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ENRICHED SILICA FROM OIL PALM BIOMASS FOR MAGNETIC SOLID PHASE EXTRACTION OF ORGANOCHLORINE PESTICIDE: CHARACTERIZATION AND METHOD DEVELOPMENT

(Silika yang Diperkayakan daripada Biomas Kelapa Sawit untuk Pengekstrakan Fasa Pepejal Magnetik Organoklorin Racun Serangga: Ciri dan Pembangunan Kaedah)

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Abstract

This study focused on preparing magnetic silica bio-sorbent made from oil palm fronds and developing methods for analyzing trace amounts of organochlorine pesticides, including Aldrin, Dieldrin, and Heptachlor. The bio-sorbent, namely $Fe_3O_4@SiO_2$, was prepared through the sol-gel method by combining silica particles derived from oil palm fronds with commercial ferrous (II) oxide. The physical and chemical properties of the bio-sorbents were analyzed using ATR-FTIR, FESEM, EDX, and XRD. According to ATR-FTIR, the bio-sorbent contained absorption bands at 1100 cm^{-1} and 500-600 cm^{-1}, indicating the functional groups of Si-O and Fe-O. FESEM and EDX studies show the particles have a rough and irregular surface morphology that is composed of 63.9% oxygen, 16.97% silica, and 19.04% ferrous atomic weight. Meanwhile, XRD analysis confirmed that the bio-sorbent was composed of face-centered cubic Fe_3O_4 and amorphous SiO_2, with multiple peaks appearing at 2θ = 22.978 (101), 30.20 (220), 35.60 (311), and 57.50. A magnetic solid-phase extraction method using the synthesized bio-sorbent was developed prior to gas chromatography-mass spectrometry analysis of the selected OCPs. The optimal extraction conditions were determined via one variable at a time (OVAT) and resulted as follows: extraction time, 5 min; desorption solvent, ethyl acetate; desorption time, 5 min; mass of sorbent, 40 mg. The analytical performance of the method was evaluated under these conditions, with a detection limit of 0.1-0.53 mg/L and an extraction recovery of 80-92%. Several linear ranges were obtained for Heptachlor, Aldrin, and Dieldrin, including 0.6-1.8, 0.1-0.3, and 0.2-0.6 mg/L, respectively. The effectiveness of the bio-sorbent was proven by removing pesticides from actual paddy water samples, with calibration curves showing linearity over a wide range of values. The intra- and inter-day precisions were 0.50-1.86% and 0.69-2.54%, respectively.

Keywords: bio-sorbent magnetic silica, organochlorine, paddy water samples, magnetic solid phase extraction

Abstrak

Kajian ini bertujuan untuk menghasilkan biosorbent silika magnetik daripada pelepah kelapa sawit dan membangunkan kaedah untuk menganalisis jumlah jejak racun serangga organoklorin seperti Heptachlor, Aldrin, dan Dieldrin. Bio-sorben iaitu Fe_3O_4-SiO_2 telah disediakan melalui kaedah sol-gel dengan menggabungkan zarah silika yang diperolehi daripada pelepah kelapa sawit dengan ferus (II) oksida komersial. Sifat fizikal dan kimia bio-sorben telah dianalisis menggunakan ATR-FTIR, FESEM, EDX, dan XRD. Menurut ATR-FTIR, bio-sorben mengandungi julat penyerapan pada 1100 cm^{-1} dan 500-600 cm^{-1}, yang menunjukkan kumpulan fungsi Si-O dan Fe-O. Kajian FESEM dan EDX menunjukkan bahawa partikel mempunyai morfologi permukaan yang kasar dan tidak teratur yang terdiri daripada 63.9% oksigen, 16.97% silika, dan 19.04% berat atom ferus. Sementara itu, analisis XRD mengesahkan bahawa bio-sorben terdiri daripada Fe_3O_4 kubik berpusat muka dan SiO_2 amorfus, dengan pelbagai puncak yang muncul pada 2θ = 22.978 (101), 30.20 (220), 35.60 (311), dan 57.50. Pembangunan kaedah pengekstrakan fasa pepejal magnet dengan menggunakan bio-sorben yang disintesis telah dijalankan diikuti analisis oleh kromatografi gas spektrometri jisim (GC-MS) daripada OCP yang terpilih. Keadaan pengekstrakan optimum ditentukan melalui satu parameter pada satu masa dan hasilnya seperti berikut: masa pengekstrakan 5 min; pelarut desorpsi, etil esitat; masa desorpsi, minit, dan sorbent jisim 40 mg. Prestasi analisis kaedah dinilai di bawah keadaan ini, dengan had pengesanan 0.1-0.53 mg/L dan pemulihan pengekstrakan 80-92%. Beberapa julat linear telah diperolehi untukHeptachlor, Aldrin dan Dieldrin, termasuk 0.6-1.8, 0.1-0.3, dan 0.2-0.6 mg/L masing-masing. Keberkesanan biosorben telah dibuktikan dengan mengeluarkan racun perosak daripada sampel air padi sebenar, dengan lengkung penentukuran menunjukkan kelinearan ke atas julat nilai yang luas.Ketepatan dalam dan antara hari ditemui dalam julat 0.50-1.86% dan 0.69-2.54%, masing-masing.

