Optimising the Operating Parameters of Oil Palm Frond Silica-based Dispersive Solid Phase Extraction for Determination of Organochlorine Pesticides

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This study investigated the development of silica particles derived from oil palm fronds (OPF-Si) as a potential sorbent for determining organochlorine pesticides (OCPs) in aqueous samples. The technology applied is the dispersive solid-phase extraction (DSPE) followed by a chromatography-electron capture detector (GC-ECD). The OPF-Si was prepared via acid and thermal treatment and characterised using FT-IR and XRD to confirm its structural formation. Aldrin and Dieldrin were selected as the model analytes to examine the feasibility and performance of the OPF-Si-based DSPE to detect OCPs. The one-factor-at-a-time (OFAT) experimental approach was employed to investigate four significant variables for DSPE, including extraction time, desorption time, desorption solvent and mass of sorbent. As a result, the optimum extraction conditions were as follows: 40 mg of mass sorbent, 15 min extraction time, and n-hexane as desorption solvent at 5 min desorption time via sonication. The prepared sorbent showed a high affinity towards OCPs through hydrogen bonding and hydrophobic interaction.

Keywords: Dispersive solid phase extraction; organochlorine pesticides; oil palm frond; silica

Silica, also known as silicon dioxide (SiO_2), has been widely applied in the industry because of its safe and non-toxic nature. In addition, it has many remarkable applications due to its controllable pore size, modifiable surface, strong mechanical properties and comparatively inert chemical composition [1]. Most of the silica was extracted from various silica sources to produce chemical precursors, such as inorganic chemical compounds found naturally in sand, quartz, or flint with various shapes, including gel, crystalline, and amorphous forms [2]. However, this conventional method of silica extraction requires high-temperature conditions and massive energy consumption during the production process, increasing the risks for global warming and requiring higher production costs [3].

Hence, re-utilising agricultural and industrial waste is a crucial long-term strategy to create sustainable industry cycles [4]. Several industrial wastes have been reused as SiO_2 precursors, including powerplant fly ash [5], rice husk ash [6-7], sugarcane bagasse ash [8], palm kernel shell ash [9-10] and oil palm fronds [11-12]. Abdul Razak et al. [13] emphasised the simple procedure of chemical routes for silica production from agricultural waste. The process includes acid leaching or alkaline treatment, followed by either hydrothermal, co-precipitation or sol-gel. This method eliminates the high production cost of commercial silica precursor synthesis that relies on templates and surfactants. Therefore, it greatly benefits future chemical processes towards cleaner production and a circular economy.

Organochlorine pesticides (OCPs) are organic compounds that have a cyclic structure and a variable number of chlorine atoms. It was excessively used in the agricultural industry until the 1980s to protect cultivated plants from insects, weeds, fungi, and bacterial attacks. OCPs compound has been classified as persistent organic pollutants (POPs) with a high half-life of compound up to 15 years and difficulty to be naturally degraded in the environment [14]. Their lipophilic and non-biodegradable properties lead to bioaccumulation and assimilation in living tissue. OCPs cause toxic effects on aquatic organisms, disrupt the food chain and eventually cause harm to human health and natural ecology [15-17]. Consequently, this organic compound was reported to increase the risk of hormone-related cancers, endocrine-disrupting human reproductive system, gastrointestinal adsorption and neurodegenerative disorders because of progressive damage to cells and the nervous system [18-21].

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Hence, the use of OCPs was banned in the Stockholm Convention, and their agricultural or domestic usage was not allowed in many European Countries [22]. However, the occurrence of OCPs-related diseases was recently reported in South Africa [23], Jiuxi Valley, China [24] and Andra Pradesh, India [25], indicating that it is still being used illegally.

OCPs are usually determined using gas chromatographic techniques, with electron capture (ECD) and mass spectrometric (MS) detection [26-27]. Besides chromatographic variables, optimisation parameters of extraction in sample pre-treatment techniques always play a significant role in enhancing the determination of targeted analytes. Among these techniques, classical solvent extraction (LLE) [28] and solid-phase extraction (SPE) [29-30] could be mentioned for aqueous samples. In terms of accuracy and precision, both techniques have simple procedures and give logically known results but suffer from several drawbacks such as time consumption, high labour and materials costs and long-time exposure to hazardous organic solvents. Therefore, dispersive solid-phase extraction (DSPE) has been considered an efficient technique to establish the easy, fast, and economical analysis method of its features of simple operating procedure and less solvent consumption [8,10]. The principle of DSPE refers to the dispersion of a solid sorbent within liquid samples in the extraction isolation and clean-up of different analytes from complex matrices. In the DSPE, sorbents are commonly used to adsorb analytes in bulk samples [8] or interfering compounds [31].

Therefore, the present study focuses on re-utilising the oil palm frond as a silica precursor to prepare silica sorbent to determine selected organo-chlorine pesticides (OCPs). DSPE was applied in the aqueous sample before the gas chromatography electron capture detector (GC- ECD). Several important extraction parameters of DSPE, such as extraction time, desorption time, desorption solvent and mass of sorbent, were optimised using one factor at a time (OFAT) to understand the mechanism of interaction between sorbent and targeted analyte.
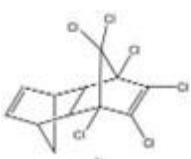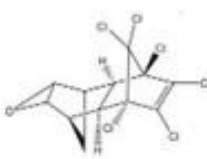
MATERIALS AND METHODS

Reagents, Materials, and Instrumentation

The oil palm fronds were collected from the oil palm plantation. Analytical grade n-hexane, dichloromethane, ethyl acetate and acetone were obtained from Merck (Darmstadt, Germany). Hydrochloric acid (HCl, 37%) was purchased from QReC Chemicals (New Zealand). Pesticide standards of aldrin and Dieldrin were purchased from Sigma-Aldrich (purity assay in the range of 98-101%). The chemical structures and properties of the studied OCPs in this work are shown in Table 1. A stock solution of each analyte was made by dissolving 10 mg of pure powder in 10 mL of methanol and keeping the solution at 4°C.

