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Sustainable Sorbents: Oil Palm Empty Fruit Bunch-Derived Activated Carbon-Alginate Beads for Organochlorine Pesticides Extraction in Water Samples

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Pesticide residues in environmental water necessitate the urgent development of rapid and accurate determination methods for effectively monitoring and managing these contaminants. In response, micro-solid phase extraction (μ-SPE) using oil palm empty fruit bunch derived activated carbon-alginate beads (Alg-EFBAC-beads) was developed as a sample preparation method for extracting three organochlorine pesticides (OCPs) in water samples before gas chromatography-mass spectrometry (GC-MS) analysis. Essential parameters, including extraction time, desorption solvent, desorption time, and sorbent mass, were optimized using one variable at a time approach. Under the optimized conditions, the method showed good linearity ($R^2 > 0.9777$) in the concentration ranges of 1-10, 0.1-1.0, and 0.2-1.4 mg/L for heptachlor, aldrin, and dieldrin, respectively. The applicability of the method was demonstrated through the analysis of selected pesticides in agricultural paddy water, with average recoveries ranging from 85 to 95%. The limits of detection (LOD) were between 0.04 and 0.29 mg/L. The greenness of the method was evaluated using the Analytical GREEnness Metric Approach (AGREE), demonstrating its viability as a sustainable solution for environmental monitoring and analysis of organochlorine pesticides in aqueous environments.

Keywords: Micro-solid phase extraction (μ -SPE); OPEFB-derived activated carbon; alginate beads; organochlorine pesticides; environmental monitoring; sustainable materials

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Organochlorine pesticides (OCPs), a class of synthetic compounds extensively utilized in agriculture and public health during the mid-20th century, have garnered recognition as persistent organic pollutants (POPs). The development of OCPs, initiated in the 1940s with the introduction of dichlorodiphenyltrichloroethane (DDT), paved the way for subsequent pesticides like heptachlor, aldrin, and lindane, used widely in pest control [1]. Their inherent resistance to degradation and ability to bioaccumulate in the food chain have led to severe environmental and health consequences [2-4]. Additionally, prolonged exposure to OCPs has been correlated with chronic diseases, including cancers [5], neurological disorders [6], and reproductive issues [7, 8].

Given the far-reaching consequences of OCP contamination, developing a sample preparation and analytical methodology with high sensitivity, selectivity, and efficiency for accurately quantifying OCP concentrations is crucial. Despite the exploration of various new sample preparation techniques, such as micro-solid-phase extraction (μ-SPE) [9], microwave-assisted magnetic solid phase extraction (MAE-MSPE) [10], solid phase microextraction (SPME) [11], mechanochemical magnetic solid phase extraction (MCMSPE) [12], surpassing the limitations of existing techniques and ensuring comprehensive OCP analysis remains a critical area of research.

The focus on advancing extraction methodologies has led to a noteworthy exploration of sorbent-based techniques. Specifically, there is a growing interest in natural or green sorbents, driven by the desire for environmentally friendly and sustainable approaches to sample preparation [13, 14]. Green sorbents, derived from renewable sources including fruit peel [15-19], oil palm empty fruit bunch (OPEFB) [20, 21], rice husk [22], and peanut shell [23,24] exhibit unique characteristics that enhance their selectivity and effectiveness in analyte extraction. This shift towards green sorbents aligns with the principles of green chemistry, prioritizing methods that minimize environmental impact and resource consumption [25,26]. Researchers aim not only to overcome the limitations of current techniques

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but also to contribute to developing environmentally friendly and economically viable approaches for comprehensive trace analysis.

As a significant producer of palm oil, Malaysia confronts challenges related to the generation of substantial amounts of biomass by-products, including empty fruit bunches (EFB), oil palm fronds (OPF), oil palm trunks (OPT), and palm kernel shells (PKS) [27]. These materials possess significant potential for diverse applications, such as energy production, soil conditioning, and the creation of value-added products. Recognizing the abundance of these by-products and the underutilization issue, which may contribute to waste accumulation and disposal problems, repurposing them as sorbent materials in extraction methodologies offers a promising solution. This dual-purpose approach not only addresses the challenge of biomass disposal but also contributes to the development of sustainable and economically viable methods, with the potential to transform environmental challenges into opportunities for innovation and positive impact in analyte extraction.

Acknowledging the imperative for an enhanced sample preparation technique and leveraging the potential of biomass materials, this study evaluated the effectiveness of activated carbon derived from OPEFB as a sorbent. Activated carbon, widely acknowledged and extensively utilized in water treatment, has demonstrated notable efficacy in the removal of diverse contaminants from water, encompassing volatile organic compounds (VOCs) [28, 29], pesticides [30,31], pharmaceuticals [32-34], dyes [35, 36], and odor-causing compound [37]. Furthermore, encapsulating activated carbon in alginate beads will create a synergistic sorbent system. Due to the porous structure of alginate, the pollutant solution can pass through while remaining in contact with activated carbon [38]. The activated carbon component ensures strong adsorption, while alginate beads contribute to mechanical stability and structural integrity [39-42]. The ion-exchange properties of alginate further enhance sorbent selectivity [43, 44], making it well-suited for extracting a diverse range of contaminants. Additionally, the bead form minimizes mass loss [45] overcomes waste challenges [40] and reduces regeneration costs [46-48].