Kata kunci: bio-sorben silika magnet, organoklorin, sampel air padi, pengekstrakan fasa pepejal magnet

Introduction

In Malaysia, vast areas are devoted to cultivating oil palm, a significant agricultural product [1]. However, oil palm farming is associated with several environmental issues, such as deforestation and the accumulation of agricultural waste in the form of oil palm fronds (OPF). These fronds are often allowed to deteriorate or burn, resulting in greenhouse gas (GHG) emissions and air pollution [2]. Consequently, developing new uses for OPF can help reduce waste, generate economic benefits, and mitigate the negative environmental impact of oil palm farming. Researchers have devised various methods to convert palm oil biomass into valuable goods with added value, thereby decreasing the amount of palm oil biomass produced. One such valuable product is silica, which is found in the frond leaves of oil palms. Commercial silica is typically used as a precursor for other materials in industrial manufacturing that are costly and energy-intensive. Silica, on the other hand, is extracted from agricultural waste at moderate temperatures, resulting in an enormously cost-effective product [3]. Therefore, the production of silica from palm oil biomass can meet industrial demands because it can be used as a precursor in the manufacture of glass and cement, as well as in the biological sector as a catalyst carrier or adsorbent for metal removal. According to a study by Onoja et al. [4], acid-treated OPF ash contains up to 95.30% silica (SiO_2). Their controllable particle size, large surface area, great biocompatibility, and adsorptive properties make them useful in numerous technical applications, including low-loss, subwavelength-diameter single-mode optical waveguides, nanoscale optical sensors, atomic trapping and guiding [5, 6].

In agriculture, pesticides are utilized as plant protection products because they enhance crop quality and productivity. Despite their usefulness, pesticides are immature, environmentally stable, and easily dispersed. In 2016, the overall usage of pesticides, such as herbicides, fungicides, and insecticides, rose by 5.5 million tons per year, according to statistics from the Food and Agricultural Organisation (FAO) [7]. This increase was due to the growing demand for food, as it was anticipated that the world rice output would increase by 42% by 2050 [7]. Unfortunately, only 0.3% of the applied pesticides are necessary to affect the target insect, with the remaining 99.7% being leached into the ground, air, and water [9]. After being sprayed on crops, pesticides can leave the site through multiple mechanisms, including biodegradation, runoff, leaching, and volatilization. Pesticide runoff takes a long time to decompose, leading to soil contamination that could seriously impact human health if people are exposed to it.

Most pesticides have very low allowed residual limits, sometimes in the range of parts per trillion; therefore, enhanced sample collection and extraction methods are required to meet these low concentration levels. The presence of matrix molecules from complex matrices, such as soil, in the extract can interfere with the signal response of the instrument in detecting the target compound [10]. Conventional sample preparation techniques for OCPs can be laborious and time-consuming because multiple stages are required [11]. A more recent method called Magnetic solid-phase extraction (MSPE) uses magnetic particles as adsorbents. This method is beneficial because it is simpler, more sensitive, and more selective than conventional solid-phase extraction (SPE) approaches [12]. It also allows for the rapid and efficient purification and concentration of pesticide samples. One of MSPE's key benefits is its ability to remove various pesticides from complex samples, owing to the large surface area and strong binding capacity of magnetic particles. The application of MSPE is eco-friendly because it does not utilize harsh chemicals, and the magnetic particles can be easily recycled, reducing the waste produced during analysis.

This study aimed to create and utilize sensitive extraction methods using Fe_3O_4-SiO_2-based magnetic solid phase extraction (MSPE) in combination with gas chromatography-mass spectrometry (GC-MS) for the determination of three organochlorinated (Aldrin, Dieldrin, and Heptachlor) in paddy water samples. The extraction parameters were optimized, including the extraction time, desorption solvent, desorption time, and sorbent mass, using the one-variable-at-a-time (OVAT) approach. The development of Fe_3O_4-SiO_2 from OPF was driven by an environmentally friendly concept, which was to adopt sustainable techniques by converting waste biomass into value-added silica-based adsorbent materials.

Materials and Methods

Chemical and reagents

All HPLC-grade solvents, including n-hexane, acetonitrile, acetone, ethanol, and ethyl acetate, were purchased from Merck (Germany). Additionally, reagents, such as ferrous oxide (Fe_3O_4), were acquired from Sigma-Aldrich. Three organochlorine pesticides, namely Aldrin, Dieldrin, and Heptachlor, with purity assay $\geq$ 99.9%, were purchased from Sigma-Aldrich. Standard stock solutions of aldrin, dieldrin, and heptachlor at concentrations of 1000 mg/L were prepared in acetonitrile. The prepared stock solutions were stored at 4°C until use. Working solutions of the standard mixtures were prepared by diluting standard stock solutions with acetonitrile.

Instrumentation

The FT-IR spectra were generated using an ATR-FTIR spectrometer (PerkinElmer Spectrum ONE FTIR with Universal ATR Polarization L1250064 ZnSe crystal) in transmittance mode over the wavenumber range of 4000-550 cm^{-1}. FESEM (Zeiss Supra 40VP FESEM) equipped with an EDX spectrometer was used for FESEM-EDX. XRD patterns and crystallinity behavior were obtained through XRD measurements using an X’Pert Pro X-Ray Diffractometer with Cu Kα radiation from 40 kV and 30 mA applied to the sample with a 2θ range of 5–100°.

Chromatographic analysis was conducted using a gas chromatography (Agilent 7890 B) system with a mass spectrometer detector (MS). Chromatographic separations were achieved on an HP-5 fused silica capillary (30 m x 0.32 mm, Agilent Technologies, USA). Helium was the carrier gas with a make-up gas flow rate of 1.1971 mL/min. The column temperature program began at 150 °C for 1 min, then increased to 200 °C at a rate of 30°C/min, held for 2 min, followed by an increase to 250 °C at a rate of 10°C/min, held for 2 min, and finally a ramp increase to 280 °C at a rate of 20°C/min. Splitless injection was maintained throughout the experiment to maintain the GC-MS interface at 250 °C.

