



Original Research Article

**Development of MIL-101(Fe)/Silica Aerogel Nanohybrid for Chlorpyrifos
Extraction in Soil Using Magnetic Fiber Headspace Solid-Phase
Microextraction Combined with Gas Chromatography-Mass Spectrometry**

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ABSTRACT

A hybrid material combining silica aerogel with MIL-101(Fe) was synthesized and effectively utilized as a fiber coating for the headspace solid-phase microextraction of Chlorpyrifos. The nanohybrid was characterized using a range of analytical techniques. Employing a magnetic field, generated with a pair of permanent disc magnets, on the coated steel fiber significantly enhanced the extraction efficiency for the majority of the target components. Optimization of key parameters influencing the extraction performance was conducted using a one-variable-at-a-time approach. The optimized conditions included a temperature of 120 °C, water addition of 10 μ L, and an extraction time of 10 minutes. The prepared fiber demonstrated stability and could be reused multiple times without noticeable deterioration in efficiency. For precision assessment, five repeat analyses were carried out, yielding a relative standard deviation (RSD) of 5.1% for peak areas associated with the target compound. Furthermore, the method proved highly reliable and effective when applied to real-world scenarios, successfully extracting and identifying Chlorpyrifos from soil samples. The results highlight the robustness, reproducibility, and practical utility of this innovative approach in analytical applications.

Keywords: Silica aerogel, Metal-organic framework, Magnetic fiber, solid-phase microextraction, Chlorpyrifos

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Introduction

Silica aerogels (SAs) are lightweight solids characterized by high porosity, low density, low thermal conductivity, and large surface areas [1-3]. Thanks to these unique properties, SAs have been employed in diverse applications such as drug delivery, catalysis, gas storage, thermal insulation, sensing technologies, and extraction methods [4-6]. To enhance the mechanical and physical properties of SAs, they can be tailored through the incorporation of various materials during the silica sol formation stage. Examples of such additives include Pt, Ag, RuO₂, SnO₂, TiO₂, ZnO, carbon nanotubes, quantum dots, SiO₂ nanowires, and metal-organic frameworks (MOFs) [7-10]. Recently, MOFs a class of crystalline materials have garnered significant attention due to their distinct features. These materials consist of metal clusters connected by organic linkers, resulting in a porous structure with tunable pore sizes and very high surface areas. Because of these properties, MOFs are increasingly used in applications like gas separation and storage, catalysis, and sample preparation [11-14].

In modern agriculture, chemical compounds like pesticides play a critical role in pest control and boosting crop yields. However, their widespread use poses environmental risks, as these chemicals may leach into ecosystems and act as pollutants. Organophosphorus and organochlorine pesticides are particularly concerning due to their high mutagenic and carcinogenic potential, posing serious health risks to humans and animals. To monitor and analyze pesticides in complex matrices such as water, soil, and food samples, efficient extraction methods are essential [15-18].

Solid-phase microextraction (SPME) has emerged as a simple, rapid, cost-effective, and environmentally friendly approach for extracting compounds from diverse matrices [19-21]. In recent years, studies have reported enhancements in SPME efficiency through the application of magnetic fields. In this study, composites of MIL-101(Fe) MOFs and SAs were synthesized by adding the MOFs into a silica sol mixture followed by ambient pressure drying. The composites, as well as the pure aerogel, were characterized using various techniques and tested as coatings for steel SPME fibers. Furthermore, the impact of magnetizing these MOF/SA-coated fibers on the extraction efficiency of Chlorpyrifos was investigated.

Experimental

Reagents and materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, N,N-Dimethylformamide (DMF), NaBH_4 , HNO_3 , NaCl, HCl and NaOH were supplied from Sigma-Aldrich. Terephthalic acid (H_2BDC) methanol, tetraethyl orthosilicate (TEOS), ammonia, hexane, trimethylchlorosilane (TMCS) and other chemicals with high purity were purchased from Merck and used without additional purification.