The chromatographic analysis for OCPs was performed by gas chromatograph with electron capture detector, GC-ECD, an Agilent 7890A GC-ECD equipped with an HP-5 column (30 m length x 320 µm ID x 0.25 µm film thickness). Helium was used as carrier gas (1 mL min^{-1}), while nitrogen (60 mL min^{-1}) was used as make-up gas. The injection port was set at 260°C, and the detector temperature was set at 270°C. The oven temperature was programmed from 150°C to 200°C at 30°C min^{-1}, then raised to 244°C at 3°C min^{-1} and 20°C min^{-1} at 260°C. OCPs were identified based on their retention times. The prepared sorbent was characterised using Perkin Elmer Fourier Transform infrared, FTIR (Spectrum 400 Perkin Elmer, Waltham, MA, USA) spectrometer in the range of 400 to 4000 cm^{-1} using potassium bromide pellet form. The crystallo- graphic structure of the prepared sorbent was examined using X-ray Diffraction, XRD (Rigaku Mini- flex II X-ray Diffractometer) with Cu Kα radiation (40 kV/40 mA, wavelength =0.1504 nm) at a scanning rate of

Table 1. Chemical structures and chemical properties of aldrin and Dieldrin [32].

Properties	Aldrin	Dieldrin
Molecular formula	$C_{12}H_8Cl_6$	$C_{12}H_8Cl_6O$
Molecular weight	364.9 g/mol	380.91 g/mol
Boiling point	145°C	385°C
Solubility in water	0.003%	0.02%

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2°C/min. The diffraction pattern was recorded at 2θ angle between 10º and 90º.

Preparation of Palm Frond Silica Sorbent (OPF-Si)

The procedure described was adopted from a previous study [33] with minor modifications. Freshly harvested oil palm fronds (OPF) were separated from the petiole and sorted to remove unwanted materials. The OPF was then left in the oven at 70°C for 48 hours to dry. The dried OPF were cut into smaller pieces and ground into fine powder. The OPF powder was dispersed into 1 M HCl and constantly stirred for 2 hours at 400 rpm. The dispersion was allowed to cool at room temperature. The wet powder was washed with distilled water until the acid-treated OPF reached neutrality at pH 7. The neutralised OPF was filtered and dried in an oven at 80ºC for 24 hours. Then, the OPF powder was calcined in the preheated furnace at 600ºC for 14 hours with a ramping time of 5 hours and a hold time of 9 hours at the rate of 2°C/min. The white ash of treated OPF-Si was harvested and stored in capped vials at room temperature for

further analysis.

Dispersive Solid Phase Extraction (DSPE)

A 40 mg of OPF-Si sorbent was added into a 50-mL centrifuge tube containing 10 mL (a dilution of 1:9) of the aqueous sample. The sample was vortexed for 15 min at 900 rpm. The sorbent was then separated from the solution by centrifugation at a speed of 4000 rpm for 3 min, and the supernatant was discarded. The desorption of analytes was performed with 500 µL of solvent under ultrasonication for 5 min, and the solution was filtered through a 0.45 µm polypropylene syringe filter. The solution was then pre-concentrated to 300 µL under a gentle stream of nitrogen gas for analyte enrichment. A 2 µL aliquot of the final extract was analysed by GC-ECD. Figure 1 illustrates the schematic dispersive solid phase extraction (DSPE) method.

The parameters for DSPE performance were investigated and summarised in Table 2. The DSPE method was optimised in triplicate with deionised water spiked with 1 mg/L of selected OCPs.
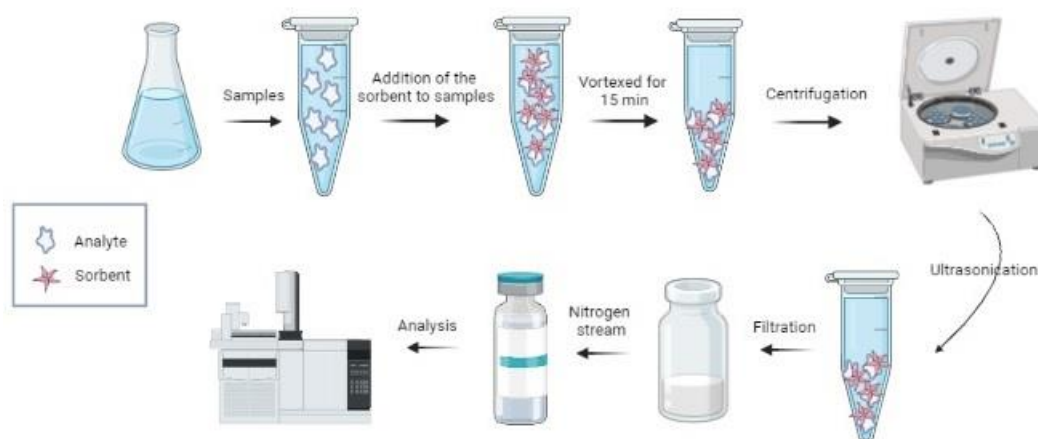

Figure 1. Schematic dispersive solid phase extraction (DSPE) method.