Preparation of silica derived from oil palm frond

Oil palm fronds (OPF) were manually separated and washed with water to eliminate impurities. The sample was oven-dried (70 ˚C for 48h) and cut into smaller pieces before ground into fine powder. The following chemical treatment of OPF was adapted from the literature [13]. Briefly, OPF powder (50.0 g) was dispersed in HCl (1.0 M, 500Ml) and constantly stirred (400 rpm) for 2 h. The dispersion was cooled to room temperature and rinsed with distilled water until the washings reached a neutral phase. The neutralized OPF was then filtered and dried in an oven (80) for 24h. The OPF powder was heated in a preheated furnace at 600°C for 14h. The temperature gradually increased over 5 h, then maintained for 9 h. The rate of temperature increase was 2°C/min. White ash from the treated OPF-Si was collected and stored in airtight containers at room temperature for further examination.

Preparation of sodium silicate (Na_2SiO_3)

Sodium silicate (Na_2SiO_3) was prepared using a modified procedure reported by Onoja et al. [14] by mixing OPF-SiO_2 (10.0 g) and 3.5M NaOH (82 mL) in a paraffin oil bath at 100 °C for 4 hours with constant stirring (200 rpm). The resulting sodium silicate solution was filtered using Whatman 41 filter paper at room temperature, and the filtrate was placed in a polypropylene vial with a screw-on cover for analysis.

Preparation of magnetic silica $Fe_3O_4@SiO_2$

The preparation of magnetic OPF-Silica was based on the developed method by Azmayawati et al. (2018) with minor modifications [14]. First, 1 g of Fe_3O_4 was diluted in 20 mL distilled water and ultrasonicated for 10 min. Subsequently, 5 mL of Na_2SiO_3 was diluted in 80 mL of distilled water and mixed with the Fe_3O_4 solution. The mixture was then ultrasonicated for an additional 20 min. Next, hydrochloric acid (HCl) was added dropwise while stirring the mixture at room temperature until the pH reached 7. The gel was aged and left at room temperature for 24 hours. The solution was then washed and vacuum-filtered to remove the gel. The sorbent was oven-dried for 24 h at 80°C and stored in a desiccator until needed.

Collection and pre-treatment of paddy water samples

Water samples from the paddy fields were collected in propylene bottles from Sawah Padi Bukit Gambir, Johor. The bottles were protected from UV by being covered with aluminum foil and kept at 4ºC. The samples were filtered twice using Whatman 125 mm filter papers to remove colloidal particles, and the filtered solutions were stored in glass bottles before analysis.

Magnetic solid phase extraction procedure

A 50 mg sample of $Fe_3O_4@SiO_2$ powder was added to a 10 mL aqueous solution containing 3 ppm of heptachlor, 0.5 ppm Aldrin, and 1 ppm of dieldrin. The mixture was vortexed in 5 min to allow the adsorption process. The solution was then separated by magnetic force and discarded. 1 mL of the desorption solvent acetonitrile (ACN) was added for the desorption of the targeted analytes and further sonicated for 5 minutes. The sorbent was separated by magnetic force, and the remaining ACN was concentrated to 0.5 mL via nitrogen before GC-MS analysis.

Results and Discussion

Characterization of the prepared adsorbent

The characteristics of the synthesized adsorbents were studied using ATR-FTIR, FESEM-EDX, and XRD. An ATR-FTIR study was conducted to compare the spectral data and discern any changes in the chemical characteristics of the prepared bio-sorbent. The origin of the Fe_3O_4 spectrum (Figure 1(a)) shows the vibrational mode at 586 cm^{-1} (stretching vibrations of the Fe−O bonds) and 1648 cm^{-1} (bending vibrations of Fe_3O_4 bound water), which is similar to a previous study reported by Lesiak et al. [1]. In contrast, the spectrum of SiO_2 -OPF (Figure 1 (b)) exhibits a wide peak at 3430 cm^{-1}, indicating the presence of silanol (Si-OH) groups and antisymmetric and symmetric stretching vibrations of siloxane groups at wavenumbers of 1073 cm^{-1} and 805 cm^{-1}, respectively [Onoja et al. (2017)]. The spectrum of $Fe_3O_4@SiO_2$ (Figure 1(c)) exhibits distinct peaks at 3366 cm^{-1}, 1629 cm^{-1}, 1088 cm^{-1}, 809 $cm^{-1,}$ and 577 cm^{-1}, which correspond to the stretching vibrations of the O-H, Fe-O, and siloxane groups, respectively, as reported by Zhang et al. [15]. In addition, the exhibited peaks were similar to those seen in the Fe_3O_4 and SiO_2-OPF spectra but with significantly reduced intensities. This suggests that SiO_2 was effectively integrated into Fe_3O_4, as supported by the corresponding EDX analysis as shown in Figure 2(b).

