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Layered Double Hydroxide/Polyethylene Glycol Nanocomposite as a Solid-Phase Microextraction Fiber Coating for Pesticide Determination in Cucumber and Tomato Samples

Marzieh Piryaei[1]✉ | Mir Mahdi Abolghasemi[1] | Hamed Faramarzi[1]

1. Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh, Iran
Corresponding Author's Email: m.piryaei@maragheh.ac.ir

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ABSTRACT

A novel layered double hydroxide/polyethylene glycol (LDH/PEG) nanocomposite was synthesized via a co-precipitation method and evaluated for the first time as a headspace solid-phase microextraction (HS-SPME) fiber coating for the simultaneous determination of thirteen multiclass pesticides (diazinon, fenitrothion, malathion, chlorpyrifos, penconazole, profenofos, cyproconazole, diniconazole, propiconazole, tebuconazole, fenpropathrin, phenothrin, and phosalone) in cucumber and tomato samples. The morphology and structure of the prepared SPME fiber were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Key extraction parameters including extraction temperature, sample pH, and extraction time were systematically optimized. Under the optimal conditions, the method showed linear ranges of 0.1–1000 µg L^{-1} for chlorpyrifos and cyproconazole, and 1–1000 µg L^{-1} for the other analytes, with coefficients of determination (R^2) between 0.985 and 0.998. Limits of detection (LODs) ranged from 0.05 to 0.50 µg L^{-1}, and relative standard deviations (RSDs) at 1000 µg L^{-1} were 3.9–8.9% (n = 3). The proposed HS-SPME method using the LDH/PEG nanocomposite fiber exhibited good analytical performance with LODs and RSDs comparable or superior to those reported in previous studies. The developed method was successfully applied to real cucumber and tomato samples with satisfactory relative recoveries.

1. INTRODUCTION

The steady growth of the global population and the consequent increase in food demand have intensified public and scientific concern about pesticide residues in food [1, 2]. Pesticides, while beneficial for crop protection, can cause adverse effects on the environment and pose potential health risks to organisms [3-5]. The need to monitor pesticide levels in food has driven the development of various analytical methods [6-9]. among which solid-phase microextraction (SPME) has gained considerable attention[10, 11]. SPME, first introduced in 1990 [12], enables simultaneous extraction and preconcentration of analytes in a single step. The headspace mode (HS-SPME) was later developed to eliminate matrix effects: the fiber is placed in the headspace above the sample, and the analytes partition among the three phases (sample, headspace, and fiber coating) [13-17].

Layered double hydroxides (LDHs) are a class of natural or synthetic anionic clays consisting of positively charged brucite-like layers and exchangeable interlayer anions. Hydrotalcite, $[Mg_6Al_2(OH)_{16}]CO_3{\cdot}4H_2O$, is the most well-known representative[18-22] The general formula of LDHs is $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}_{x/n}{\cdot}mH_2O]$, where M^{II} and M^{III} are divalent and trivalent metal cations, respectively, and A^{n-} is the interlayer anion [23, 24]. Owing to their two-dimensional structure, large surface area, ion-exchange capacity, and thermal stability, LDHs are increasingly used as adsorbents in analytical chemistry, including in solid-phase extraction[25, 26]. Common synthesis methods include co-precipitation, ion exchange, hydrothermal treatment, and calcination [27, 28]. LDH nanostructures modified with polyethylene glycol (PEG) can increase the LDH adsorption capacity.[29, 30].

Recent studies have shown that modification of LDHs with polyethylene glycol (PEG) reduces particle agglomeration and increases the number of accessible

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active sites, thereby significantly enhancing the adsorption capacity toward organic pollutants [31, 32]. Inspired by these findings, in the present work an LDH/PEG nanocomposite was prepared and, for the first time, applied as an HS-SPME fiber coating for the extraction and determination of a wide range of pesticides (organophosphates, triazoles, and pyrethroids) in cucumber and tomato samples. After thorough characterization, the effects of the main extraction parameters were optimized, and the analytical performance of the method was evaluated and compared with that of previously reported techniques.