Table 2. Extraction parameters involved in the optimisation process.

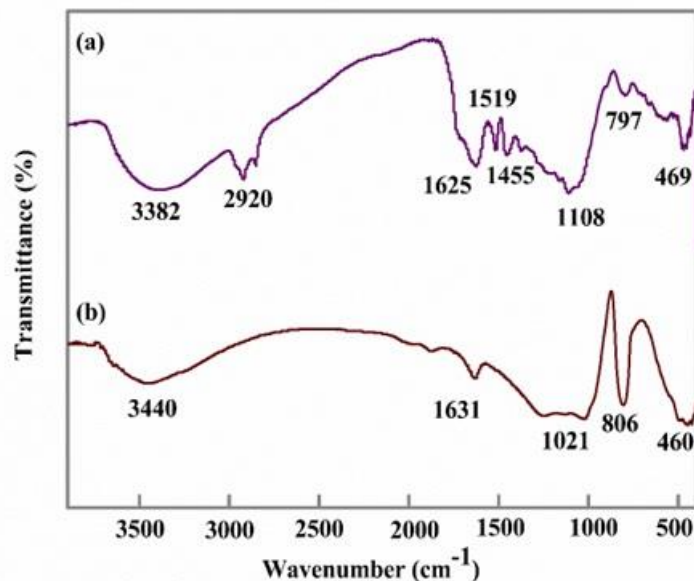| Parameter	Optimised DSPE Conditions
Extraction time (min)	5, 10, 15, 20, 25
Desorption time (min)	1, 2.5, 5, 7.5
Type of desorption solvent	n-hexane, dichloromethane, ethyl acetate, acetone
Sorbent dosage (mg)	20, 40, 60, 80

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Figure 2. The FTIR spectrum of (a) OPF and (b) OPF-Si

RESULTS AND DISCUSSION

Characterisation of Palm Frond Silica

Fourier Transform Infrared Spectroscopy (FTIR)

Silica prepared from acid-leached OPF was further characterised using FTIR and compared with raw OPF to observe changes in their composition. As shown in Figure 2(a), the FTIR spectroscopy displayed the presence of the adsorption bands of O-H stretching vibrations at 3382 cm^{-1} that were caused by intra-intermolecular hydrogen bonding. However, the O-H stretching vibration bands were shifted to 3440 cm^{-1} (Figure 2 (b)) with slightly decreased intensity bands. It may be attributed to the tightly bonded hydrogen in the silanol chain, which constrains the bonding vibrations, as was previously documented [34]. The presence of lignin in OPF was indicated by the emergence of a band at 2920 cm^{-1} due to the CH_2 stretching vibrations of carbonyl groups present in lignin [35]. Similarly, the aromatic rings of lignin at 1519 cm^{-1} and 1455 cm^{-1} (Figure 2(b)) were ascribed to the stretching vibrations of C=C [36]. The vibrational bands for hemicellulose and lignin functional groups CH_2, C=C, and C-O-C, disappeared in the spectra of OPF-Si. This observation suggests that most hemicellulose and lignin were eliminated during the acid treatment [37].

Additionally, two distinct peaks were observed at 1631 cm^{-1} and 1625 cm^{-1}, corresponding to the stretching vibrations caused by the biopolymer's O-H bending [38]. On the other hand, a band at 1108 cm^{-1} and 1021 cm^{-1} corresponds to C-O-C stretching due to the pyranose ring and glycosidic linkages between glucose units in the cellulose, respectively [39].

Siloxane (Si-O-Si) stretching vibrations are responsible for the 797 cm^{-1} and 806 cm^{-1} bands, while the 469 cm^{-1} and 460 cm^{-1} bands are due to siloxane terminating vibrations in OPF and OPF-Si, respectively [40].

X-ray Diffraction (XRD)

The result obtained by XRD for OPF-Si is shown in Figure 3. The data confirms that the extracted silica is predominantly an amorphous solid, as described by Onoja et al. [33]. A higher difference (diffraction peak at $2\theta = 24.0$) shows an XRD pattern typical of amorphous materials, which is also characteristic of mesoporous silica nanoparticles [41]. Figure 3 illustrates the XRD patterns of OPF and OPF-Si. Both samples are subjectively evaluated for peak identification using the International Centre for Diffraction Data (ICDD). Apart from the existence of amorphous materials, the diffractogram of OPF (Figure 3(a)) revealed the presence of two main mineral phases. The compounds are cristobalite (SiO_2) and hematite (Fe_2O_3), with ICDD card numbers 01-080-3756 and 01-080-5411. The outcome is comparable to results that were published from a prior study on agricultural biomass [42]. However, in Figure 3 (b) for OPF-Si, the peak related to hematite, labelled H in the diffractogram, vanished. This occurrence is caused by a decrease in the concentrations of the AAEMs after the acid leaching and thermal treatment procedures. While the Bragg angles at $2\theta = 24°$ confirm the presence of the amorphous character of silica as the predominant component in OPF-Si, which is made from calcined agricultural biomass [43-44].
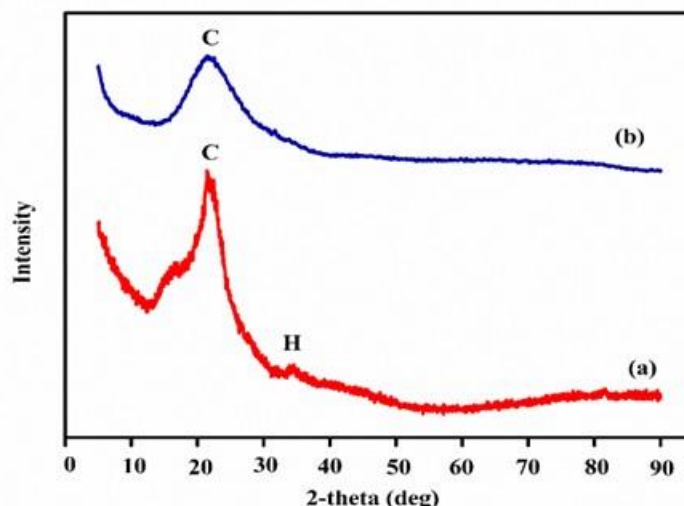
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Figure 3. XRD pattern (a) OPF and (b) OPF-Si