This novel sorbent was scrutinized for its suitability as an adsorbent in the µ-SPE procedure for extracting and determining OCPs, specifically heptachlor, aldrin, and dieldrin. The extraction of these OCPs was coupled with gas chromatography-mass spectrometry (GC-MS) analysis applied to environmental water samples. Numerous pivotal experimental parameters influencing µ-SPE efficiency, such as extraction time, desorption time, desorption solvent, and sorbent mass, were meticulously optimized through a systematic one-variable-at-a-time (OVAT) approach. The development of biopolymer alginate beads encapsulating activated carbon from OPEFB biomass (Alg-EFBAC-beads) stems from a principled commitment to environmentally friendly practices, seeking to adopt sustainable techniques by transforming waste biomass into greener adsorbent materials. This endeavor aligns with the overarching objective of advancing analytical methodologies while contributing to the paradigm shift towards sustainable and eco-friendly practices within environmental analysis.

EXPERIMENTAL

Chemicals and Materials

Raw oil palm empty fruit bunch (OPEFB) was obtained from a local palm oil plantation around Klang Valley. Potassium hydroxide (KOH) pellet was purchased from R&M chemicals, hydrochloric acid (HCl) from Riendemann Schmidt chemicals (Grade AR, 37%), sodium alginate from Orec (New Zealand), and calcium chloride ($CaCl_2$) from HmbG Chemicals (Germany). All solvents (n-hexane, acetonitrile (ACN), acetone, ethanol, and ethyl acetate (EA)) of HPLC grade were purchased from Merck (Darmstadt, Germany).

The OCP standards (heptachlor, aldrin, and dieldrin) were purchased from Sigma-Aldrich. Standard stock solutions of heptachlor, aldrin, and dieldrin with a concentration of 1000 mg/L were prepared in ACN. Respective stock solutions were stored in the refrigerator at 4 °C before use. Working solutions were prepared freshly by diluting standard stock solutions with ACN.

Instrumentation

The FT-IR spectra were generated using an ATR-FT-IR spectrometer (Perkin Elmer Spectrum ONE FTIR with Universal ATR Polarization L1250064 ZnSe crystal) in transmittance mode over wavenumber 4000–550 cm^{-1} range at room temperature using 8 scans and at a resolution of 4 cm^{-1}. A field emission scanning electron microscopy (FESEM) (Zeiss Supra 40VP) equipped with an energy dispersive X-ray (EDX) spectrometer was used to perform the SEM-EDX.

The chromatographic analysis for the targeted analyte was performed by a gas chromatograph equipped with a mass spectrometer (GC-MS) operating with an automatic sampler (Agilent Technology, USA). Separation was performed using an HP-5MS ultra inert fused silica capillary column (30 m length, 250 µm internal diameter, and 0.25 µm film thickness; (Agilent Technology, USA) coated with (5% phenyl)-methylpolysiloxane. Helium gas was used as the carrier. Quantitative data acquisition and processing were performed using the MassHunter Software (Agilent Technology, USA) with full scan mode. The following temperature program was incorporated: initial temperature, 150 °C hold for 1 min; raise to 200 °C at a heating rate of 30 °C min^{-1} and held for 2 min; raised to 250 °C at 10 °C min^{-1} and held for 2 min; raised to 280 °C at 20 °C min^{-1}. The injection volume was 1 μL in a splitless mode.

Preparation of Activated Carbon from Oil Palm Empty Fruit Bunch (EFBAC)

The preparation of activated carbon followed a modified method based on a prior study [49]. OPEFB fibers were initially washed and oven-dried at 35 ℃ overnight. Subsequently, the dried fibers underwent charring at 500 ℃ in a muffle furnace for 2 hours to eliminate lignin, which possesses a complex chemical structure and hinders pore formation during activation. The carbonized material was then ground with a KOH pellet of weight ratio 1:1 and subjected to activation in a tubular furnace at 800 ℃ for 2 hours with a constant flow of hydrogen gas. Following activation, the resulting activated carbon underwent rinsing with distilled water and 1.0 M hydrochloric acid until reaching a neutral pH (6~7), monitored using a pH meter. The final step involved drying the activated carbon in an oven at 80 ℃.

Preparation of Oil Palm Empty Fruit Bunch-Activated Carbon-Alginate Beads (Alg-EFBAC-beads)

The preparation of Alg-EFBAC-beads followed a procedure adapted from existing literature, with slight modifications as specified in [38]. Initially, a 2% (w/v) sodium alginate solution was prepared in distilled water at room temperature, undergoing an hour of stirring for thorough homogenization. Subsequently, 0.1 g of EFBAC was introduced to the solution and further homogenized. The blended mixture was then dispensed through a syringe into a 4% (w/v) multivalent cation ($CaCl_2$) solution. Bead formation occurred promptly upon contact with the calcium ions. Following formation, the beads underwent filtration and extensive rinsing with distilled water to eliminate excess $CaCl_2$ solution. The final step involved oven-drying the composite Alg-EFBAC-beads at approximately 100 °C for 24 hours. The resultant beads were subsequently stored in desiccators for future use. This encapsulation method is illustrated in Figure 1.