Apparatus

Compound separation, measurement, and identification were performed using a gas chromatograph-mass spectrometer (GC-MS) system (SCION SQ W/436, SSL-T21; SCION-MS detector). Separation was achieved on a fused silica capillary column (15 m \times 0.25 mm i.d., 0.25 μm film thickness; DBX-5, 95% polydimethylsiloxane, 5% phenyl). Helium (99.999% purity) was used as the carrier gas. Samples were directly injected (1 μL) using a GC-MS microsyringe. Surface morphology and elemental analysis were investigated using a field emission scanning electron microscope (FE-SEM; Tescan Mira3 LMU, Czech Republic) equipped with an energy-dispersive X-ray (EDX) spectrometer. X-ray diffraction (XRD) patterns were acquired using a STOE STADI P powder diffractometer (Germany) with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Thermal stability was assessed using a DSC-1 differential scanning calorimeter (Toledo) with a thermal analyzer.

Synthesis of MIL-101(Fe)

For the fabrication of MIL-101(Fe), 2.68 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.824g H_2BDC were added to 30 ml of DMF and were sonicated for 10 min. The final solution was transferred to a Teflon-lined autoclave and heated at 110 C for 20 h. The obtained product was washed several times via DMF and dried at 50 C.

Synthesis of SA and its hybrids with the MOF

MIL-101(Fe)/SA hybrid material was synthesized using a sol-gel method. First, MIL-101(Fe) (0.3 g) was dispersed in ethanol (11.7 mL) via sonication for 15 min. Water (1.8 mL) and TEOS (5.5 mL) were then added, and the pH was adjusted to 2.0 with HCl. The mixture was stirred for 90 min, followed by the addition of concentrated ammonia solution (25%, 20 μL), and further

mixing for 10 min. The resulting gel was aged in ethanol for 48 h to facilitate solvent exchange. Ambient pressure drying was achieved by immersing the gel in a mixture of TMCS/ethanol/n-hexane (18:9:7 v/v/v) for 48 h at 35 °C. After washing with hexane, the gel was dried in an oven sequentially at 55 °C for 24 h, 85 °C for 12 h, and 135 °C for 6 h to ensure complete solvent removal. Pure silica aerogel (SA) was also prepared using the same procedure, but without the addition of MIL-101(Fe).

GC-MS analysis

Chlorpyrifos separation and identification were performed using GC-MS. The column temperature program was as follows: initial hold at 80 °C for 1 min, followed by an increase to 200 °C at a rate of 20 °C/min, held for 1 min, and then a final ramp to 280 °C at 8 °C/min, held for 5 min. The injection port and detector temperatures were maintained at 280 °C and 300 °C, respectively. Helium was used as the carrier gas at a flow rate of 1 mL/min. A splitless injection system was employed. The ionization chamber temperature was 200 °C, and the ionization energy was 70 eV.

Preparation of the SPME holder and fiber

A custom SPME holder was fabricated from 19-gauge and 21-gauge stainless steel needles. A 2-cm section of the 19-gauge needle was cut, and a septum was inserted at one end to ensure a gas-tight seal. The 21-gauge needle was then passed through the septum and inside the 19-gauge needle. To prepare the SPME fiber, a 1-cm length of 23-gauge stainless steel wire, roughened with epoxy adhesive, was coated with a thin, uniform layer of absorbent powder. This was achieved by inserting the wire into the powder. The coated fiber was then dried in an oven at 65 °C for 48 h to remove residual solvent from the epoxy adhesive. Finally, the fiber was conditioned and cleaned by exposure to helium gas within the GC injector at 250 °C for 10 min.