Optimisation of DSPE Conditions

Optimisation of numerous variables is required to establish a DSPE procedure for the determination of aldrin and Dieldrin. Significant parameters that might affect DSPE performance [45], including extraction time, desorption time, solvent, and sorbent dosage, were thoroughly investigated. At the same time, other parameters such as room temperature, vortex speed (900 rpm), sample volume (10 mL), and desorption solvent volume (500 μL) were kept constant. The trials were carried out in triplicate (n=3), and the means of results were used for optimisation.

Extraction Time

The principle behind DSPE is the diffusion of analytes from the sample matrix to the extraction phase with the ultimate goal of reaching equilibrium between the phases. Theoretically, a longer extraction time will allocate more time for adsorption. However, a sufficient amount of time is required for a close system of DSPE to reach adsorption equilibrium where the adsorption and desorption rates become constant [46]. Therefore, the highest extraction efficiency was achieved when the extraction time reached equilibrium. In this experiment, the influence of extraction time between the analyte and sorbent was investigated by varying the agitation time from 5 to 25 min.

The experimental results depicted in Figure 4 demonstrate that the recovery of OCPs increased gradually with the progression of extraction time from 5 to 15 min. This observation suggests that the adsorption of OCPs increases over time as the large surface area of silica sorbent allows larger effective contact between sorbent and targeted analytes for swift mass transfer [47]. After 15 min, the recovery of OCPs remained plateau, indicating that the adsorption equilibrium has been achieved and the adsorption process has been completed. Therefore, the DSPE procedure was carried out employing 15 min of extraction time in all further stages of this work.
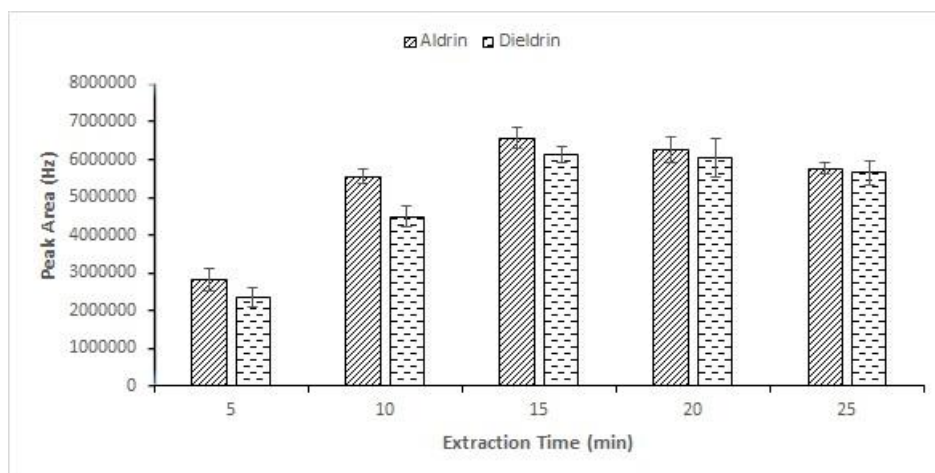

Figure 4. The effect of extraction time on the DSPE method for extraction of OCPs
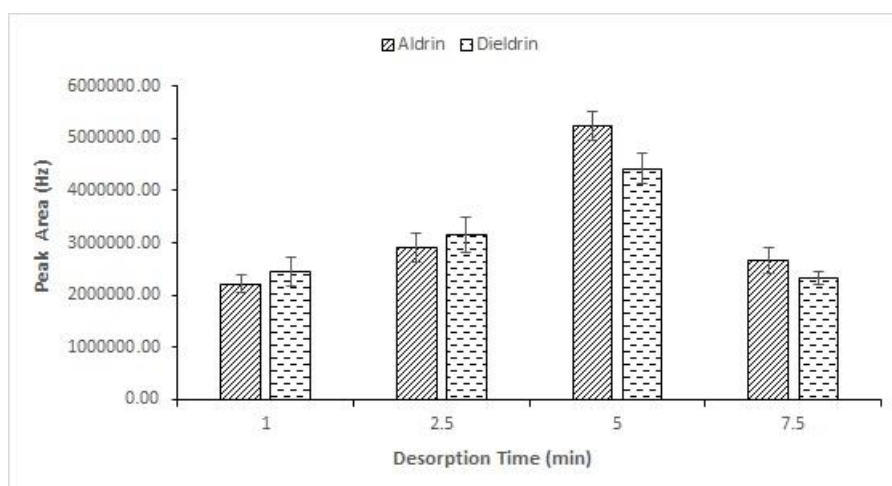
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Figure 5. The effect of desorption time on the DSPE method for extraction of OPCs

Desorption Time

Desorption time is the time required for the analyte to be eluted from the sorbent surface. The DSPE procedure requires sufficient desorption time to achieve the desorption equilibria [48]. The effect of desorption time was studied for 1-7.5 minutes using a sonicator to determine the minimum amount of time required for complete elution. Desorption time refers to the time it takes to desorb all the analytes from the sorbent. Based on Figure 5, the extraction efficiency of the analytes increased by increasing the desorption times by up to 5 minutes. This fact demonstrates that the recovery of OCPs increases as time progresses before finally reaching a saturation state, indicating that the state of desorption equilibrium has been achieved [45]. However, a further increase in desorption time and decrease at 7.5 minutes showed significant decreases in OCP recovery of OCPs, most likely due to re-adsorption of the target analytes onto the sorbent [49] and possibly because of increased temperature with prolonged sonication [50], which can cause decomposition of analytes. Therefore, 5 min desorption time was selected as the optimum time.

