextraction (SPME) [19] methods. Magnetic Solid Phase extraction (MSPE) proposed method offers a simplicity and minimizing the usage of organic solvent. However, a lot of studies need to be done before this method could be adopted as routine analysis.

Table II. Assessment of the suggested technique with various methods used for extraction and determination of OPPs values

Adsorbent	Method	Detector	Matrix	Recovery (%)	References
	MSPE	HPLC/UV	Water	87.1	This study
Fe_3O_4-MCM-41					
Fe_3O_4-SBA-15	MSPE	HPLC/UV	Water	97.5	This study
C-G/Fe_3O_4	SPME	HPLC/UV	Water	>70	[19]
	DSPE	GC-MS	Vegetables	70.3	[18]
GCB/PSA/Fe_3O_4	SPE	GC-MS	Fruits	89.7	[20]
Molecular imprinted polymer					

IV. CONCLUSION

In this research, the combination benefits of sizable surface area of mesoporous silica and magnetic properties Fe_3O_4 produce the successfully synthesized Fe_3O_4-SBA-15 and Fe_3O_4-MCM-41 sorbent for preconcentration of OPPs pesticides in water samples. The Fe_3O_4-SBA-15 showed outstanding recoveries (97.5%) as MSPE sorbent for selected analysis compared Fe_3O_4-MCM-41 (87.1%) to due to SBA-15 has wider pores (10 nm) than MCM-41 (5.1 nm) obtained from nitrogen adsorption-desorption analysis. These results indicate that the sorbents endowed great and are promising a wide range of applications in the field of analytical chemistry which offer simple, cheap, efficient, sensitive and environment friendly for trace analysis of OOPs in water samples.

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