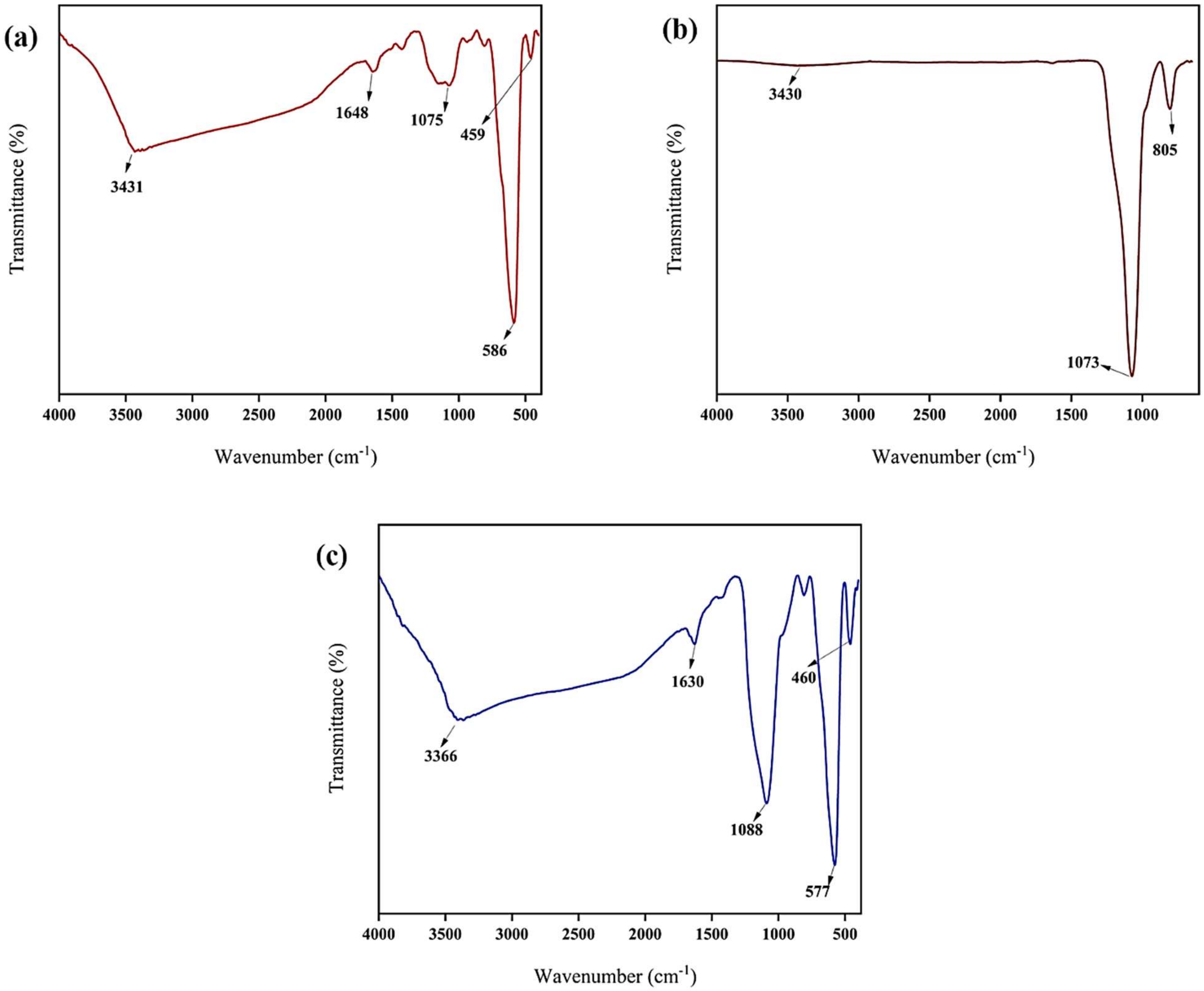

Figure 1. The ATR-FTIR spectra of the as-prepared (a) Fe_3O_4, (b) SiO_2 and (c) $Fe_3O_4@SiO_2$

Figure 2(a) depicts the FESEM micrographs of Fe_3O_4-SiO_2. As shown in Figure 2(a), the particles were obtained in agglomerated particles, rough surface structure, and the presence of cavities [14, 17]. Fe_3O_4 particles have a cubic shape and aggregate because of their high surface energy and adhesion properties. Nonetheless, the absence of a cubic structure in the FESEM images suggests that SiO2 has coated the magnetite and acted as a core to protect the magnetite from oxidation under acidic conditions, similar to a description by previous work [17].

The FESEM micrograph of Fe_3O_4-SiO_2 was further analyzed by mapping the elemental composition using energy-dispersive X-ray (EDX) analysis, as shown in Figure 2(b). Based on the result, the prepared bio-sorbent mainly consisted of 41.5 wt. % iron (Fe), 39.9 wt.% oxygen (O), and 18.6 wt.% silicon (Si), which correlated with the expected elements in Fe_3O_4-SiO_2. The high percentage of O could be from ferrous oxide and Si-OH in the silica layer, which acts as a shell for the core of the sorbent. The presence of Si can be interpreted as evidence of the successful synthesis of magnetic silica.

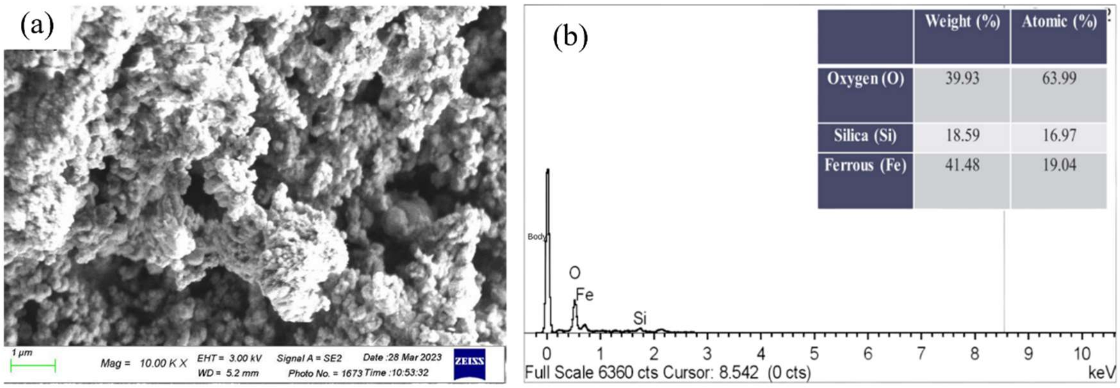

Figure 2. FESEM micrographs of the (a) Fe3O4-SiO₂ and (b) EDX spectrum from specific regions of $Fe_3O_4@SiO_2$

The XRD diffractograms of each sample were analyzed to evaluate the impact of crystallinity on the sorbents. The diffractograms of $Fe_3O_4@SiO_2$, Fe_3O_4, and SiO_2 are shown in Figure. 3. The SiO_2 sample in Figure 3(a) displays a broad peak and a Bragg angle of $2\theta = 22.978°$ corresponding to the (101) Miller indices (ICDD No. 01-083-2300), indicating that it is in an amorphous form, which is consistent with previous studies [18]. While, the diffraction peaks seen at angles 2θ~ 30.20 (220), 35.60 (311), and 57.50 can be attributed to the face-centered cubic structure of Fe_3O_4 as documented in the JCPDS file number 85-1436 [19]. The diffraction pattern depicted in Figure 3c indicates a displacement of the peak, signifying that the presence of Fe_3O_4 has resulted in the shift. This alteration suggests that $Fe_3O_4@SiO_2$ particles have been formed successfully, with the magnetite phase being integrated into the silica surface [20]. With comparison, both peaks were present on the diffractogram of Fe_3O_4-SiO_2.

