Magnetic Solid Phase Extraction based on Amino-functionalized Magnetic Starch for Analysis of Organochlorine Pesticides

Dana Ayu MUSTOFA, Jirasak GAMONCHUANG, Rodjana BURAKHAM*

Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

*Corresponding author: Rodjana Burakham, Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand; Fax: +66 4320 2373; Tel: +66 4300 9700 ext. 42174; e-mail: rodjbu@kku.ac.th
Abstract

A magnetic starch modified with 3,5-diaminobenzoic acid and 3-aminopropyltriethoxysilane (Fe-starch@DABA-APTES) was synthesized and applied as adsorbent for extraction of organochlorine pesticides (OCPs). The magnetic solid-phase extraction was developed using 75 mg of the sorbent and 15 mL sample solution. Extraction was conducted on a vortex mixer for 40 s. The adsorbent was collected using an external magnet before eluting the analytes using 0.5 mL methanol. Quantification of the analytes was performed using gas chromatography with micro-electron capture detector. Linearity was obtained for the studied OCPs in the range between 0.01–2.00 μg L⁻¹. The detection and quantification limits were obtained in the ranges of 0.5–4.0 and 1.5–15.0 ng L⁻¹, respectively, with the enrichment factors of up to 39. The precision in terms of intra- and inter-day relative standard deviations (RSDs) were below 4.75%, and 9.25%, respectively. The developed method has been applied in natural water and agricultural product samples. The recoveries ranged between 59.83–132.67% (RSDs<10.73%).

Keywords: solid phase extraction; magnetic material; diaminobenzoic acid; aminopropyltriethoxysilane; organochlorine; gas chromatography
Introduction

Organochlorine pesticides (OCPs) are listed in the class of persistent organic pollutants (POPs), which have been extensively used for controlling pests and diseases in crop production. Recently, these compounds have been banned in many countries due to their persistence in the environment and bioaccumulation in humans and other animals. However, they are still applied in some developing countries, widespread in the environment and remain for a very long time. The accumulation of OCPs in the environment and food chain is of great concern. Therefore, existing analytical techniques, including gas chromatography with electron capture detector (GC-ECD)\textsuperscript{1-5} and gas chromatography with mass spectrometry (GC-MS)\textsuperscript{6-8} have been dedicated for the determination of OCPs. However, efficient sample preparation method is essential to obtain reliable analytical results.

The aims of sample preparation are to enrich the concentration of target analytes usually present in sample at very low concentrations and to clean–up the samples by removing interferences before applying instrumental analysis. Magnetic solid phase extraction (MSPE) has currently attracted much attention in sample preparation technology. The method is based on direct dispersion of the magnetic sorbents into sample solution. Extraction is facilitated by shaking, applying vortex mixing, or ultrasonication. Separation of the solid sorbent from the solution is much rapid and convenient by using external magnetic field, which avoids the traditional centrifugation or filtration process. The extraction efficiency of MSPE could be greatly enhanced by integration of functional groups on the magnetic elements, which provide more active sites. Nowadays, extensive research has been carried out to develop new sorbent materials with efficient extraction capacity for the group of target analytes.
Zerovalent iron particles are becoming a popular choice due to their excellent properties, including high magnetization value, small size, and large active surface area. Zerovalent iron consists of a core as principal zerovalent or metallic iron, and mixed valent oxide shell which derive from the oxidation of the metallic iron. However, there are some limitations by using bare zerovalent iron, i.e. low selectivity for the target analytes, easy oxidation, low acid resistant and high aggregation as well as low dispersibility in sample solution. Therefore, several coating materials are proposed for modifying the surface of zerovalent iron to reduce the above-mentioned problems. Surface modification can not only improve the dispersibility of the magnetic materials but also create active surface to selectively interact with the target molecules. Different types of both inorganic and organic materials have been reported for coating onto the surface of magnetic core, such as silica, polymer, surfactants, and carbonaceous. Starch is natural polysaccharide that has been studied lately for balancing the magnetism and the van der Waals interaction on the magnetic surface because its compatibility for further modification. Potato starch shows high average swelling power, with the granules volume increasing until 100 times from their original volume. Repulsion between phosphate groups on adjacent chains increases hydration by weakening the extent of bonding within the crystalline domain. The properties of starch also gain the attention, such as low cost, biodegradability, and easily available.