Extraction by the MF-HS-SPME system

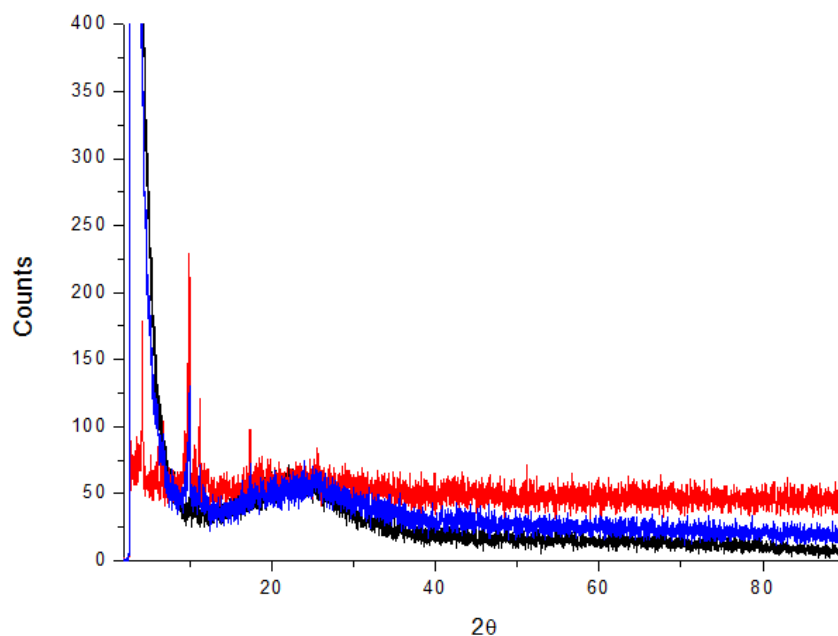
Sand, predominantly composed of metal oxides, silica (-SiO₂), and active silanol (-OH) groups, closely resembles natural soils, making it a useful model material for experimental purposes. To simulate such a system, 10 grams of standard soil were accurately weighed and placed in a

custom-designed container equipped with a Teflon lid. A total of 100 μL of a 100 ppm standard solution mixture was then applied to the sand model via spraying, and the container was vigorously shaken by hand to ensure even distribution. Subsequently, 10 μL of water was added to the sample, followed by two additional rounds of vigorous shaking to promote uniform water penetration throughout the sample. Next, an SPME fiber holder was carefully introduced into the vial through its septum. To impose a magnetic field on the SPME fiber, a pair of permanent neodymium (NdFeB) disc magnets was attached to the holder. Throughout the experiments, the needle's position was maintained at a consistent height relative to the sample surface for accuracy. The fiber was then gradually lowered to allow exposure to the sample's headspace. The vial containing the sample was placed in a sand bath and heated at 120°C for 10 minutes. Once the exposure period concluded, the fiber was retracted into the holder with care and promptly transferred to the GC injection port for thermal desorption and subsequent analysis.

Results and discussion

Characterization of the adsorbents

Figure 1 illustrates the XRD patterns of MIL-101(Fe) and MIL-101(Fe)/SA compounds. The XRD pattern of MIL-101(Fe) aligns well with data previously reported in the literature. Additionally, the characteristic diffraction peaks of both MIL-101(Fe) and MIL-101(Fe)/SA are evident in the silica-based composites. These findings confirm the successful preparation of the hybrid materials.



Figur.1. The XRD Pattern of Adsorbents

Morphology

The surface morphology of the prepared fibers was analyzed through their SEM images. Figure 2 presents the SEM image of a fiber coated with MIL-101(Fe)/SA, revealing a porous and uniform coating on the fiber, which has an approximate diameter of 170 μm .



Figur.2. The morphology of the surface structure of the prepared fiber

Thermal stability studies

Figure 3 presents the DSC spectra of MIL-101(Fe)/SA, highlighting the thermal stability of these compounds. The endothermic peaks observed in the spectra can be attributed to the evaporation of water or solvent during the drying process.