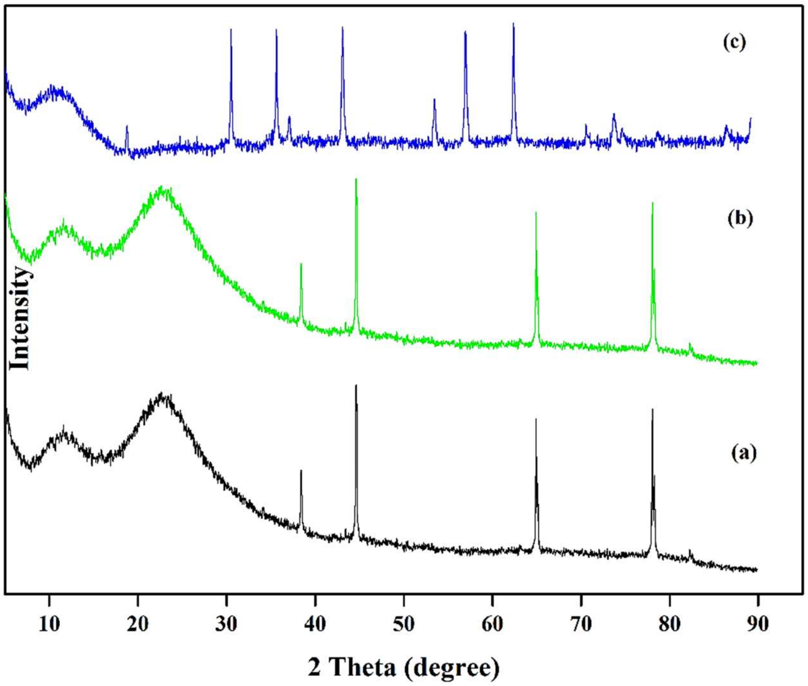

Figure 3. XRD patterns of (a) SiO_2, (b) Fe_3O_4 and (c) Fe_3O_4-SiO_2

Optimization of extraction conditions

The performance of the sorbent was assessed by MSPE for OCPs analysis in aqueous samples to determine the optimum extraction parameters. The one-variable-at-time (OVAT) approach was used to optimize the following MSPE parameters: extraction time, desorption solvent type, desorption time, and amount of sorbent. This approach reduces the use of chemicals, labor, and time. The optimization process involved utilizing distilled water spiked with heptachlor, aldrin, and dieldrin solutions. These solutions were prepared to achieve final concentrations of 3, 0.5, and 1 mg/L in 10 mL of water.

Effect of extraction time

The parameter of extraction time in analytical chemistry pertains to the period during which the extraction process isolates specific analytes from a sample matrix. The efficiency and effectiveness of the extraction procedure can be significantly influenced by critical factors. Precise optimization of the extraction time is crucial for obtaining reliable and accurate analytical results. This study focused on the impact of various extraction durations, ranging from 2.5 to 10 min, on the peak area of the analytes. Figure 4(a) illustrates the correlation between the peak area and extraction time, showing a significant increase in analyte extraction from 2.5 minutes to 5 min. However, the trend gradually decreases from 7.5 minutes to 10 minutes. This suggests that the most efficient extraction time for analyte adsorption onto the magnetic silica was 5 min. The decrease in trend may be because as the extraction time prolongs, there is an increased probability of analyte degradation or instability, leading to loss or alteration of the analyte and inaccurate, unreliable analytical outcomes [21]. Thus, 5 minutes of extraction time was selected for further experiments.

Effect of desorption solvent

The selection of the desorption solvent is crucial for facilitating the elution of the desired analytes from the sorbent material, which ultimately affects the overall efficiency and selectivity of the extraction process. As shown in Figure 4(b), ethyl acetate demonstrated the most favorable performance compared with other solvents such as n-hexane, acetonitrile, ethanol, and acetone. Ethyl acetate may have a greater selectivity towards chlorinated analytes than less polar solvents such as n-hexane, ethanol, acetonitrile, and acetone. This method enables the selective separation of heptachlor, aldrin, and dieldrin, reducing interference from other constituents in the sample matrix. Ethyl acetate is a solvent with moderate polarity (4.4) with favorable solubility characteristics for various organic molecules. Heptachlor, aldrin, and dieldrin are examples of chlorinated organic compounds. Owing to its moderate polarity (with dieldrin having a relative polarity of 5.40, heptachlor at 6.10, and aldrin at 6.75), ethyl acetate effectively dissolves these analytes from the sorbent material [22]. Therefore, ethyl acetate was selected as the desorption solvent for the subsequent analysis.

Effect of desorption time

Desorption time is a crucial parameter in extraction processes in analytical chemistry because it affects the efficiency and completeness of eluting target analytes from the extraction medium. The time range between 2.5 minutes and 10 min was examined, and the results showed that at 5 min, heptachlor and dieldrin were desorbed the most, while 7.5 minutes was required for aldrin. Proper control and optimization of desorption time are essential to achieve accurate and reproducible analytical results. The optimum desorption time was chosen as the one that was standardized for all three analytes. The differences in aldrin levels at 5 and 7.5 minutes were insignificant; therefore, the latter was accepted. A declining trend was observed as the sonication time was increased (from 7.5 to 10 minutes). This phenomenon may be attributed to the thermal effects caused by the sonicator, leading to the degradation of the analyte over time [23]. Therefore, 5 min was selected as the optimal desorption time.