2. EXPERIMENTAL

2.1. Materials

The studied pesticides (diazinon, fenitrothion, malathion, chlorpyrifos, penconazole, profenofos, cyproconazole, diniconazole, propiconazole, tebuconazole, fenpropathrin, phenothrin, and phosalone) were purchased from Arya Company, Iran. A stock solution (1000 mg L^{-1}) of the pesticide mixture was prepared in methanol and stored at 4 °C. Standard working solutions at different concentrations were obtained by diluting the stock solution with distilled water.

$Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $NaNO_3$, NaOH, dichloromethane, polyethylene glycol 6000, chlorosulfonic acid, ethanol, hydrochloric acid, phosphoric acid, ammonia, and sodium chloride (all of analytical grade) were purchased from Merck and Fluka. Stainless steel wires (diameter 200 µm) obtained from the core of spinal needles (B. Braun) were used as fiber substrates.

2.2. Apparatus

Gas chromatographic analysis was performed on an Agilent 7890B GC (USA) equipped with a flame ionization detector (FID) and a split/splitless injector. Separation was carried out on an HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Hydrogen was supplied by a HyGen 200 hydrogen generator (England). The column oven was initially held at 70 °C for 2 min, then ramped to 300 °C at 8 °C min^{-1} and held for 5 min. The injector temperature was 275 °C, and all injections were performed in splitless mode for 2 min.

X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer (Germany) using Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 3–80°. The morphology of the synthesized fiber was examined with a Phenom ProX scanning electron microscope (Phenom Co., the Netherlands). FT-IR spectra were acquired on a Bruker VECTOR22 spectrophotometer (Germany). Thermogravimetric analysis was conducted on a Mettler Toledo TGA/SDTA 851 instrument (Switzerland). A custom-made SPME holder was used to handle the fiber.

2.3. The Real Samples

Cucumber and tomato samples were collected from Gog Tappeh village, Miandoab, Urmia, Iran. The samples were grated and centrifuged at 15,000 rpm for 15 min to remove solid debris. The supernatants were filtered and centrifuged again at 4,000 rpm for 10 min. The pH of the final extracts was adjusted to 7 before analysis.

2.4. Synthesis of LDH/PEG Nanocomposite Fiber

Synthesis of LDH :$Mg(NO_3)_2 \cdot 6H_2O$ (10.25 g), $Al(NO_3)_3 \cdot 9H_2O$ (7.50 g), and $NaNO_3$ (2.83 g) were dissolved in 186.6 mL of distilled water in a round-bottom flask. The pH of the solution was adjusted to 9.5 using 6% ammonia solution under stirring. The mixture was then stirred at 65 °C for 2 h under a nitrogen atmosphere. The resulting precipitate was collected by filtration, washed thoroughly with distilled water, and dried at 70 °C, yielding the LDH powder. The yield of this synthesis was 86% (based on the theoretical mass calculated from the metal precursors).

Synthesis of PEG sulfonate (PEGs):Sulfonated polyethylene glycol (PEGs) was prepared according to a modified literature procedure [31, 35]. Polyethylene glycol 6000 (2 g) was dissolved in 20 mL of anhydrous dichloromethane in a round-bottom flask under nitrogen atmosphere. The solution was cooled to 0 °C using an ice bath. Chlorosulfonic acid (1.5 mL) was added dropwise over 30 min with continuous stirring. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for an additional 4 h. After completion of the reaction, the excess dichloromethane was removed under reduced pressure. The residue was slowly poured into 50 mL of ice-cold distilled water under vigorous stirring. The pH of the resulting solution was carefully adjusted to 7–8 by gradual addition of 10% NaOH solution. The product was precipitated by adding excess ethanol, collected by filtration, washed several times with ethanol, and dried under vacuum at 60 °C for 24 h. The yield of the sulfonated PEG (PEGs) was 82%.

Preparation of LDH/PEG nanocomposite:A dispersion of PEGs in distilled water (100 mL) and a suspension of LDH powder in distilled water (100 mL) were prepared separately and then mixed together. The mixture was stirred under a nitrogen atmosphere at 65 °C for 4 days. The solid product was separated by filtration, washed sequentially with water and ethanol, and dried at 60 °C, yielding the LDH/PEG nanocomposite as a white powder. The yield of the LDH/PEG nanocomposite was 81%.