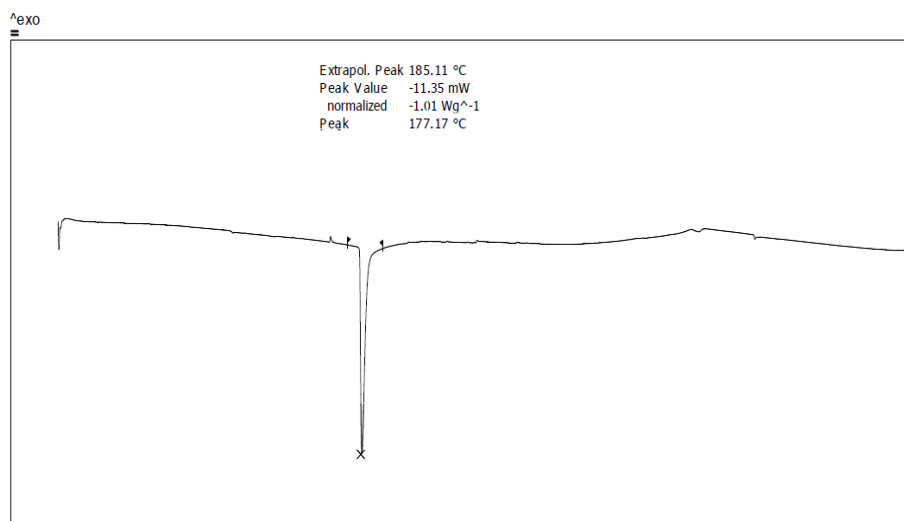


Figure.3. The DSC spectra of MIL-101(Fe)/SA

Optimization of Parameters by One at a Time Method

To optimize the extraction of Chlorpyrifos using the MF-HS-SPME method, various factors influencing the technique's efficiency were thoroughly examined. These included the type of sorbent used, the extraction temperature, the impact of water addition, and the duration of the extraction process.

Selection of Adsorbent

The study investigated the impact of different adsorbent types on the extraction of a compound from soil using the solid-phase microextraction (SPME) method in the headspace under a magnetic field. Three adsorbents, MIL-101(Fe)/silica aerogel, MIL-101(Fe), and silica aerogel were tested. Based on the results illustrated in Fig. 4, MIL-101(Fe)/silica aerogel demonstrated the most effective performance compared to the other two adsorbents. Consequently, this

adsorbent was identified as the optimal choice and was utilized in the subsequent stages of the study.

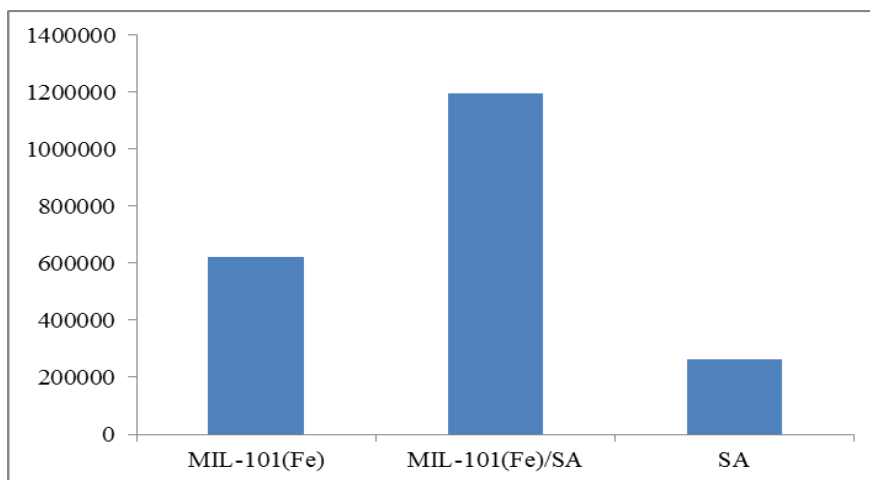


Figure. 4. Effect of the adsorbent type on extraction efficiency

Effect of the magnetic field

An SPME fiber coated with an MIL-101(Fe)/SA composite was employed to study the influence of a magnetic field on the extraction efficiency of the HS-SPME system. The extraction efficiencies were evaluated both in the absence and presence of a magnetic field generated by a pair of permanent disc magnets. The results clearly showed that applying the magnetic field significantly enhanced the extraction efficiency of the analyte. Consequently, the magnetic field was identified as a key parameter in the extraction process and was incorporated into subsequent experiments (refer to Fig. 5).