Collection and Pretreatment of Paddy Water Sample

The paddy water sample was collected from Bukit Gambir paddy field, Gerisek, Johor, Malaysia (Longitude: 102.629259, Latitude: 2.195476). The water was filtered twice through Whatman 125 mm filter papers, followed by a 0.45 μm membrane filter to remove colloidal particles. The filtered water sample was kept in glass bottles, covered with aluminum foil, and stored in a chiller at 4 °C until the following analysis.

Micro-Solid Phase Extraction (μ -SPE) Procedure for OCP Determination

First, 10 mL of the filtered water sample was transferred into a tube and spiked with the appropriate amount of OCPs. Approximately 50 mg of the Alg-EFBAC-beads adsorbent was added to the solution and stirred at 900 rpm for 15 min using a carousel. The supernatant containing non-adsorbed components was discarded. The target OCPs were desorbed from the Alg-EFBAC beads using 1 mL of n-hexane as the desorption solvent and sonicated for 7 min. The solvent was then collected and dried with a gentle stream of nitrogen gas.

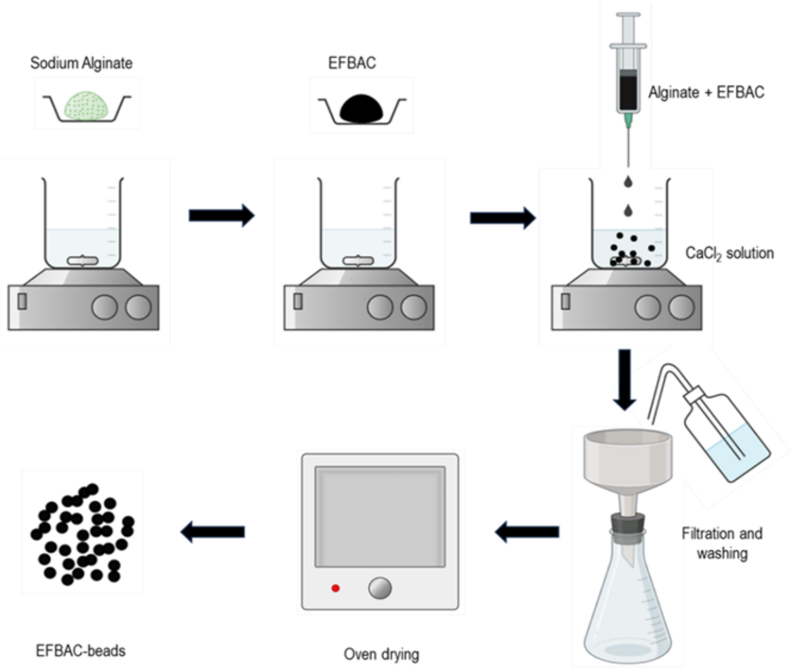


Figure 1. Schematic diagram preparation of Alg-EFBAC-beads sorbent.

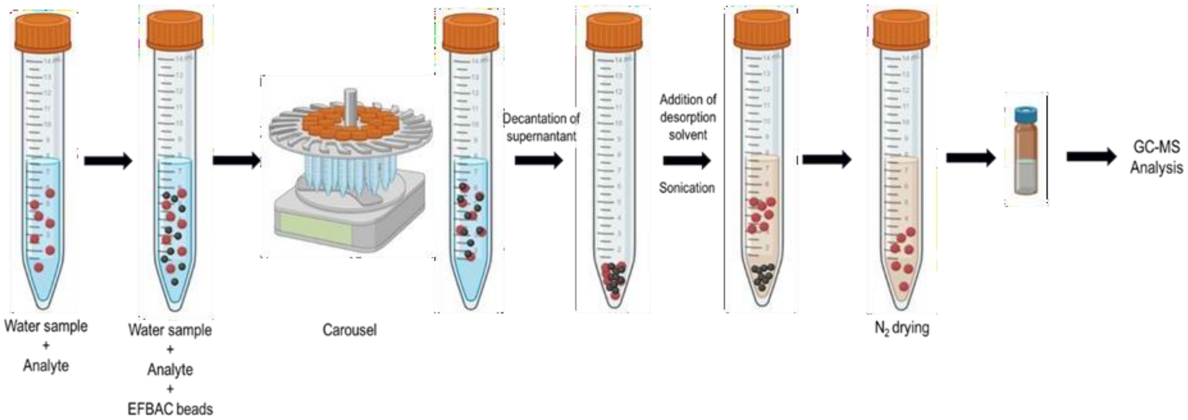


Figure 2. Schematic diagram of µ-SPE procedure by using EFBAC beads as sorbent.

Finally, 500 µL of the clean extract was analyzed via the GC-MS system for quantitative analysis. Figure 2 depicts a visual summary of the method. The method was adapted and modified from the previous study [50].