Fiber coating:A small amount of the synthesized LDH/PEG powder was spread into a thin layer on a glass plate. A stainless-steel spinal needle (200 µm diameter) was dipped into a silicone-based glue and then gently rolled over the powder to coat the surface with the nanocomposite. The coated fiber was dried in an oven at 60 °C for 24 h. Before first use, the fiber was conditioned in the GC injector at 275 °C for 1 h under a stream of carrier gas.

2.5. HS-SPME Extraction Process

An aliquot (5 mL) of the aqueous sample containing the target analytes and 1 g of NaCl (20% w/v) was placed in a 15 mL glass vial equipped with a magnetic stir bar. The vial was sealed and placed on a stirrer at a controlled temperature. The fiber was exposed to the headspace for a fixed contact time, during which equilibration of the volatile analytes between the sample, headspace, and fiber

coating was established. After extraction, the fiber was immediately transferred to the injection port of the GC, where thermal desorption of the analytes occurred at 275 °C. All experiments were performed in triplicate.

3. RESULT AND DISCUSSION

3.1. LDH/PEGs Nanocomposites as an SPME Fiber Coating

Layered double hydroxides (LDHs) are widely used in various fields due to their unique properties, including high anion exchange capacity, large specific surface area, tunable chemical composition, and excellent thermal stability. The adsorption performance of LDHs is strongly influenced by their morphology, surface area, and degree of particle agglomeration.

Previous studies have demonstrated that modification of LDHs with polyethylene glycol (PEG) significantly enhances their adsorption capacity toward organic pollutants. Mandal et al. (2019) reported that incorporation of PEG into LDHs effectively reduces particle agglomeration, leading to better dispersion and an increased number of accessible active sites for adsorption [24]. This improved dispersibility and higher surface availability result in superior adsorption performance compared to unmodified LDHs.

Inspired by these findings, in the present work, an LDH/PEG nanocomposite was synthesized and applied, for the first time, as a novel coating for headspace solid-phase microextraction (HS-SPME) of thirteen multiclass pesticides (including organophosphates, triazoles, and pyrethroids) in cucumber and tomato samples. Although PEG-modified LDHs have been previously investigated for the removal of dyes and organic pollutants from aqueous solutions [31, 32], there is no report on their application as a coating material in solid-phase microextraction. Most previous studies using LDH-based materials in microextraction have focused on single-class analytes or simpler sample matrices. The present study introduces, for the first time, the use of LDH/PEG nanocomposite as an HS-SPME fiber coating for the simultaneous extraction of a wide range of multiclass pesticides (including organophosphates, triazoles, and pyrethroids) from complex vegetable matrices such as cucumber and tomato. This work aims to fill this research gap by combining the high surface area and thermal stability of LDH with the improved dispersibility and compatibility offered by PEG.The morphology and structural properties of the prepared fiber coating were systematically characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

To achieve maximum extraction efficiency, key operational parameters affecting the HS-SPME procedure-including extraction temperature, sample pH, and extraction time-were optimized. The analytical performance of the developed method (linearity, limit of detection, limit of quantification, and repeatability) was evaluated under the optimized conditions.

3.2. XRD Study

The crystal structure of the synthesized LDH/PEGs was investigated by X-ray diffraction (XRD) analysis over the 2θ range of 5–80°. The resulting XRD pattern is shown in Figure 1a. Indexed diffraction peaks were observed at 2θ = 10.8°, 21.6°, 34.8°, 37.6°, 45.7°, 61.1° and 62.2°, confirming the successful formation of the LDH/PEG structure [31]. These peak positions are in excellent agreement with the data reported by Yan [33]. Furthermore, the absence of any extraneous reflections demonstrates that the synthesized product is phase pure and free of crystalline impurities.