Effect of mass sorbent

The adsorption capacity of the target analytes is influenced by the mass of the sorbent and its effect on both the adsorption capacity and the equilibrium between the sorbent and the sample matrix. The optimal sorbent mass for this extraction was 30 mg, as shown in Figure 4(d), with the highest extraction efficiency. This is because 30 mg of sorbent offers sufficient surface area for the target analytes (heptachlor, aldrin, and dieldrin) to bind. Increasing the sorbent mass beyond this limit might not result in improved extraction effectiveness, as it could cause the sorbent particles to become overcrowded and limit mass transfer, thereby decreasing the extraction efficiency. Additionally, higher sorbent masses can saturate the active binding sites in the sorbent, leading to declining returns in extraction efficiency [24].

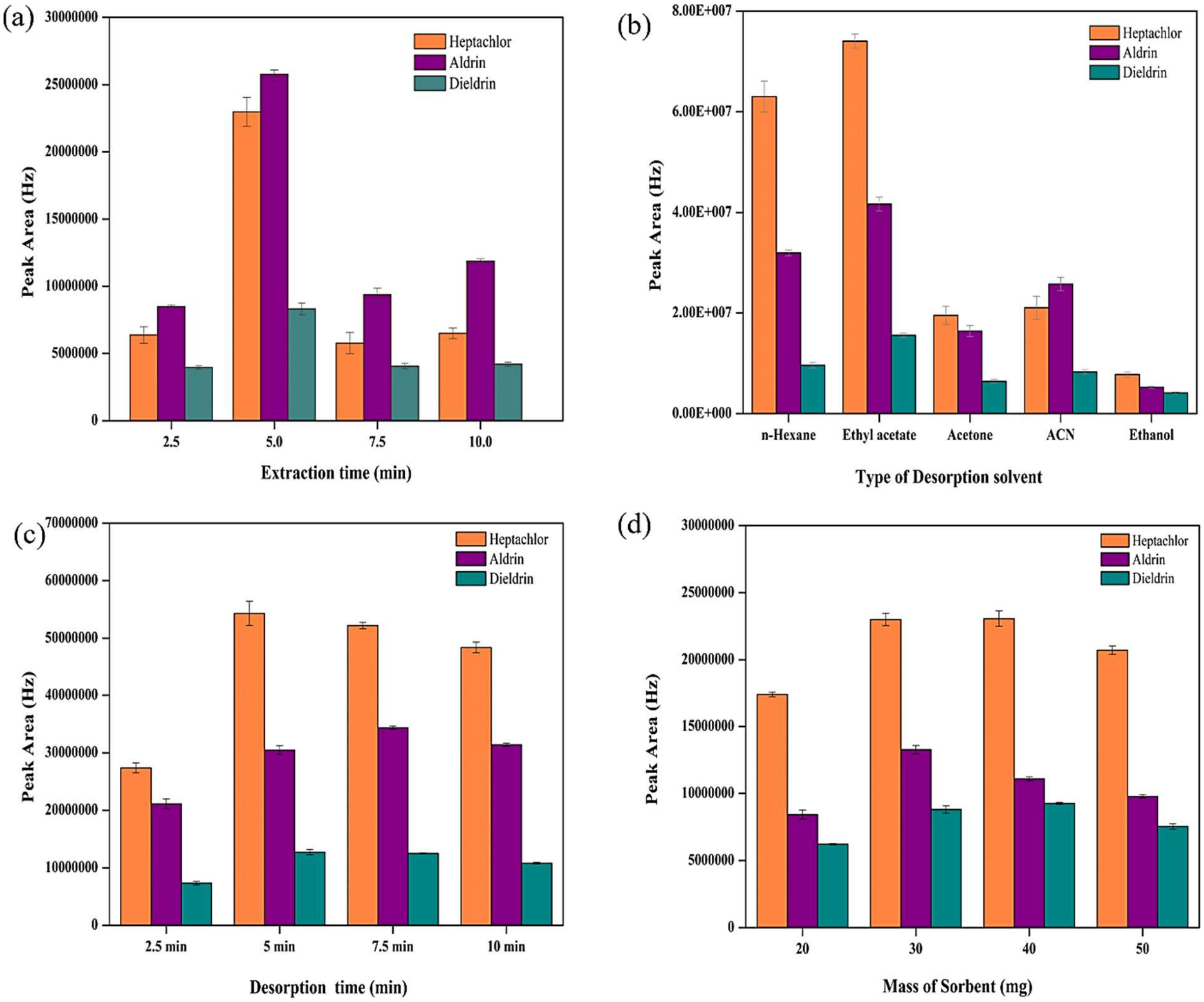

Figure 4. MSPE optimization conditions. (a) Extraction time (b) type of desorption solvent (c) desorption time (d) mass of sorbent

Method validation: Analytical performance

The accuracy of the proposed method for the magnetic solid-phase extraction of $Fe_3O_4@SiO_2$ was evaluated by analyzing certain organic pollutants in a water sample obtained from a paddy field. To determine the reliability of $Fe_3O_4@SiO_2$ for extracting three specific pollutants (heptachlor, aldrin, and dieldrin), a matrix-matched calibration approach was employed. The method was validated by calculating the limit of detection (LOD) and limit of quantification (LOQ) using the linear regression approach, standard deviation, and slope of the calibration curve. Calibration curves were generated using the least-squares approach, and peak areas were plotted against concentration. A strong linear relationship was observed between heptachlor, aldrin, and dieldrin, with R^2 values ranging from 0.98 to 0.99.