Desorption Solvent

The selection of a suitable desorption solvent is important in the microextraction technique to ensure high recovery and sensitivity in extraction method performance [51]. Therefore, characteristics such as extraction capability, solubility, and compatibility with the GC system must be considered in this study. Several organic solvents were used, namely n-hexane, dichloromethane, ethyl acetate and acetone, with polarity indexes of 0.1, 3.1, 4.4 and 5.1, respectively. Non-polar solvents should give better results than polar solvents due to the relative water insolubility of aldrin and Dieldrin (Table 1). Based on the result, n-hexane showed the highest desorption efficiency (Figure 6) due to its low polarity index and strongest affinity for the OCPs due to its strong hydrophobic effect [52]. However, dipole-dipole interaction and hydrogen bonding between the targeted analytes and sorbent (OPF-Si) should not be disregarded. Therefore, further experiments were carried out using 500 µL of n-hexane as a desorption solvent.
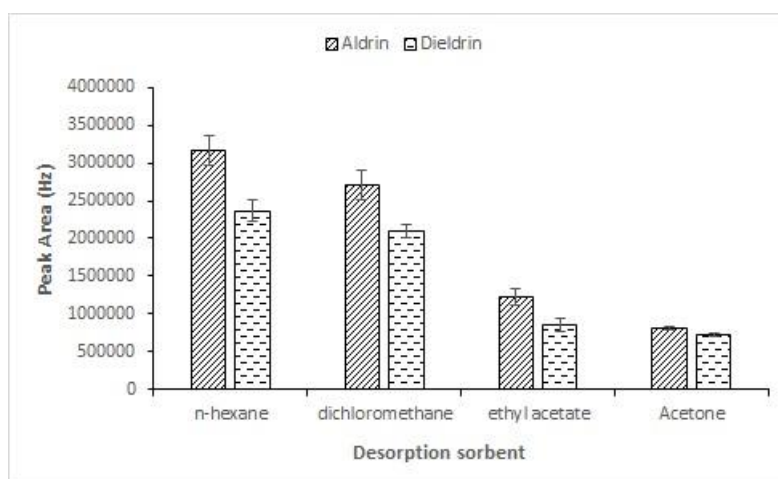

Figure 6. The effect of desorption solvent on the DSPE method for extraction of OPCs

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Figure 7. The effect of sorbent dosage on the DSPE method for extraction of OCPs

Sorbent Dosage

The amount of sorbent is another important parameter to be considered in the DSPE procedure. Generally, an increase in the amount of adsorbent will increase the number of adsorption sites that may occupy the adsorbate particles during the extraction procedure [53]. In order to determine the minimum amount of sorbent sufficient to extract the total amount of OCPs per sample, the influence of the mass of silica sorbent on the recovery of the targeted OCPs was investigated in the range between 20 and 80 mg. Based on the obtained results (Figure 7), the recoveries of OCPs increased when the sorbent mass increased from 20-40 mg. However, a further increase in the mass of sorbent did not improve the extraction efficiency of OCPs. This observation might be because of the saturation of sorption sites for the selected sample volume. Thus, excessive sorbents used resulted in more difficult desorption and required a higher volume of desorption solvent [50]. It can be concluded that 40 mg of the sorbent is adequate to provide sufficient active sites for quantitative extraction of OCPs in 10 mL of sample.

CONCLUSION

Remarkable parameters of the DSPE technique based on a new silica sorbent enriched from oil palm frond (OPF) for determining OCPs before GC-ECD analysis have been successfully optimised in this study by using the OFAT approach. The finding suggested that 40 mg of mass sorbent, 15 min extraction time, and n-hexane as desorption solvent at 5 min desorption time via sonication can be further used to investigate the trace determination of OCPs in various real samples. Furthermore, the experimental value of optimisation parameters showed that the dominant interaction between aldrin and dieldrin is via hydrophobic interaction, dipole-dipole and Hydrogen bonding interaction. The findings of this study will therefore provide a reference for future investigations using OCPs and silica sorbents.

REFERENCES

1. Chen, L., Liu, J., Zhang, Y., Zhang, G., Kang, Y., Chen A., Feng, X., Shao, L. (2018) The Toxicity of Silica Nanoparticles to the Immune System. *Nanomedicine*, **13**, 1939–1962.

2. Nor Surayah Osman and Norzahir Sapawe (2019) Waste Material As an Alternative Source of Silica Precursor in Silica Nanoparticle Synthesis – A Review. *Materials Today: Proceedings*, **19**, 1267–1272.

3. Bergna, H. E., Roberts, W. O. (2006) *Taylor & Francis*, 9–37.

4. Imoisili, P. E., Ukoba, K. O., Jen, T. C. (2020) Synthesis and Characterization of Amorphous Mesoporous Silica from Palm Kernel Shell Ash. *Bol. La Soc. Esp. Ceram. Y. Vidr.*, **59**, 159–164.