3.3. FT-IR Analysis

The chemical structure and functional groups of the synthesized LDH/PEGs were examined by Fourier-transform infrared (FT-IR) spectroscopy. The recorded spectrum is displayed in Figure 1b. The broad and intense absorption band centered at approximately 3419 cm^{-1} and the band observed at 1634 cm^{-1} are assigned to the stretching and bending vibrations of metal-bound hydroxyl groups and interlayer water molecules, respectively [34]. The peak around 1356 cm^{-1} is attributed to the stretching vibrations of nitrate (N–O) and carbonate (C–O) ions. The absorption bands in the region of 450–700 cm^{-1} are related to the stretching and bending vibrations of Al–OH and Mg–OH groups. Furthermore, the characteristic peaks at 1110, 1185, and 2900 cm^{-1} correspond, respectively, to the bending vibrations of C–O–H bonds and the stretching vibrations of C–H bonds of the PEG component, confirming the successful incorporation of PEG into the LDH structure.[31, 35].

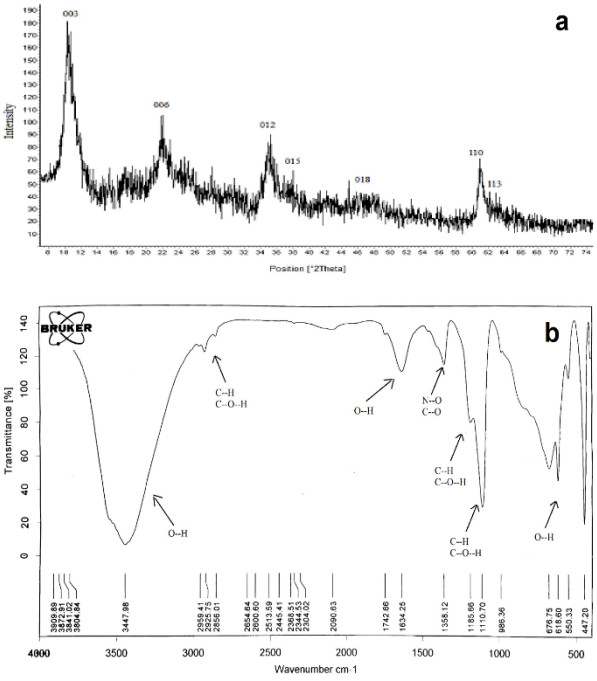


Fig. 1. (a) The XRD pattern, (b) FT-IR spectra of LDH / PEG

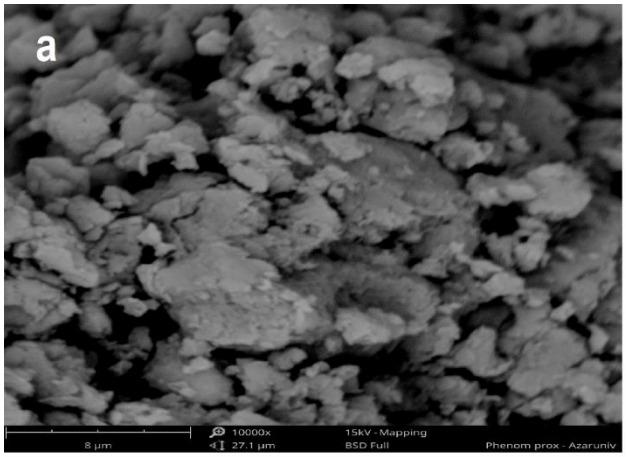
3.4. Scanning Electron Microscopy (SEM)

The surface morphology of the LDH/PEG nanocomposite was investigated using scanning electron microscopy (SEM). As shown in Figure 2a, the nanocomposite exhibits a platelet-like layered structure characteristic of LDHs, with particles appearing as irregular aggregates. Some degree of agglomeration is observed, which is common in LDH-based materials due to strong interlayer hydrogen bonding and van der Waals interactions. However, the incorporation of PEG appears to reduce the compactness of the aggregates compared to unmodified LDHs, leading to a more open and rough surface morphology. This rough and less agglomerated structure is beneficial for SPME applications as it increases the available surface area and facilitates analyte diffusion and adsorption. The particle size distribution was roughly estimated to be in the range of 50–300 nm.

The observed morphology confirms the successful formation of the LDH/PEG nanocomposite and supports the improved adsorption capacity expected from PEG modification, which acts as a spacer and dispersant between the LDH layers.