Method Validation

The validity of the developed method was systematically assessed across critical parameters, including linearity (R^2), limit of detection (LOD), limit of quantification (LOQ), precision (% relative standard deviations), and accuracy (% relative recovery). The validation experiments were meticulously conducted under optimal experimental conditions, utilizing a blank water sample for matrix validation. The matrix-matched calibration curves were generated for each OCP, incorporating a minimum of five concentrations ranging from 0.1 to 10 mg/L in water. The studied linear range and determination coefficient (R^2) were calculated from the regression equation of the pesticide's peak area and concentration. LODs and LOQs were determined through linear regression of the calibration curve according to Eq. (1) and Eq. (2), respectively, where σ: standard deviation and m: slope.

$$LOD = \frac{3\sigma}{m} \qquad (1)$$

$$LOQ = \frac{10\sigma}{m} \qquad (2)$$

The precision analysis was presented as relative standard deviations (% RSDs), calculated intra-day and inter-day with a sample size of n = 3 at low and high OCP concentrations. The relative recovery values (% RR) were computed using Eq. (3), where C_{found}, C_{real}, and C_{added} are the final concentration of OCPs after the addition of OCP solution to actual samples, the primary concentration of OCPs in real samples, and the concentration of defined amounts of OPP standard solution added to real samples, respectively.

$$\%RR = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \qquad (3)$$

The enrichment factor (EF) is expressed as the ratio of the concentration of analyte found in the final desorption solvent phase (C_{eluent}) to the initial concentration of analyte in the original water phase (C_{aq}), as shown in Eq. (4). This rigorous validation protocol ensures the robustness and reliability of the developed methodology, affirming its capability for precise and accurate quantification of OCPs in water samples.

$$EF = \frac{C_{eluent}}{C_{aq}} \qquad (4)$$

RESULTS AND DISCUSSION

Characterization of Alg-EFBAC-Beads

FTIR analysis was performed to observe changes in the composition of EFBAC upon encapsulation with the alginate matrix. The FTIR results are presented in Figure 3, and the spectra of EFBAC and alginate beads obtained in this study are similar to previous reports [51-53]. A broad stretch at 3331 cm^{-1} assigned to OH functions in alginate beads, while a slight shift to 3349 cm^{-1} was observed in the OH peak stretching upon forming Alg-EFBAC-beads. The lower intensity of this peak for EFBAC was due to the moisture vaporization during carbonization [51]. This shifting suggests that EFBAC interacts with alginate chains through intermolecular hydrogen bonds [54]. The bands at 1598 cm^{-1} (alginate beads) and 1601 cm^{-1} (Alg-EFBAC-beads) were associated with COO$^-$ asymmetric and symmetric stretching, with Alg-EFBAC-beads exhibiting a more prominent band. The shift results from the negative charge of the carboxyl group in alginate interacting electrostatically with the positive charge of EFBAC [52] The peak observed in the range of 1078 to 1027 cm^{-1} in all three compounds corresponds to the C-O-C functional groups [54]. The presence of -OH and C-O-C functional groups in Alg-EFBAC-beads, serving as active sites for interactions and, consequently, facilitating the adsorption of the targeted analytes possible [53]. Table 1 compares vibration bands among EFBAC, alginate beads, and Alg-EFBAC beads.

The surface interaction and homogeneity of Alg-EFBAC beads were investigated using FESEM (Figure 4). At a magnification of 45X, the shape of composite beads can be described as spherical. At a magnification of 5kX, the rough and uneven surface is due to the cavity from the crosslinking operation (Figure 4b). The arrangement of pores on the surface should be regarded as a factor contributing to an increase in the specific surface area and permeability of composite beads. Additionally, these cavities aid in the diffusion of pores during adsorption, emphasizing the significance of the inner specific surface with minimal diffusion resistance in the composite beads, thereby enhancing adsorption potential and rate [53,55].

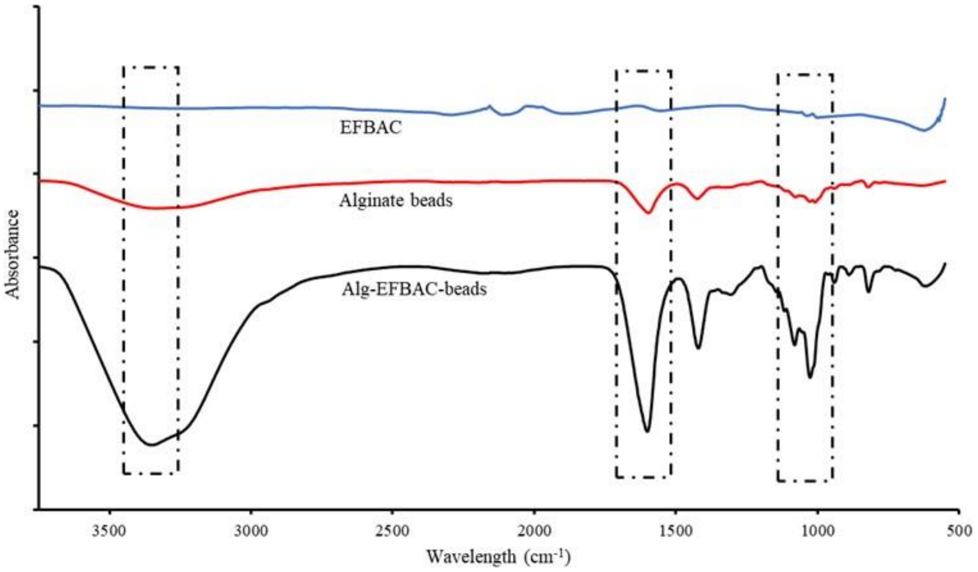


Figure 3. FTIR spectra of EFBAC, alginate beads, and Alg-EFBAC beads.