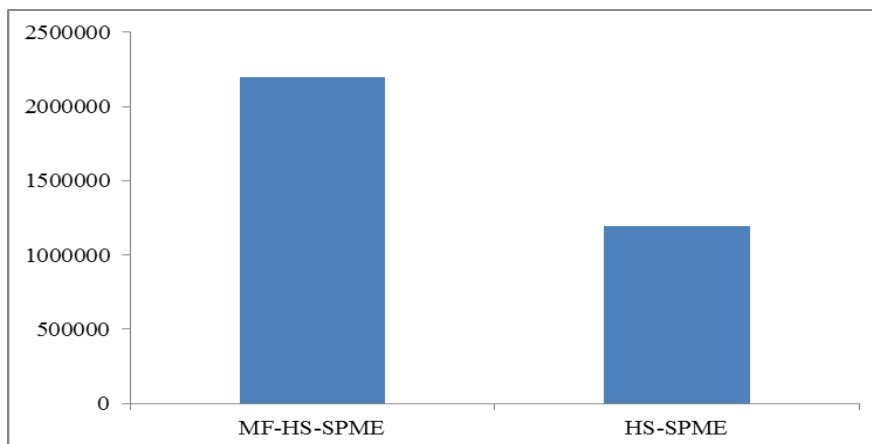


Figure. 5. Effect of the magnetic field on extraction efficiency

Effect of extraction temperature

Elevating the sample temperature enhances the release of analytes from the matrix, thereby improving mass transfer to the headspace. Additionally, sample heating influences extraction kinetics by accelerating the extraction rate. To evaluate the impact of extraction temperature on the proposed MF-HS-SPME method, experiments were conducted using sand samples, monitoring the peak area of extracted Chlorpyrifos across various sample temperatures. The results are presented in Fig. 6. A consistent increase in peak area was observed as the sample matrix temperature rose, reaching an optimal point at 120 °C. However, at higher temperatures, the pressure inside the extraction vial increased undesirably.

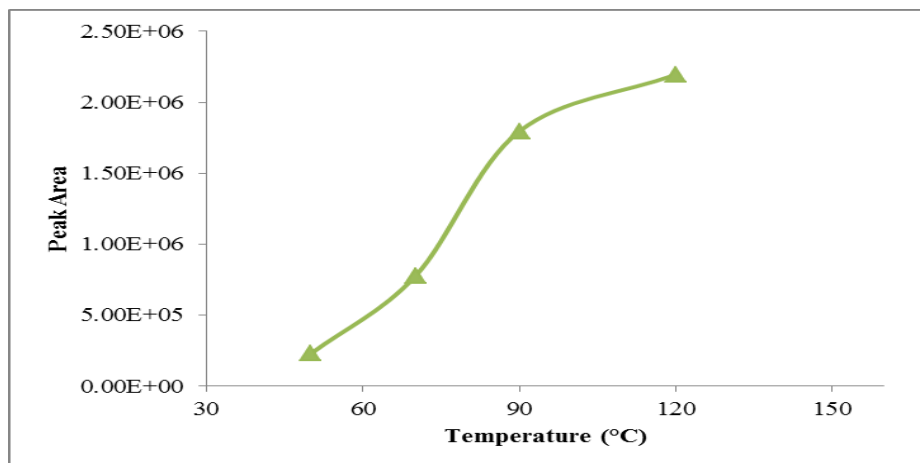


Figure.6. Effect of extraction temperature on extraction efficiency

Effect of moisture

The results indicate that moisture exhibits a beneficial impact on the response up to a volume of 10 μl . However, introducing water into the sample leads to saturation of the vapor phase with water, which minimizes the evaporation of the sample components. Additionally, a thin water layer may develop on the fiber coating. Under these circumstances, the analyte tends to adsorb onto this water layer rather than directly onto the fiber, ultimately decreasing the quantity of extracted compounds (refer to Fig. 7).