In this work, we proposed a newly synthesized Fe-starch@DABA-APTES sorbent by combination of zerovalent iron with starch as magnetic materials and modified with diaminobenzoic acid (DABA) and (3-aminopropyl)triethoxysilane (APTES) for enrichment of OCPs. DABA has benzene ring that could generate the π-π interaction within the sorbent and target analytes. APTES is organosilane coupling agent that may connect chemically reactive amino groups and stable in aqueous solution. The amino silane is the most common functional group
that usually used because of their availability and low cost. Both APTES and DABA contain amino-end group in their structures that give important major to improve the hydrophilicity for adsorbing the target analytes. The functional groups, morphology, and magnetic properties of this magnetic material were investigated by various techniques, including Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and vibrating sample magnetometry (VSM). The prepared sorbent has been applied to develop the MSPE procedure for preconcentration of OCPs prior to quantification by GC-µECD technique. Seven types of OCPs with structural analogues of (i) hexachlorobicyclic class (dieldrin, endrin, aldrin, isobenzan, and endosulfan), (ii) heptachlorobicyclic class (heptachlor), and (iii) octachlorobicyclic class (chlordane) were studied.

The proposed MSPE using Fe-starch@DABA-APTES as sorbent was further applied to enrich the desired analytes in environmental samples and agricultural products.

Experimental
Chemicals

All the chemicals used were at least an analytical reagent grade. Ferrous sulfate heptahydrate was purchased from Carlo Erba (France). Potato starch, DABA, and APTES were obtained from Acrös (China). Sodium borohydride was supplied from AppliChem (India). Ammonium hydroxide was received from Qrèc (New Zealand). Methanol, acetone, acetonitrile, and n-hexane were obtained from Merck (Germany). All OCP standards, including endosulfan, heptachlor, isobenzan, aldrin, chlordane, dieldrin, and endrin, were purchased from Ehrenstorfer (Germany). Stock standard solutions of each OCP at concentration of 1000 mg L⁻¹ were prepared in methanol. Deionized water (18.2 MΩ·cm) was obtained from a Simplicity® ultrapure water system Type 1 (Millipore, Darmstadt, Germany).
Instrumentation

Fourier transform infrared spectra was investigated on a Perkin Elmer Spectrum One FTIR spectrometer between 400 and 4000 cm$^{-1}$ using a standard KBr disk method. A PANalytical, EMPYREAN X-ray diffractometer using monochromatic Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm) in a 2$\theta$ range of 10° to 80° was used for crystal structure characterization of sorbent. The morphology and structure of sorbent were analyzed using a FEI, Helios NanoLab G3 CX dual beam scanning electron microscope with focused ion beam (FIB-SEM) and a FEI, Tecnai G$^2$ 20 transmission electron microscope coupled with energy dispersive X-ray analysis (EDX), working at the voltage of 200 kV. Magnetic property was measured by a Lake Shore (VSM 7403) vibrating sample magnetometer at 298 K with applied magnetic field (H) of ± 10000 Oe. The surface area and pore size analyzer model BELSORP - mini X (MicrotracBEL Corp., Japan) was used for measurement of the specific surface area of the material. CHN analyses were performed using a PerkinElmer PE 2400 CHNS analyzer.

Gas chromatograph equipped with a micro-electron capture detector, Agilent GC7980 system (Agilent Technology, USA), was used for analysis. The OCPs was separated on a HP-5 fused silica capillary column (30 m × 0.25 mm, 0.25 µm film thickness, Agilent, USA). The injection volume was 1 µL with split ratio of 35:1. Ultrapure N$_2$ (99.999 %) with a flow rate of 1 mL min$^{-1}$ was used as carrier gas. The temperature of injector and ECD detector was set at 270 and 320 °C, respectively. The oven temperature program was started at 160 °C for 0.5 min, raised to 180 °C at a rate of 20 °C min$^{-1}$ and held for 0.5 min, raised to 190 °C at 20 °C min$^{-1}$ and held for 0.5 min, raised to 250 °C at 40 °C min$^{-1}$ and held for 4 min, and then to 300 °C at 25 °C min$^{-1}$ and held for 2 min.