Table 1. Comparison of vibration bands between EFBAC, alginate beads, and EFBAC beads

Vibrational mode	EFBAC (cm^{-1})	Alginate beads (cm^{-1})	Alg-EFBAC-beads (cm^{-1})
-OH	-	3331	3349
COO^-	-	1598	1601
C-O-C	-	1078 - 1027	1084

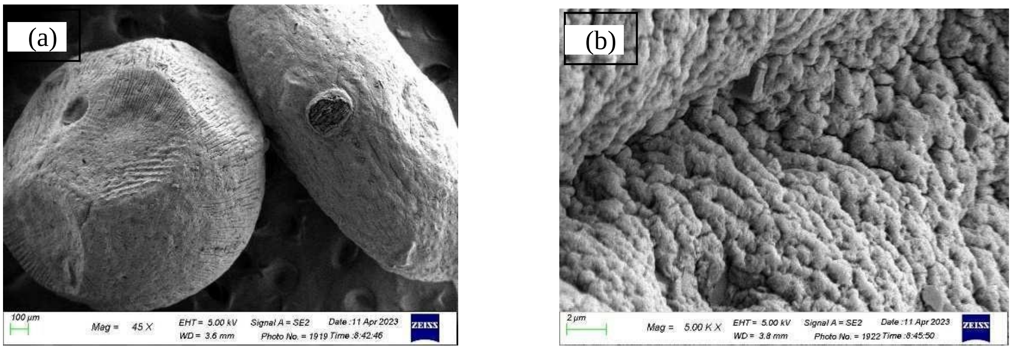
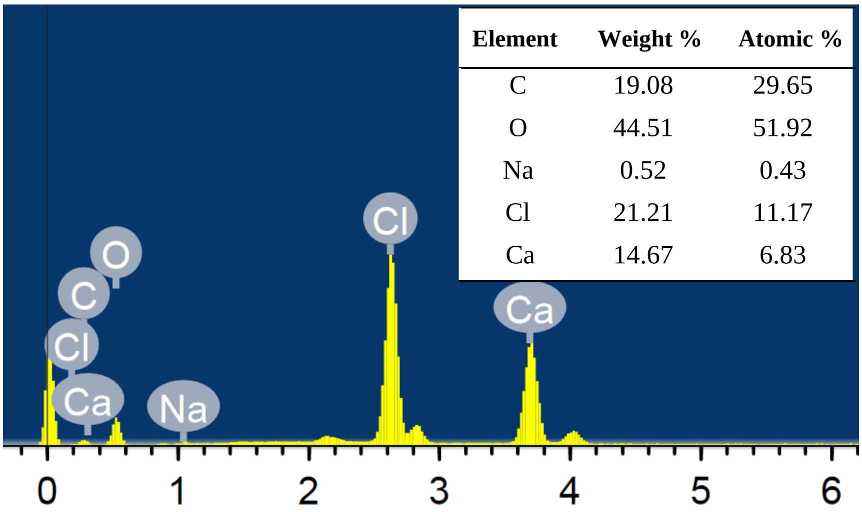


Figure 4. FESEM images of Alg-EFBAC beads under (a) 45X magnification and (b) 5KX magnification.



Element	Weight %	Atomic %
C	19.08	29.65
O	44.51	51.92
Na	0.52	0.43
Cl	21.21	11.17
Ca	14.67	6.83

Figure 5. EDX analysis of Alg-EFBAC-beads.

Table 2. Optimization parameters of µ-SPE.

Parameter	Condition
Extraction time (min)	2.5, 5, 7.5, 10, 15
Desorption solvent	n-hexane, ethyl acetate, acetone,acetonitrile, ethanol
Desorption time (min)	3, 5, 7, 10
Mass sorbent (mg)	30, 40, 50, 60

The EDX analysis of Alg-EFBAC beads, as presented in Figure 5, demonstrated predominant carbon (29.65%) and oxygen (51.92%) content, originating primarily from EFBAC and alginate. A minor presence of chlorine (11.17%), calcium (6.83%), and a trace of sodium (0.43%) were attributed to residual sodium alginate and calcium (II) chloride used as crosslinking agents, respectively. The elevated chloride concentration resulted from the substantial amount of calcium chloride dissolved in the alginate beads during the dropping process of the alginate solution into excess calcium chloride, aligning with previous research [56]. The result proves the absence of impurity peaks, which is consistent with findings observed in the FTIR analysis.