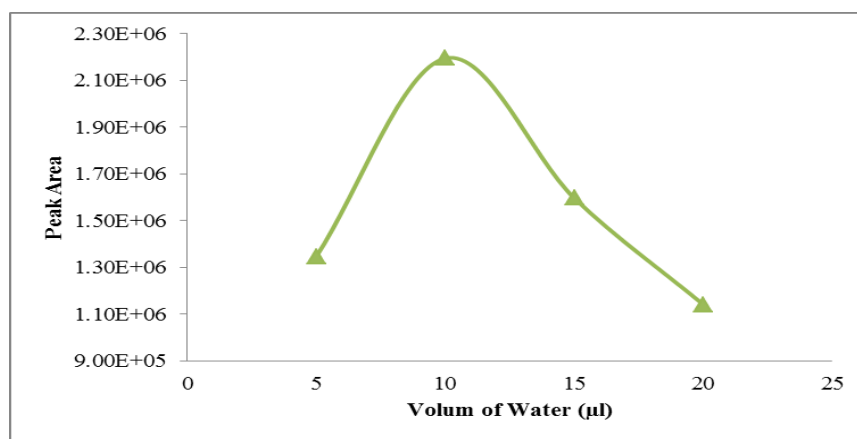


Figure.7. Effect of moisture on extraction efficiency

Analytical performances

Following optimization of the factors for the developed method and based on the results obtained during the optimization process, the calibration curve demonstrated strong linearity, with determination coefficients reaching 0.992 (Table 1). The repeatability of the MF-HS-SPME method was evaluated under optimal conditions. The relative standard deviations (RSDs) of peak areas, derived from five replications, were within 5.1%. Additionally, a single fiber used in this study remained effective for at least 30 injections within a month, showing no significant changes in its properties. This suggests that the fiber possesses satisfactory thermal stability.

Table 1. Limit of detection (LOD), limit of quantitation (LOQ), linear dynamic range (LDR), correlation coefficient (R^2) and regression equation for Chlorpyrifos in the sand samples analyzed by MF-HS-SPME method

Regression equation	R^2	LOD (ng g^{-1})	LOQ (ng g^{-1})	LDR ($\mu\text{g g}^{-1}$)	RSD
$y=411918x+1649.5$	0.992	0.41	1.21	0.0012 -10	5.1

Real Sample

To evaluate the efficiency of the applied method for extracting compounds, three soil samples from agricultural land were analyzed under the established optimal conditions, as shown in Table 2.

Table 2. Amount of Chlorpyrifos ($\mu\text{g g}^{-1}$) in three soil samples determined by the MF-HS-SPME method.

*N.D: Not Detected

Sample	Added	Found
Soil 1	-	N.D*
	1	0.92 (± 0.4)
Soil 2	-	N.D*
	1	0.99 (± 0.11)
Soil 3	-	N.D
	1	1.05 (± 0.02)

Conclusion

The MIL-101(Fe)/SA nanocomposites, characterized by high porosity and thermal stability, were successfully synthesized and analyzed. A solid-phase microextraction (SPME) fiber coated with the MIL-101(Fe)/SA sorbent demonstrated effective extraction of the target analyte from soil samples. The findings indicated that applying a magnetic field to the MIL-101(Fe)/SA SPME fiber using a permanent magnet could significantly enhance the efficiency of the headspace solid-phase microextraction (HS-SPME) method. The fiber exhibited excellent durability, allowing multiple uses without any noticeable alteration in its properties. Overall, the magnetic field-enhanced HS-SPME (MF-HS-SPME) approach proved to be both efficient and reliable, making it a viable method for the extraction and identification of the analyte.

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