5. Lü, J., Liu, J., Wei, Y., Jiang, K., Fan, S., Liu, J., Jiang, G. (2007) Preparation of Single-Walled Carbon Nanotube Fiber Coating for Solid-Phase Microextraction of Organochlorine Pesticides in Lake Water and Wastewater. *J. Sep. Sci.*, **30**, 2138–2143.

6. Mostafalou, S., Abdollahi, M. (2017) Pesticides: An Update of Human Exposure and Toxicity, Arch. *Toxicol.*, **91**, 549–599

33   Nordiana Suhada Mohmad Tahiruddin, Nur Husna Zainal Abidin, Azreen Asyikin Mhd Kamal, Nor Suhaila Mohamad Hanapi, Nursyamsyila Mat Hadzir, Sheela Chandren, and Wan Nazihah Wan Ibrahim

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7.   Barriada-Pereira, M., González-Castro, M. J., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., Fernández-Fernández, E. (2004) Determination of 21 organochlorine pesticides in tree leaves using solid-phase extraction clean-up cartridges. *J Chromatogr A.*, **1061 (2)**, 133–139

8.   Li, N., Zhu, Q., Yang, Y., Huang, J., Dang, X. & Chen, H. (2015) A novel dispersive solid phase extraction method using metal-organic framework MIL-101 as the adsorbent for the analysis of benzophenones in toner. *Talanta*, **132**, 713–718.

9.   Barceló, D. (1993) Environmental Protection Agency and other methods for the determination of priority pesticides and their transformation products in water. *J. Chromatogr. A.*, **643**, 117–143.

10.   Liu, L., Xia, L., Wu, C., Qu, F., Li, G., Sun, Z. & You, J. (2016) Zirconium (IV)-based metal organic framework (UIO-67) as efficient sorbent in dispersive solid phase extraction of plant growth regulator from fruits coupled with HPLC fluorescence detection. *Talanta*, **154**, 23–30.

11.   Emmanuel Onoja, Sheela Chandren, Fazira Ilyana Abdul Razak, Roswanira Abdul Wahab (2018) Extraction of nanosilica from oil palm leaves and its application as support for lipase immobilization. *Journal of Biotechnology*, **283**, 81–96.

12.   Roslan, A. M., Zahari, M. A. K. M., Hassan, M. A., Shirai, Y. (2014) Investigation of Oil Palm Frond Properties for Use as Biomaterials and Biofuels. *Trop. Agric. Dev.*, **58**, 245 26–29

13.   Nurina Adriana Abdul Razak, Nur Hidayati Othman, Muhammad Shafiq Mat Shayuti, Aidah Jumahat, Napisah Sapiai, Woei Jye Lau (2022) Agricultural and industrial waste-derived mesoporous silica nanoparticles: A review on chemical synthesis route. *Journal of Environmental Chemical Engineering*, **10**, 107322

14.   Dehao Tang, Xingjian Liub, Haijun He, Zhenang Cui, Huayang Gan, Zhen Xia (2020) Distribution, sources and ecological risks of organochlorine compounds (DDTs, HCHs and PCBs) in surface sediments from the Pearl River Estuary, China. *Marine Pollution Bulletin*, **152**, 110942.

15.   Hua, S., Gong, J. -L., Zeng, G. -M., Yao, F. -B., Guo, M., Ou, X. -M. (2017) Remediation of organochlorine pesticides contaminated lake sediment using activated carbon and carbon nanotubes. *Chemosphere*, **177**, 65–76.

16.   Temoka, C., Wang, J., Bi, Y., Deyerling, D., Pfister, G., Henkelmann, B., Schramm, K. -W. (2016) Concentrations and mass fluxes estimation of organochlorine pesticides in three gorges reservoir with virtual organisms using in situ PRC-based sampling rate. *Chemosphere*, **144**, 1521–1529.

17.   Günter, A., Balsaa, P., Werres, F., Schmidt, T. C. (2016) Influence of the drying step within 395 disk-based solid-phase extraction both on the recovery and the limit of quantification of 396 organochlorine pesticides in surface waters including suspended particulate matter. *J. 397 Chromatogr. A.*, **1450**, 1–8.

18.   Luo, Y. B., Li, X., Jiang, X. Y., Cai, B. D., Zhu, F. P., Zhang, H. F., Chen, Z. G., Pang, Y. Q., Feng, Y. Q. (2015) Magnetic graphene as modified quick, easy, cheap, effective, rugged and safe adsorbent for the determination of organochlorine pesticide residues in tobacco. *J. Chromatogr. A.*, **1406**, 1–9.

19.   Tankiewicz, M., Fenik, J., Biziuk, M. (2011) Solventless and solvent-minimized sample preparation techniques for determining currently used pesticides in water samples: a review. *Talanta*, **86**, 8–22.

20.   Mostafalou S., Abdollahi, M. (2017) Pesticides: an update of human exposure and toxicity. *Arch. Toxicol.*, **91**, 549–599.

21.   Qiu, X., Zhu, T., Li, J., Pan, H., Li, Q., Miao, G., Gong, J. (2004) Organochlorine pesticides in the air around the Taihu lake, China. *Environ. Sci. Technol.*, **38**, 1368– 1374.

22.   United nations environment programme, Stockholm convention on persistent organic pollutants (POPs), Secr. Stock. Conv. (2018) 1–77. http://www.pops.int/theConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx.

23.   Thompson, L. A., Darwish, W. S., Ikenaka, Y., Nakayama, S. M., Mizukawa, H. & Ishizuka, M. (2017) Organochlorine pesticide contamination of foods in Africa: Incidence and public health. *The Journal of Veterinary Medical Science*, **79(4)**, 751–764.