Preparation of the Fe-starch@DABA-APTES sorbent
The Fe-starch@DABA-APTES sorbent was synthesized by adding 0.82 g of FeSO₄·7H₂O and 2.68 g of potato starch in a glass bottle. Then, 180 mL water was added, and the mixture was stirred for 10 min before adding the NaBH₄ solution (0.21 g in 20 mL water). The black magnetic particles were obtained, which were separated from the solution by external magnet. The solid particles were washed with water at least 3 times before adding to 170 mL ethanol in the reactor. To functionalize the magnetic sorbent, NH₄OH solution (28%, 4 mL) and DABA were sequentially added, and the mixture was stirred for 30 min. Then, APTES was added and shaken for 3 h. The Fe-starch@DABA-APTES product was collected and washed with ethanol for 3 times. The product was then dried in an oven at temperature of 110 °C for 3 h.

Collection and pretreatment of the samples

Reservoir water samples were taken from Lam Pao Dam, Kalasin province, and local lake in Khon Kaen University, Khon Kaen, Thailand, and were filtered through filter paper before analysis. The vegetables and fruits were collected from local markets in Khon Kaen province, Thailand, and were chopped in small size and blend homogeneously. A 25 g of each sample was weighed, and 25 mL of water was added. The mixture was shaken for 15 min and centrifuged for 5 min at 3500 rpm. The supernatant was filtered before adding to the centrifuge tube containing 400 mg primary secondary amine (PSA) and centrifuge for 3 min at 5000 rpm. The obtained supernatant was filtered through 0.45 µm membrane filter before applying MSPE procedure.

MSPE procedure

The MSPE procedure for preconcentration of OCPs was developed using Fe-starch@DABA-APTES as sorbent. The extraction process was started by direct dispersion of the sorbent (75 mg) in a sample solution (15 mL). Extraction process was accelerated using vortex mixer for 40 s. Then, the magnetic sorbent interacted with the target analytes were collected using
external magnet, while the supernatant was discarded. After that, the analytes were eluted from the sorbent using 0.5 mL methanol by fierce vortex for 40 s. After separating from the sorbent, the eluate was filtered through a 0.45 µm membrane filter before further analyzed by GC-µECD. The schematic diagram of the MSPE procedure is shown in Fig. 1.

**Results and Discussion**

**Characterization of the sorbent**

The FTIR technique was used to confirm the chemical structure of the synthesized magnetic sorbent. The FTIR spectrum shown in Fig. S1(a) indicated the vibration peaks at 2931, 1645, 1414, 1151, 1082, and 1000 cm\(^{-1}\), indicating C–H stretching, vibration mode of OH species, CH\(_2\) symmetric vibration, C–O–C asymmetric stretching, and C–O stretching of characteristic vibration of starch, respectively. Furthermore, the characteristic vibration of C–O–C in the ring of starch were also found at 927 and 762 cm\(^{-1}\). The vibration of zerovalent iron on starch were observed at 581 and 520 cm\(^{-1}\), which assigned to Fe–O vibration mode. The results confirmed the existence of zerovalent iron on the surface of starch. The FTIR spectrum of Fe-starch@APTES was shown in Fig. S1(b), the observed band around 3427 cm\(^{-1}\) attributed to the vibration mode of –NH stretching. The vibration peaks at 1021, 970, 849 and 765 cm\(^{-1}\) were observed, which assigned to the vibration of Si–O–C bond, Fe–O–Si and the Si–C bond of characteristic vibration of APTES, respectively. The characteristic vibration peaks of both of zerovalent iron and starch were also observed at the same wavenumber. These results supported that APTES was successfully modified on Fe-starch surface. From the FTIR spectrum of Fe-starch@DABA as shown in Fig. S1(c), the observed peaks at 3416 and 1389 cm\(^{-1}\) were assigned to the stretching vibration of the –NH group of amino. Additional peak at 1563 cm\(^{-1}\) corresponded to aromatic C=C stretching mode of DABA. The characteristic vibration peaks due to Fe-starch (in Fig. S1(a)) were also found,
which proved the success modification of DABA onto the Fe-starch. Fig. S1(d) presented the FTIR spectrum of APTES and DABA modified Fe-starch. All characteristic vibration peaks due to Fe-starch, APTES, and DABA were observed, confirming the successful coating of APTES and DABA onto Fe-starch surface.