The limit of detection (LOD) was found to be 0.53-1.50 mg/L. The mean squared prediction error (MSPE) of Fe_3O_4-SiO_2 was evaluated in the context of pesticide analysis of paddy water samples.

Table 1. Performance of the proposed method under optimized conditions

Samples	**Analytes**	**Linearity (mg/L)**	**Regression coefficient, R ²**	**LOD (mg/L)**	**LOQ (mg/L)**
Paddy water	Heptachlor	0.6-2.4	0.99	0.53	1.62
	Aldrin	0.1-0.4	0.98	0.10	4.59
	Dieldrin	0.2-0.8	0.99	0.16	1.89

Analysis of real sample

The MSPE method, which utilizes $Fe_3O_4@SiO_2$, has been effectively used to analyze paddy water samples. The experiment involved adding spiked water samples to achieve final concentrations of 0.1 and 2.4 mg/L for heptachlor, 0.1 and 0.4 mg/L for aldrin, and 0.2 and 0.8 mg/L for dieldrin to conduct relative recovery tests. The results (Table 2) showed that the relative recoveries of the pesticides were within the standard range specified by AOAC International (2016), ranging from 80% to 95%. The intra- and inter-day precisions exhibited relative standard deviations within 0.50-1.86% and 0.69-2.54%, respectively. These results demonstrated the effectiveness of $Fe_3O_4@SiO_2$-MSPE as a technology for extracting pesticides from aqueous matrices. This study compared the new $Fe_3O_4@SiO_2$-MSPE method to conventional SPE methods that have already been published [25]. The results showed that the SPE method has recoveries ranging from 75.9 to 112.1 %, upon comparison with previous studies that used magnetic solid phase extraction to identify OCPs, the extraction time was shorter than that of conventional SPE. Figure 5 displays the gas chromatograms showing the presence of heptachlor, aldrin, and dieldrin in water samples from paddy fields.

Table 2. Method precision for intra-day and inter-day (%RSD) and percent recovery (%ER)

Analytes	**Concentration (mg/L)**	**Inter-day RSD (%, n=9)**	**Intra-day RSD (%, n=3)**	**ER (%)**
Heptachlor	0.6	1.86	2.54	80%
	1.8	0.93	1.93	90%
Aldrin	0.1	1.43	1.98	81%
	0.3	1.12	1.83	90%
Dieldrin	0.2	0.50	1.71	88%
	0.6	1.69	0.69	92%

Green assessment profile

New microextraction techniques are being developed to meet the demand for analytical sample preparation methods that are faster, less invasive, more selective, and require fewer resources. The AGREE calculator (shown in Figure 6) was used to evaluate the long-term feasibility of the proposed $Fe_3O_4@SiO_2$-MSPE procedure. The evaluation is considered eco-friendly because it meets a set of standards, such as reducing the number of extra sample treatments (4), avoiding derivatization during analysis and extraction (6), and using less energy (9), and fewer potentially harmful solvents (12). However, its primary limitation is that the target analytes must be determined offline, which means that $Fe_3O_4@SiO_2$ must be integrated into online or inline procedures.

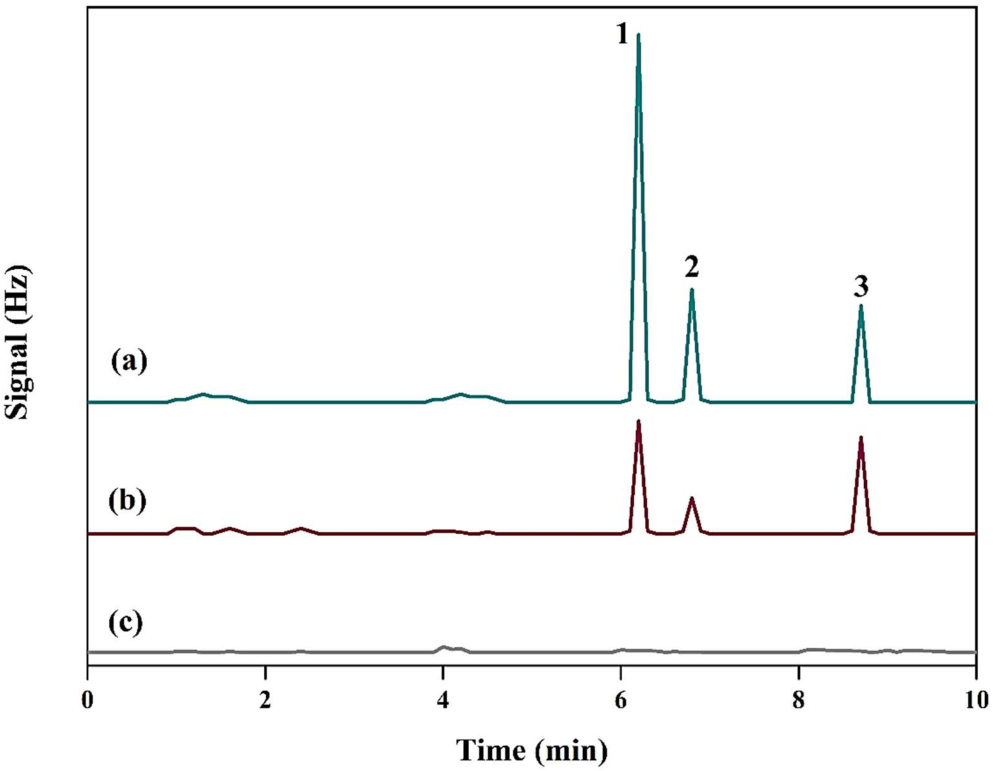

Figure 5. Chromatogram obtained from $Fe_3O_4@SiO_2$ MSPE-GC-MS of (a) blank of paddy water (b) and (c) paddy water spiked with at range 0.1 mg/L to 2.4 mg/L of analytes respectively. Chromatographic peaks: (1) Heptachlor, (2) Dieldrin, and (3) Aldrin.