Optimization of µ-SPE Parameters

The investigation into optimal extraction parameters aimed at enhancing the efficiency of the µ-SPE technique, utilizing the synthesized EFBAC beads as an adsorbent, involved exploring several significant factors. These factors included extraction time, the type of desorption solvent, desorption time, and the sorbent mass. The optimization process employed an OVAT approach, with other parameters constant throughout the experiments. OVAT was chosen because of the simplicity of the system and the limited number of parameters under consideration. With only four parameters to be examined, OVAT provides a practical and straightforward approach, allowing for a focused exploration of individual factors while ensuring resource efficiency. Distilled water spiked with OCPs in 10 mL of distilled water samples served as the medium for optimization. Notably, the elution solvent's volume was consistently fixed at 1 mL, as this volume ensured complete immersion of the adsorbent. Therefore, a detailed study of the elution solvent's volume was not undertaken. The summary of optimized parameter ranges for the technique is presented in Table 2.

Effect of Extraction Time

Sufficient extraction time is crucial for establishing equilibrium between the adsorbent and the sample solution, ensuring an optimal interaction between the analyte and adsorbent. Therefore, the influence of extraction time was studied in the range of 2.5 to 15 minutes. As shown in Figure 6a, the adsorption capacity of OCPs rapidly increased from 2.5 to 15 minutes of extraction, where the highest extraction efficiency was obtained at 15 minutes. This has shown that the analyte saturation was completed as time went on at all the inactive sites within the surface area of the sorbent. Therefore, 15 minutes was selected as the optimal time and was used in further experiments. Further extraction time was not included in this study as an increase in extraction time may lead to a higher likelihood of decreased analyte extraction [57,58] and an increase in errors [59].

Effect of Type of Desorption Solvent

The choice of desorption solvent is critical in extracting target analytes from sorbent material, significantly influencing extraction efficiency and analyte recovery. This investigation employed five organic solvents, n-hexane, ethyl acetate, acetone, acetonitrile, and ethanol, as desorption solvents for eluting OCPs from Alg-EFBAC-beads. Each solvent's efficiency in achieving maximum desorption was evaluated, with n-hexane demonstrating superior performance, as shown in Figure 6b. The higher efficiency of n-hexane to the target compounds (heptachlor, aldrin, and dieldrin) is likely attributed to its nonpolar nature, providing optimal solubility and selectivity for these hydrophobic OCPs (log P values: heptachlor 5.4, aldrin 6.5, dieldrin 5.4) [60]. Consequently, n-hexane was consistently chosen as the desorption solvent in subsequent experiments, maintaining a fixed total volume of 1 mL, as mentioned earlier.

Effect of Desorption Time

Desorption time, the duration during which the analytes are adequately released from the sorbent, directly influences the effectiveness of analyte recovery and the overall performance of the extraction method. In this study, the effect of desorption time was investigated within a range of 3-10 minutes of sonication. Figure 6c demonstrates a slight increase in extraction efficiency of Alg-EFBAC beads with a desorption time of up to 7 minutes, reaching maximum efficiency at this duration. However, as the desorption time extends to 10 minutes, the efficiency of extraction decreases, likely attributed to the heat generated by the sonicator, leading to the degradation of the analyte during the sonication step [50]. Consequently, the optimum desorption time was set at 7 min.

Effect of Sorbent Mass

The appropriate sorbent mass is essential to ensure maximum extraction efficiency by providing sufficient binding sites for the analytes. The Alg-EFBAC beads' mass varied between 30 and 60 mg to optimize the sorbent mass. As illustrated in Figure 6d, the highest extraction efficiency was attained at a sorbent mass of 60 mg, indicating an increase in active adsorption sites. However, it was not recommended to increase the sorbent mass further, as doing so would lead to increased waste generation during cleanup, contradicting the first principle of the 12 Principles of Green Chemistry [61]. Considering the need to reduce the sorbent amount and overall extraction efficiency, 50 mg was chosen as the optimum sorbent mass.