The morphology of as-prepared magnetic sorbents were shown in SEM images (Fig. S2). The spherical-like shape of zerovalent iron with connecting to each other (chain-like) was observed (Fig. S2(a)). The zerovalent iron chain was randomly arranged on surface of starch particles. After modification with DABA and APTES, their polymeric-linkage with irregular and sheet-like shapes were observed (Fig. S2(b)). This result could confirm the successful coating of DABA and APTES on the surface of Fe-starch. Furthermore, TEM was carried out to confirm the coating layer on Fe-starch. From the TEM image of Fe-starch (Fig. S3(a) and (b)), zerovalent iron connected in chains with thin iron oxide shell thickness was observed. After coating with DABA and APTES (Fig. S3(c) and (d)), the shell was encapsulated on zerovalent iron with thickness of about 6 nm. Therefore, these results confirmed that the chain of zerovalent iron was arranged on starch particles and was then coated by DABA and APTES layers.

The XRD patterns of as-synthesized sorbents, Fe-starch and Fe-starch@DABA-APTES, were presented in Fig. S4. The diffraction peak due to the characteristic of Fe-starch was observed only at 2θ of 45°, corresponding to (110) crystal planes of zerovalent iron, which matched well with standard pattern for Joint Committee on Powder Diffraction Standard (JCPDS No.87-0721). Moreover, the strong diffraction peak at 2θ of 17° and the broad band from 10° to 25° were also observed, belonging to the characteristic XRD pattern of tomato starch. After modifying DABA and APTES, the XRD pattern of zerovalent iron disappeared due to the coating of amorphous phase of DABA and APTES onto Fe-starch. In contrast, XRD pattern of potato starch was not
significant change with applying DABA and APTES because both modified materials mainly coated on zerovalent iron.

Specific surface area of the sorbent was measured by the Brunauer-Emmett-Teller (BET) method. From N₂ adsorption/desorption isotherm, the Fe-starch@DABA-APTES exhibited non-porous materials, and its surface area of 2.09 m² g⁻¹ was obtained. Elemental analysis was carried out to confirm the existence of coating components on magnetic material. The percentages of C:H:N in Fe-starch@DABA and Fe-starch@DABA-APTES were found to be 34.87:6.22:0.10 and 38.22:6.54:0.64, respectively. The contents of DABA and APTES on the magnetic sorbent could be calculated as 15.6% and 84.4%, respectively.

The magnetic properties of as-synthesized sorbents were measured by vibrating sample magnetometer with applying magnetic field (H) of ± 10000 Oe at 298 K. The results showed ferromagnetic behavior with saturation magnetization of 15.80 and 5.31 emu g⁻¹ for Fe-starch and Fe-starch@DABA-APTES, respectively (Fig. S5). The decrease of magnetization of Fe-starch@DABA-APTES, compared to Fe-starch, was due to the obstructing of non-magnetic materials (DABA and APTES) onto zerovalent iron surface. Although the magnetization of the proposed magnetic sorbent was decreased, it was good enough for use in MSPE.

**Optimization of the MSPE conditions**

To find the optimum MSPE condition for preconcentration of OCPs, different parameters influencing the extraction efficiency of the method were studied. These include the sorbent amount, vortex time during adsorption and desorption processes, type of desorption solvent and its volume, and sample volume. The standard solution of OCPs containing 1 µg mL⁻¹ each was analyzed, and peak areas obtained from GC-µECD system were used for evaluation of the
extraction efficiency. All experiments were carried out in triplicates (n=3). Respective figures are given in the Supporting Information.