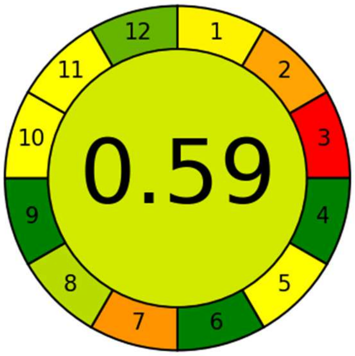

Figure 6. AGREE analysis of the method developed in this study

Proposed adsorption mechanism

Various interactions can occur between the sorbent and sorbate compounds, potentially affecting the extraction efficiency. These interactions, including electrostatic forces, hydrogen bonding, and hydrophobicity, can either attract or repel compounds involved. The properties of the sorbent materials, such as surface area, porosity, and sorption surface morphology, may also influence the extraction process of sorbate compounds [26]. The possible interactions between $Fe_3O_4@SiO_2$ and the OCPs include hydrogen bonding and van der Waals interactions, as schematically illustrated in Figure

7. $Fe_3O_4@SiO_2$ is sensitive to chlorinated groups of OCPs in its structure (aldrin and heptachlor) via van der Waals forces. Furthermore, silica has a polar functional group that interacts with the OCP molecule in a manner that makes it stick together, and the hydroxyl group of silica and the chlorine atom in the OCP compounds form strong hydrogen bonds. This interaction is facilitated by forming hydrogen bonds between the hydroxyl groups on silica and the anionic groups present in heptachlor molecules [27].

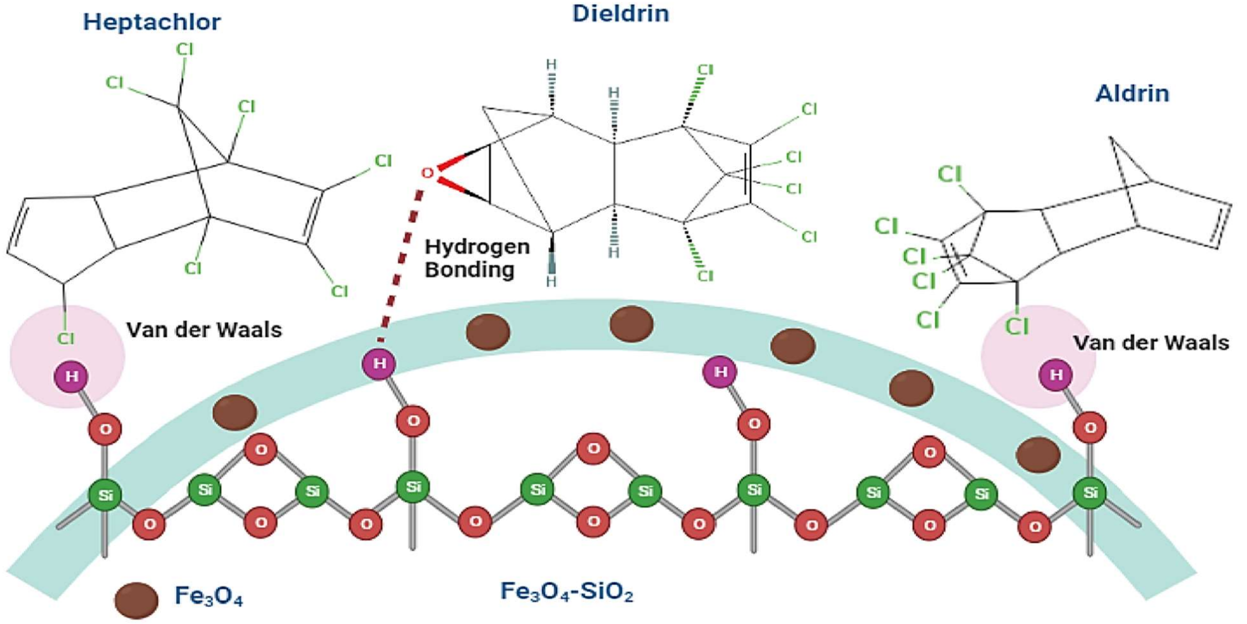

Figure 7. Schematic diagram of proposed interactions between sorbent and analytes

Conclusion

In summary, the present study included synthesizing a $Fe_3O_4@SiO_2$ composite material, which was then used as a magnetic sorbent in the magnetic solid-phase extraction (MSPE) method. This approach was coupled with gas chromatography-mass spectrometry (GC-MS) to quantify trace amounts of organochlorine pesticides (OCPs) in water samples collected from paddy fields. The main aim of this study is to develop a material that exhibits both environmentally friendly properties and magnetic sensitivity. The synthesizing and fabricating of a composite material consisting of $Fe_3O_4@SiO_2$ was successfully achieved via the sol-gel technique. The successful synthesis of Fe_3O_4 and its efficient extraction of organochlorine pesticides (OCPs) within a short timeframe was confirmed by the use of Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and X-ray diffraction (XRD) methods. Significantly, the MSPE procedure offers efficient extraction within a short time frame (5 min) and only uses a small quantity of sorbent (40 mg). In addition, the suggested methodology demonstrated a low limit of detection (LOD), a broad range of linearity, and satisfactory accuracy. The use of the MSPE approach, combined with the GC-MS method, proved to be successful in analyzing organochlorine pesticide (OCP) residues in paddy samples. The findings obtained in this study exhibited good values for recoveries, enrichment factors, and relative standard deviations (RSDs), which significantly improved the sensitivity and simplicity of the sample preparation technique. Furthermore, the Fe_3O_4-SiO_2 adsorbent may be conveniently synthesized using abundant biomass sources, presenting supplementary benefits like cost-efficiency and ecological sustainability.

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