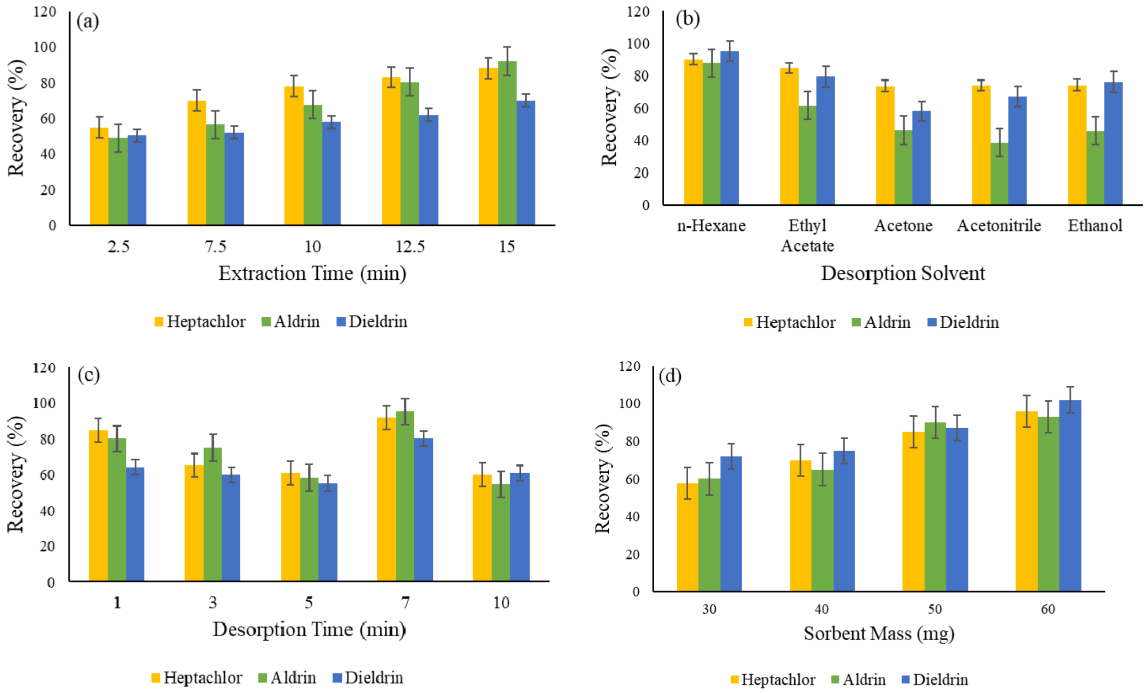


Figure 6. µ-SPE optimization condition. (a) extraction time, (b) desorption solvent, (c) desorption time, and (d) sorbent mass.

The possible interaction between Alg-EFBAC beads and analytes may encompass hydrophobic and hydrogen bonding. The hydrophobic surface of activated carbon could potentially accommodate chlorinated hydrocarbons owing to their nonpolar nature [62]. Hydrogen bonding might occur among the analytes, alginate, and activated carbon due to the presence of hydroxyl groups on the alginate and some carbonyl groups on the activated carbon, as observed in FTIR spectra [63,64]. Moreover, the anticipated high porosity of activated carbon enhances the interaction surface, while the alginate coating acts as a pre-concentration layer, capturing analytes through weaker interactions before reaching the activated carbon, thereby facilitating efficient extraction [48].

Analytical Performance of µ-SPE

The analytical data, including linearity, LODs, LOQs, and precision using Alg-EFBAC-beads adsorbent for the µ-SPE-GC-MS analysis of OCPs in water samples, is presented in Table 3. The method was analyzed against a paddy water sample, and the chromatograms of heptachlor, aldrin, and dieldrin are presented in Figure 7. The matrix-matched calibration curve for each OCP shows good linearity with a corresponding determination coefficient (R^2) of 0.98-0.99. The LOD and LOQ varied between 0.04 and 0.29 mg/L and 0.12-0.88 mg/L respectively for the analyzed OCPs.

As indicated in Table 4, the system precision, defined at two concentration levels for each OCP, ranged between 0.15% and 0.71% for intra-day RSDs (n = 3) and 0.07%-0.77% for inter-day RSDs (n = 3), respectively. The low values signify high precision and good repeatability of measurements, ensuring the reliability of experimental results and the consistency of the developed methods. This method also produced satisfactory recoveries (RR%) in the range of 85% to 95%, which fall within the guidelines for standard method performance requirements [65]. The enrichment factors (EFs) for the targeted analytes, ranging from 2.18 to 3.06, indicate an increase in analyte concentration after the µ-SPE procedure.

Table 3. Analytical data of Alg-EFBAC-beads - µ-SPE – GC-MS method for determining OCPs in water.

Analytes	Linearity (mg/L)	R^2	LOD (mg/L)	LOQ (mg/L)
Heptachlor	1.0-10	0.98	0.29	0.88
Aldrin	0.1-1.0	0.99	0.04	0.12
Dieldrin	0.2-1.4	0.99	0.07	0.19

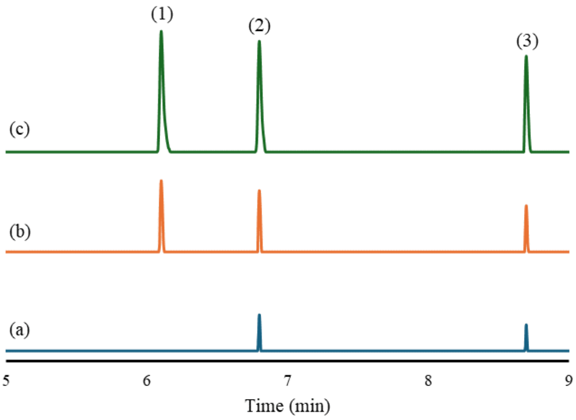


Figure 7. The chromatogram of paddy water at (a) unspiked, (b) spiked (lowest concentration), and (c) spiked(highest concentration). Peak identifications: 1. Heptachlor, 2. Aldrin, 3. Dieldrin.

Table 4. Precision for intra-day and inter-day (%RSD), percentage of relative recovery (%RR), and enrichment factor (EF).

Analytes	Spike Level (mg/L)	Intra-day RSD % (n=3)	Inter-day RSD % (n=3)	RR (%)	EF
Heptachlor	1	0.71	0.42	95	2.51
	10	0.15	0.09	87	2.18
Aldrin	0.1	0.15	0.56	86	2.25
	1	0.26	0.1	91	2.25
Dieldrin	0.2	0.63	0.77	90	2.41
	1.4	0.36	0.07	85	3.06

The effectiveness of the current approach was evaluated by comparing it with published techniques utilized for OCP analysis in water. The comparative data in Table 5 indicates that the proposed method, utilizing the Alg-EFBAC-beads adsorbent, facilitates a quicker extraction and desorption, eliminating additional centrifugation or filtration steps. Despite the increased use of sorbent, the Alg-EFBAC-beads, derived from biomass, ensure sustainability. Consequently, the developed micro solid-phase extraction method based on Alg-EFBAC-beads adheres to the principles of green analytical chemistry.