**Adsorption capacity**

In this work the synthesized Fe-starch@DABA-APTES was selected as sorbent for preconcentration of OCPs in the MSPE method. The amount of sorbent in the range from 50 to 150 mg did not influence the sorption performance for the tested OCPs solution, which nearly 100% adsorption was obtained for all analytes. Therefore, 75 mg Fe-starch@DABA-APTES was employed for the present work. The sorption capacity of the synthesized Fe-starch@DABA-APTES sorbent for MSPE of OCPs was calculated according to equation \( q = (C_0 - C_f)V \times 1000/m \), where \( q \) is sorption capacity (mg kg\(^{-1}\)), \( C_0 \) and \( C_f \) are the initial concentration of the analytes in sample solution and final concentration (μg L\(^{-1}\)), respectively, \( V \) is sample volume (L), and \( m \) is sorbent mass (g). For this purpose, 1 μg L\(^{-1}\) of OCPs standard solution was extracted under the optimum MSPE condition, and the sorption capacity of the material for the studied OCPs were obtained in the range of 177–205 mg kg\(^{-1}\), as summarized in the Table S1.

**Effect of vortex times**

The vortex agitation was used for acceleration of the MSPE during extraction (adsorption) and desorption processes. In the present work, vortex adsorption time was studied in the range of 10–60 s, while keeping other conditions as follows: 75 mg of the sorbent, 15 mL sample volume, 0.5 mL methanol as desorption solvent and 40 s vortex desorption time. The peak areas of all analytes remained in the supernatant reached minimum using vortex adsorption time of 40 s and the almost flattened out afterward (data not shown). Therefore, adsorption process could be reached after vortexing for 40 s. The adsorption of OCPs on the sorbent were found in the range of 93–100% and the equilibrium distribution of the OCPs between solid and liquid phases was
relatively fast process in this work. To study the time needed for desorption process, the vortex time was varied in the range of 10–60 s during eluting the analytes from the sorbent. The desorption efficiency reached maximum at vortex time of 40 s (data not shown), and it was selected for subsequent experiments.

*Type of desorption solvent and its volume*

The desorption solvent plays a crucial role in the desorption process. To study the effect of the solvent for desorption of seven OCPs from Fe-starch@DABA-APTES sorbent, four types of solvent were tested, including methanol, acetone, acetonitrile, and n-hexane. Other parameters were kept as follows: 75 mg sorbent, 15 mL samples solution, 40 s vortex adsorption time, 0.5 mL desorption solvent, and 40 s vortex desorption time. The results in the Fig. S6 indicated that the worst desorption capability and repeatability was obtained using n-hexane. Methanol, acetone, and acetonitrile show almost similar results, however, desorption using methanol gave the highest peak areas for most analytes. This could be due to the lower polarity index of n-hexane compared with the other solvents. Affinity between desorption solvent and the studied analytes in terms of polarity should be considered. In addition, poor eluting power may be attributed to the weaker dispersibility of the sorbents in the solvent by decreasing the polarity. Therefore, methanol was adopted as desorption solvent for further experiments.

The volume of the solvent should be enough for providing an effective elution of the target analytes from the sorbent. Therefore, the volumes of methanol between 0.5 to 2.0 mL were varied, while keeping other conditions as follows: 75 mg sorbent, 15 mL sample volume, 40 s for vortex adsorption, and 40 s for vortex desorption. The results were illustrated in Fig. S7. Increasing the volume of methanol, the peak area of most analytes decreased due to the dilution effect. However,
using methanol less than 0.5 mL, collection of eluent was problematic. Therefore 0.5 mL of methanol was used for desorption of OCPs in the proposed MSPE procedure.

**Effect of sample volume**

To maximize the enrichment factor of the MSPE procedure, the sample volume was studied in the range of 5–20 mL using 75 mg sorbent, 40 s vortex adsorption time, 0.5 mL methanol as desorption solvent, and 40 s vortex desorption time. The results in the Fig. S8 indicated that the extraction efficiency in the term of peak areas of most analytes reached the maximum at sample volume of 15 mL. Therefore, 15 mL was ultimately chosen as the proper sample volume in this work.