24.   Liu, Z., Zheng, G. & Liu, Z. (2020) Organo-chlorine Pesticides in Surface Water of Jiuxi Valley China: Distribution, Source Analysis and Risk Evaluation. *Journal of Chemistry*, 1–8.

25.   The Times of India (2020, December 7). Organo-chlorine substances suspected to have triggered mystery disease in Andhra Pradesh Eluru, Andhra Pradesh, India.

26.   Tomkins, B. A., Barnard, A. R. (2002) Determination of organochlorine pesticides in ground water using solid-phase microextraction

34 Nordiana Suhada Mohmad Tahiruddin, Nur Husna Zainal Abidin, Azreen Asyikin Mhd Kamal, Nor Suhaila Mohamad Hanapi, Nursyamsyila Mat Hadzir, Sheela Chandren, and Wan Nazihah Wan Ibrahim

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followed by dual-column gas chromatography with electron-capture detection. *J. Chromatogr. A.*, **964**, 21–33.

27. Dong, C., Zeng, Z., Yang, M. (2005) Determination of organochlorine pesticides and their derivations in water after HS-SPME using polymethylphenylvinylsiloxane-coated fiber by GC- ECD. *Water Res.*, **39**, 4204–4210.

28. Barceló, D. (1993) Environmental Protection Agency and other methods for the determination of priority pesticides and their transformation products in water. *J. Chromatogr. A.*, **643,** 117–143

29. Lü, J., Liu, J., Wei, Y., Jiang, K., Fan, S., Liu, J., Jiang, G. (2007) Preparation of single-walled carbon nanotube fiber coating for solid-phase microextraction of organochlorine pesticides in lake water and wastewater. *J. Sep. Sci.*, **30**, 2138–2143.

30. Barriada-Pereira, M., González-Castro, M. J., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., Fernández-Fernández, E. (2004) Determination of 21 organochlorine pesticides in tree leaves using solid-phase extraction clean-up cartridges. *Journal of Chromatography A.*, **1061(2)**, 133–139

31. Anastassiades, M., Lehotay, S. J., Stajnbaher, D. & Schenck, F. J. (2003) Fast and easy multi-residue method employing acetonitrile extraction/ partitioning and "Dispersive Solid-Phase Extraction" for the determination of pesticide residues in produce. *Journal of AOAC International*, **86**, 412–431.

32. do Carmo, S. N., Mendes, L. D., Corazza, G., Comelli, H., Merib, J. & Carasek, E. (2020) Determination of pesticides of different chemical classes in drinking water of the state of Santa Catarina (Brazil) using solid-phase microextraction coupled to chromatographic determinations. *Environmental Science and Pollution Research*, **27(35)**, 43870–43883.

33. Onoja, E., Attan, N., Chandren, S., Ilyana, F., Razak, A., Syazwani, A., Keyon, A., Mahat, N. A. & Wahab, R. A. (2017) Insights into the physico-chemical properties of the Malaysian oil palm leaves as an alternative source of industrial materials and bioenergy. *Malaysian Journal of Fundamental and Applied Sciences*, **13(4)**, 623–631.

34. Lionetto, F., Sole, R. D., Cannoletta, D., Vasapollo, G. & Maffezzoli, A. (2012) Monitoring Wood Degradation during Weathering by Cellulose Crystallinity. *Materials*, **5**, 1910–1922.

35. Cyran, M. & Saulnier, L. (2007) Association and Structural Diversity of Hemicelluloses in the Cell Walls of Rye Outer Layers: Comparison between Two Ryes with Opposite Breadmaking Quality. *Journal of Agricultural and Food Chemistry*, **55(6)**, 2329-41.

36. Panthapulakkal, S. & Sain, M. (2006) Bioprocess Preparation of Wheat Fiber and Characterization. *Industrial Crop Production*, **23**, 1–8.

37. Sim, K., Youn, H. J., Cho, H., Shin, H., Lee, L. H. (2012) Improvement in Pulp Properties by Alkali Pre-Extraction and subsequent Kraft Pulping with Controlling H-Factor and Alkali Charge. *Bioresources*, **74**, 5864–5878.

38. Deepa, M, Surekha, M., Thushara Bindu, V., Deepti Bhargavi, K., Deva, S. S. (2015) Gold Nanoparticles in Cancer Therapy. *International Journal of Advances in Pharmacy and Biotechnology*, **1(2)**, 19–24.

39. Alemdar, A. and Sain, M. (2008) Isolation and Characterization of Nanofibers from Agricultural Residues-Wheat Straw and Soy Hulls. *Bioresource Technology*, **99**, 1664–1671.

40. Diyana Faziha Mohamad, Nor Surayah Osman, Mohd Khairul Hanif Mohd Nazri, Azizzil Azim Mazlan, Muhammad Farhan Hanafi, Yusak Asri Mohd Esa, Mohd Izzat Ikhwan Mohd Rafi, Muhammad Naim Zailani, Nurul Nabihah Rahman, Abu Hassan Abd Rahman, Norzahir Sapawe (2019) Synthesis of Mesoporous Silica Nanoparticle from Banana Peel Ash for Removal of Phenol and Methyl Orange in Aqueous Solution. *Materials Today: Proceedings*, **19**, 1119–1125.