Environmental Impact Assessment

In alignment with Green Analytical Chemistry (GAC) principles, methods without sample treatment are ideal. Nevertheless, the exclusion of sample treatment remains a challenging endeavor, especially for complex water matrix [66]. A study involving green metrics was conducted to assess the developed method's environmental sustainability and viability. Analytical GREEnness Metric Approach (AGREE) tools were employed for this assessment.

The AGREE score, depicted in Figure 8, attains a value of 0.57 for the proposed methodologies. Notably, the principles of integrating analytical processes (Principle 4), adopting automated and miniaturized methods (Principle 5), and avoiding derivatization (Principle 6) boast perfect scores, indicating excellent performance in sample preparation, sample size, and derivatization/reagents. Strong support for waste management (Principle 7) confirms its commitment to being environmentally friendly, balancing efficiency and waste reduction. It should be mentioned that the sorbent has a high tendency to be regenerated and thus did not count as waste, and only minimal amounts of the solvents (n-hexane) were consumed during the extraction or post-analysis. While there's room for improvement in minimizing sample sizes (Principle 2), the need for in situ measurements (Principle 3), and the minimization of energy use (Principle 9), the method nonetheless demonstrates a robust foundation for a greener analytical approach, showing a dedication to ongoing improvement in all aspects of environmental responsibility.

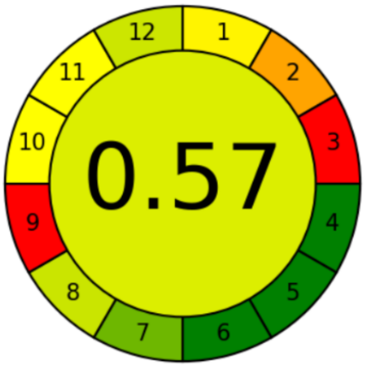


Figure 8. Results of AGREE analysis for Alg-EFBAC-beads- µ-SPE – GC-MS.

CONCLUSION

In conclusion, our developed µ-SPE method, incorporating EFBAC encapsulated in sodium alginate beads and coupled with GC-MS, proved to be a promising approach for determining OCPs in water samples. The technique demonstrated wide linearity, exceptional precision, and satisfactory relative recoveries for the targeted analytes under optimized conditions.

Table 5. Comparison with other methods for the analysis of OCPs.

SPE Mode	Method	Sorbent	Sample Volume (mL)	Sorbent Amount (mg)	Extraction Time (min)	Desorption Time (min)	Solvent Volume (µL)	LOD (µg/L)	Recoveries (%)	Ref.
SB-µ-SPE	GC-MS	[4-MA] [FeCl4]	10	1	15	30	200	0.25-3.4	89–105	[67]
µ-SPE	GC-MS	MIL-101	10	4	40	15	100	0.0025-0.016	87.6-98.6	[68]
MSPE	GC-MS/MS	M-M-ZIF-67	5	6	20	5	4000	0.07-1.03	74.9-116.3	[69]
CPME	GC-MS	PEG 300	20	3 cm	50	2	250	0.01-0.03	90.5 -105	[70]
µ-SPE	GC-MS	ZnO-CF	10	15	30	15	300	0.19-1.64	85.1-100.7	[71]
µ-SPE	GC-MS	Alg-EFBAC-Beads	10	50	15	7	1000	40 - 290	85-95	This work

SB-µ-SPE; Stir-bar supported µ-SPE, CPME; Capsule phase microextraction.
GC-MS/MS: Gas chromatography-tandem triple quadrupole mass spectrometry
[4-MA] [FeCl4]; Ionic liquid (4-methylbenzenaminium tetrachloroferrate (III), MIL-101; Chromium terephthalate-based mesoporous metal-organic; Framework material, M-M- ZIF-67; Imidazolate framework based on magnetic multiwalled carbon nanotubes, PEG 300; Poly (ethylene glycol) 300, ZnO-CF; zinc oxide nanoparticles incorporated carbon foam.

The alginate bead is a support matrix that holds the activated carbon particles in place and allows easy separation. The AGREE score affirmed the moderate greenness of the method, highlighting its environmentally friendly features. Alg-EFBAC beads hold significant potential for determining various contaminants in water matrices.

In considering avenues for future research, it is imperative to delve deeper into the molecular interactions between the sorbent (Alg-EFBAC-beads) and analytes. Employing advanced techniques such as molecular docking or density functional theory (DFT) can provide valuable insights, confirming and elucidating the nature of these interactions. Additionally, exploring the effects of varying percentages of sodium alginate in the sorbent composition is crucial. This aspect directly influences the sorbent's surface area, thereby impacting the overall efficiency of the extraction process. Furthermore, evaluating the regeneration and reusability potential of the sorbent is suggested for investigation. The implementation of online methods should be explored to enhance the environmental sustainability of the method further and elevate the AGREE value.

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