**Validation of the proposed MSPE procedure**

To validate the proposed MSPE procedures coupled with GC-µECD for determination of OCPs, linearity, sensitivity, precision, and enrichment factors were investigated under the selected condition. The calibration graphs of all OCPs were obtained in the range of 0.01–2.00 µg L\(^{-1}\) with coefficient of determination greater than 0.9935. The LODs and LOQs in the ranges of 0.5–4.0 ng L\(^{-1}\) and 1.5–15.0 ng L\(^{-1}\), respectively, were reached. The enrichment factors, calculated as the ratios of concentration of the analytes after MSPE and initial concentration, of up to 39 were obtained. The precision in terms of %RSDs of retention time and peak area for the MSPE experiments in a day (intra-day precision) and in five consecutive days (inter-day) were less than 9.25%. Table 1 summarizes the analytical features of the proposed MSPE-GC-µECD procedure. Fig. 2 shows the chromatograms of the standard OCPs obtained by direct GC-µECD and after preconcentration using MSPE procedure. To determine the precision of the inter-batch synthesized material, the Fe-starch@DABA-APTES was prepared in different five days and applied for MSPE of OCPs. The
%RSDs of the determination below 4.99 were found (Table S1), indicating that the synthesis manner gave reproducible sorbents.

The possible interaction during extraction process could be proposed that chlorine atom on OCPs could exhibit a halogen bonding or σ-hole interaction with negative charge site or electron donor group on the sorbent, involving oxygen atom from carboxylate and nitrogen atom from amino groups. This phenomenon could be explained in term of interaction of carbon-bonded chlorine (C–Cl) and oxygen or nitrogen, which chlorine was referred as halogen bond donor or nucleophilic acceptor, while oxygen and nitrogen were recognized as halogen bond acceptor or electron-rich atoms, leading to favorable interaction. In addition, the lone pair electrons of amino groups arranged around sorbent possibly interacted with the electron-deficient vinyl (unsaturated carbon bonds) of OCPs. Another possible interaction refers as intermolecular forces generated by amino group in sorbent (polar molecule) induced non-polar molecule of OCPs to generate temporary dipole. Thus, the structure of Fe-starch@DABA-APTES sorbent tended to exhibit interaction toward OCPs via halogen bonding, π-donor-acceptor interaction, and induced dipole force.

Analysis of real samples

The developed MSPE procedure using Fe-starch@DABA-APTES sorbent coupled with GC-μECD was applied to the determination of OCPs in various sample matrices. It was found that the amount of OCPs were detected in the range of 0.01–0.18 µg L⁻¹ in water samples, 0.01–0.47 µg L⁻¹ in vegetables, and 0.03–0.38 µg L⁻¹ in fruit. To evaluate the accuracy of the developed method, the recovery was studied by spiking known concentrations of OCPs standard into the samples before analysis. The recoveries at two spiked concentrations (0.20 and 0.50 µg L⁻¹) were
summarized in the Table S2. The recoveries of all studied OCPs were obtained in the range of 69.61–121.95% with RSDs below 9.76 % for water samples. In the case of vegetables, the method recoveries in the range of 59.83–132.67% with RSDs better than 10.73% were found. For fruit matrix (watermelon), the recoveries were obtained in the range of 67.41–115.37% with RSDs less than 10.03%. Generally, fruits or vegetables has a different composition of water, sugars, lipids, and colors, and these cannot be eliminated completely by the clean-up steps in pesticide residue analysis.\textsuperscript{23} The matrix effect for each pesticide was also affected by the pesticide concentration. The greater matrix effects were observed at low spiked concentration of OCPs and caused the signal enhancement or suppression of the analytes, which could affect the recovery of the method. However, the Codex Alimentarius suggests that the recoveries in the range of 50–150% are accepted for the spiked concentration of less than 1 µg kg\textsuperscript{-1} for the examination of the general U.S. Department of Agriculture (USDA) pesticide residues.\textsuperscript{24} In addition, the European Commission set the acceptable average recovery for each spiked level tested at 90–120% with the repeatability RDS of less than 20%.\textsuperscript{25} The present method showed the average recoveries of 93.62% and 86.92% for water and agricultural products, respectively, at spiked concentration of 0.20 µg L\textsuperscript{-1}, while the average recoveries of 101.56% and 89.60% were obtained for water and agricultural products, respectively, at spiked concentration of 0.50 µg L\textsuperscript{-1}. The results obtained by the proposed procedure fall within the acceptance criteria of guidance for the validation parameters.