41. Ungku Amirul Arif Ungku Abdullah, Nor Suhaila Mohamad Hanapi, Wan Nazihah Wan Ibrahim, Nursyamsyila Mat Hadzir, Nurzaimah Zaini, Ahmad Lutfi Anis and Noorfatimah Yahaya (2021) Pre-Concentration and Determination of Tetracyclines Antibiotics Residues in Water Samples Using RGO/Fe3O4 Nanocomposite as Extraction Sorbent Indones. *J. Chem.*, **21(5)**, 1196–1211.

42. Mochamad Zakki Fahmi, Abdul Haris, Ahmadi Jaya Permana, Denika Liyan Nor Wibowo, Bambang Purwanto, Yatim Lailun Nikmah and Adi Idris (2018) Bamboo Leaf-Based Carbon Dots for Efficient Tumor Imaging and Therapy. *RSV Adv.*, **8**, 38376.

43. Rafiee, E. and Shahebrahimi, S. (2012) Nano Silica with High Surface Area from Rice Husk as a Support for 12-Tungstophosphoric Acid: An Efficient Nano Catalyst in Some Organic Reactions. *Chinese Journal of Catalysis*, **33**,

35   Nordiana Suhada Mohmad Tahiruddin, Nur Husna Zainal Abidin, Azreen Asyikin Mhd Kamal, Nor Suhaila Mohamad Hanapi, Nursyamsyila Mat Hadzir, Sheela Chandren, and Wan Nazihah Wan Ibrahim

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1326–1333.

44.   Ravindran, R. & Kumar Jaiswal, A. (2015) A Comprehensive Review on Pre-Treatment Strategy for Lignocellulosic Food Industry Waste: Challenges and opportunities. *Bioresource Technology*, **199**.

45.   Peige Qin, Yixin Yang, Wenqi Li, Jing Zhang, Qian Zhou and Minghua Lu (2019) Amino-functionalized mesoporous silica nanospheres (MSN-NH2) as sorbent for extraction and concentration of synthetic dyes from foodstuffs prior to HPLC analysis. *Anal. Methods*, **11**, 105.

46.   Ungku Amirul Arif Ungku Abdullah, Nor Suhaila Mohamad Hanapi, Wan Nazihah Wan Ibrahim, Nursyamsyila Mat Hadzir, Nurzaimah Zaini, Ahmad Lutfi Anis and Noorfatimah Yahaya (2021) Pre-Concentration and Determination of Tetracyclines Antibiotics Residues in Water Samples Using RGO/Fe3O4 Nanocomposite as Extraction Sorbent Indones. *J. Chem.*, **21(5)**, 1196–1211.

47.   Nur Husna Zainal Abidina, Wan Nazihah Wan Ibrahima, Nor Suhaila Mohamad Hanapi, Nursyamsyila Mat Hadzir, Siti Kartina Abdul Karim, Noorfatimah Yahaya and Sazlinda Kamaruzaman (2022) Trace Level Quantification of Organophosphorus Pesticides from Fleshy Fruit Samples by Magnetic Solid-phase Extraction Using Fabricated SBA-15/Fe3O4 Coupled with HPLC/UV. *Anal. Bioanal. Chem. Res.*, **9(1)**, 45–57.

48.   Wan Ibrahim, W. A., Veloo, K. V. & Sanagi, M. M. (2012) Novel sol-gel hybrid methyltrimetho-xysilane-tetraethoxysilane as solid phase extraction sorbent for organophosphorus pesticides. *Journal of Chromatography A.*, **1229**, 55–62.

49.   Farah Wahidah Mohd Hassan, Muggundha Raoov, Sazlinda Kamaruzaman, Ahmad Husaini Mohamed, Wan Nazihah Wan Ibrahim, Nor

Suhaila Mohamad Hanapi, Nur Nadhirah Mohamad Zain NoorfatimahYahaya, David Da Yong Chen (2021) A rapid and efficient dispersive trehalose biosurfactant enhanced magnetic solid phase extraction for the sensitive determination of organophosphorus pesticides in cabbage (Brassica olearaceae var. capitate) samples by GC-FID. *Journal of Food Composition and Analysis*, **102**, 104057.

50.   Wan Nazihah Wan Ibrahim, Mohd Marsin Sanagi, Nor Suhaila Mohamad Hanapi, Sazlinda Kamaruzaman, Noorfatimah Yahaya, Wan Aini Wan Ibrahim (2018) Solid-phase Microextraction Based on an Agarose-Chitosan-Multi-Walled Carbon Nanotube Composite Film Combined with HPLC–UVfor the Determination of Non-steroidal Anti-Inflammatory Drugs in Aqueous Samples. *J. Sep. Sci.*, 2942–2851.

51.   Wan Ibrahim, W. A., Veloo, K. V. & Sanagi, M. M. (2012) Novel sol-gel hybrid methyltrimetho-xysilane-tetraethoxysilane as solid phase extraction sorbent for organophosphorus pesticides. *Journal of Chromatography A.*, **1229**, 55–62.

52.   Faridah Mohd Marsin, Wan Aini Wan Ibrahim, Hamid Rashidi Nodeh, Mohd Marsin Sanagi (2019) New Magnetic Oil Palm Fiber Activated Carbon-Reinforced Polypyrrole Solid Phase Extraction Combined With Gas Chromatography-Electron Capture Detection for Determination of Organochlorine Pesticides in Water Samples. *Journal of Chromatography A.*, **460638**.

53.   Amirhassan Amiri, Reza Tayebee, Abbas Abdar, Fatemeh Narenji Sani (2019) Synthesis of a zinc-based metal-organic framework with histamine as an organic linker for the dispersive solid-phase extraction of organophosphorus pesticides in water and fruit juice samples. *Journal of Chromatography A.*, **1597**, 39–45.