**Comparison of the proposed MSPE to other methods**

Some previously reported MSPE methods using different magnetic materials for the detection of OCPs by GC-ECD technique are summarized in Table S3. The proposed method is reliable for a variety of OCPs and provides adequate linear calibration range for the quantification in various sample matrices. Compared with other methods, the proposed MSPE procedure using
Fe-starch@DABA-APTES as sorbent showed a comparable sensitivity in terms of LODs or LOQs to those obtained by other works.\textsuperscript{1-5} However, simple extraction process in a short extraction time (time consumption in both adsorption and desorption processes <2 min) is beneficial for the present work. Considering the preparation of magnetic sorbent proposed in this work, the Fe-starch@DABA-APTES sorbent can be prepared easily under facile condition at ambient temperature using a short synthesizing time, and no complicated equipment is required.

**Conclusion**

In summary, a newly synthesized magnetic material based on zerovalent iron combined with starch and modified with DABA and APTES was applied for MSPE of OCPs prior to quantification by GC-\(\mu\)ECD. The sorbent was simply prepared according to the facile manner at ambient temperature and provided efficient extraction capability for the target analytes. The developed MSPE condition showed good analytical characteristics for a variety of OCPs and offered simple extraction process in a short extraction time. The proposed method has potential for the application in various sample matrices.

**Acknowledgements**

The KKU Scholarship for ASEAN and GMS countries (No. 1356/1028), Materials Chemistry Research Center, Department of Chemistry, Faculty of Science, Khon Kaen University, and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Ministry of Higher Education, Science, Research, and Innovation (Implementation Unit-IU, Khon Kaen University) are gratefully acknowledged for financial supports. R. Burakham thanks the National Research Council of Thailand (NRCT) and Khon Kaen University for supporting the Mid-Career Research Grant (NRCT5-RSA63003-05).
References

1. Z. Du, M. Liu, G. Li, *J. Sep. Sci.*, **2013**, *36*, 3387.
2. A. Mehdinia, S. Rouhani, S. Mozaffari, *Microchim. Acta*, **2016**, *183*, 1177.
3. A. Mehdinia, S. Einollahi, A. Jabbari, *Microchim. Acta*, **2016**, *183*, 2615.
4. S. Mahpishanian, H. Sereshti, *J. Chromatogr. A*, **2017**, *1485*, 32.
5. F.M. Marsin, W.A.W. Ibrahim, H.R. Nodeh, M.M. Sanagi, *J. Chromatogr. A*, **2020**, *1612*, 460638.
6. X. Huang, G. Liu, D. Xu, X. Xu, L. Li, S. Zheng, H. Lin, H. Gao, *Appl. Sci.*, **2018**, *8*, 959.
7. M. Darvishnejad, H. Ebrahizadeh, *Microchim. Acta*, **2017**, *184*, 3603.
8. M. Sajid, C. Basheer, M. Daud, A. Alsharaa, *J. Chromatogr. A*, **2017**, *1489*, 1.
9. N.C. Mueller, J. Braun, J. Bruns, M. Černík, P. Rissing, D. Rickerby, B. Nowack, *Environ. Sci. Pollut. Res.*, **2012**, *19*, 550.
10. P.Y. Wang, X.X. Wang, S.J. Yu, Y.D. Zou, J. Wang, Z.S. Chen, N.S. Alharbi, A. Alsaedi, T. Hayat, Y.T. Chen, X.K. Wang, *Chem. Eng. J.*, **2016**, *306*, 280.
11. C. McCullum, P. Tchounwou, L.S. Ding, X. Liao, Y.M. Liu, *J. Agric. Food Chem.*, **2014**, *62*, 4261.
12. T. Arai, T. Sato, H. Kanoh, K. Kaneko, K. Oguma, A. Yanagisawa, *Chem. Eur. J.*, **2018**, *14*, 882.
13. D. Zhao, L. Zhao, C.S. Zhu, Z.B. Tian, X.Y. Shen, *Carbohydr. Polym.*, **2009**, *78*, 125.
14. H. Wang, X.L. Zhao, W. Meng, P.F. Wang, F.C. Wu, Z. Tang, X.J. Han, J.P. Giesy, *Anal. Chem.*, **2015**, *87*, 7667.
15. A. Speltini, M. Sturini, F. Maraschi, A. Profumo, *Trends Environ. Anal. Chem.*, **2016**, *10*, 11.
16. N.H. Abdullah, K. Shameli, E.C. Abdullah, L.C. Abdullah, *Chinese Chem. Lett.*, **2017**, 28, 1590.

17. J. Singh, L. Kaur, O.J. McCarthy, *Adv. Potato Chem. Technol.*, **2009**, 2009, 273.

18. N. Majoul, S. Aouida, B. Bessaïs, *Appl. Surf. Sci.*, **2015**, 331, 388.

19. R.V. Manek, P.F. Builders, W.M. Kolling, M. Emeje, O.O. Kunle, *AAPS PharmSciTech.*, **2012**, 13, 379.

20. X.J. Mu, Q.T. Wang, L.P. Wang, S.D. Fried, J.P. Piquemal, K.N. Dalby, P.Y. Ren, *J. Phys. Chem. B*, **2014**, 118, 6456.

21. F.Y. Lin, Jr. A.D. MacKerell, *J. Phys. Chem. B*, **2017**, 121, 6813.

22. P. Politzer, J.S. Murray, T. Clark, *Phys. Chem.*, **2013**, 15, 11178.

23. N.-H. Kim, J.-S. Lee, K.-A. Park, Y.-H. Kim, S.-R. Lee, J.-M. Lee, I.-S. Yu, K. Jung, Y.-K. Lee, *Food Sci. Biotechnol.*, **2016**, 25, 33–40.

24. AOAC. Guidelines for single laboratory validation of chemical methods for dietary supplements and botanicals, **2002**.

25. European Commission. Analytical quality control and method validation procedures for pesticides residues analysis in food and feed, Document No. SANTE/12682/2019, **2020**.
Fig. 1 Schematic diagram of the proposed MSPE procedure for OCPs
Fig. 2 Chromatograms of OCPs obtained from direct GC-µECD and after preconcentration by the proposed MSPE method (concentration 0.5 µg L⁻¹ each)
Table 1 The analytical features of the proposed MSPE-GC-µECD for OCPs

| Analyte    | Linear range (µg L⁻¹) | Linear equation       | R²   | LOD (ng L⁻¹) | LOQ (ng L⁻¹) | %RSDs | EFs |
|------------|------------------------|------------------------|------|--------------|--------------|--------|-----|
|            |                        |                        |      |              |              |        |     |
| Intra-day  |                        |                        |      |              |              |        |     |
| Inter-day  |                        |                        |      |              |              |        |     |
| tR          | Peak area              | tR                     | Peak area |             |              |        |     |
|             |                        |                        |      |              |              |        |     |
| Endosulfan | 0.25–2.00              | 7461.7x + 1077.90      | 0.9996 | 4.0          | 15.0         | 0.11   | 2.22| 0.08 | 9.15 | 24  |
| Heptachlor | 0.01–0.75              | 12351x - 145.75        | 0.9935 | 1.0          | 3.0          | 0.11   | 3.35| 0.07 | 7.72 | 14  |
| Aldrin     | 0.01–0.75              | 20899x - 8.98         | 0.9964 | 1.0          | 2.5          | 0.12   | 4.63| 0.08 | 8.96 | 25  |
| Isobenzan  | 0.01–0.75              | 10985x + 23.33        | 0.9971 | 1.0          | 2.5          | 0.12   | 4.75| 0.08 | 5.25 | 24  |
| Chlordane  | 0.10–1.00              | 8397.2x + 197.67      | 0.9996 | 4.0          | 15.0         | 0.13   | 2.97| 0.14 | 9.25 | 39  |
| Dieldrin   | 0.01–0.75              | 14376x - 123.75       | 0.9955 | 0.5          | 1.5          | 0.15   | 4.75| 0.09 | 9.05 | 21  |
| Endrin     | 0.10–1.00              | 14551x + 439.20       | 0.9998 | 1.0          | 3.0          | 0.11   | 3.81| 0.07 | 7.85 | 22  |