3.5. Thermogravimetric Analysis (TGA)

The thermal stability of the synthesized LDH/PEG fiber was evaluated by thermogravimetric analysis (TGA). The resulting thermogram is presented in Figure 2b. According to the TGA curve, the degradation of the fiber proceeds in four distinct stages. The first stage, observed up to approximately 110 °C, corresponds to a mass loss of about 7.14 %, attributable to the removal of physically adsorbed water. In the second stage, between 110 °C and 280 °C, a mass loss of about 9.21 % occurs due to the elimination of interlayer hydroxyl and carbonate groups within the LDH structure. The third stage, extending up to around 550 °C, involves a more substantial mass reduction of approximately 17.41 %, which can be assigned to the decomposition of residual anions in the LDH layers, the collapse of the layered structure, and the degradation of free PEG within the fiber. Finally, above 550 °C, a gradual mass loss of about 3.5 % takes place, corresponding to the complete structural breakdown of the LDH/PEG composite[31].



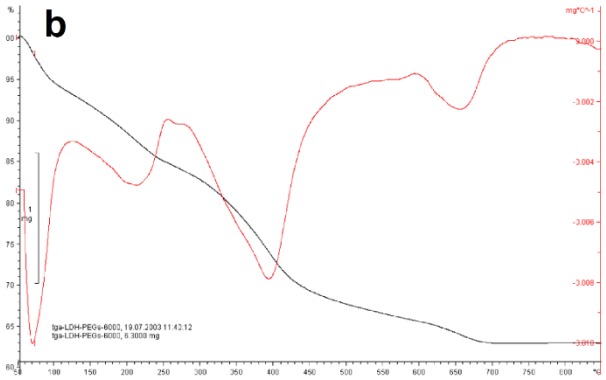


Fig. 2. (a) The SEM image and (b) TGA analysis of LDH / PEG

3.6. Optimization of SPME Procedure

Parameters such as temperature, pH and contact time that affected the extraction of analytes to the head-space and adsorption on the fiber were investigated.

3.6.1. Optimization of Extraction Temperature

In HS-SPME, temperature has a dual effect: it enhances the mass transfer of analytes into the headspace by increasing their vapor pressure, while simultaneously decreasing the distribution coefficient between the headspace and the fiber coating due to the exothermic nature of adsorption. To find the optimal temperature, the effect of this parameter was studied in the range of 75–95 °C. As shown in Figure 3a, the peak areas of most analytes increased with temperature up to 85 °C. Although no sharp decline was observed at higher temperatures, a plateau or slight decrease was noted for some compounds. Therefore, 85 °C was selected as the optimal extraction temperature, providing the highest overall efficiency while maintaining good precision and protecting both the analytes and the fiber coating.

3.6.2. Effect of pH

In the HS-SPME technique, the extraction fiber is not immersed in the sample solution; therefore, pH does not directly affect the fiber coating. However, the pH of the sample is a critical parameter that influences the distribution constant, hydrolysis, and chemical form of the analytes in the solution. Since only the neutral (molecular) form of the analytes can volatilize into the headspace, maintaining the appropriate pH is essential. The target analytes in this study are pH-sensitive and tend to undergo hydrolysis in strongly acidic or alkaline environments. For this reason, the effect of pH was not investigated under extreme pH conditions; instead, the extraction was evaluated over a moderate pH range of 4 to 8. As presented in Figure 3b, the maximum peak area and thus the highest extraction efficiency was obtained at pH 7.

3.6.3. Effect of Extraction Time

HS-SPME is an equilibrium-based microextraction technique; therefore, the amount of analyte extracted is directly related to the extraction time, making contact time a critical parameter influencing method efficiency. While the sorption of analytes onto the fiber coating increases

with time, shorter analysis times are preferred for higher sample throughput. To establish the optimal balance between extraction efficiency and analysis duration, extraction (contact) times ranging from 30 to 60 min were evaluated. The results, presented in Figure 3c, show that the analyte peak areas increased progressively with extraction time up to 50 min, after which the responses remained essentially constant. This plateau indicates that the fiber surface became saturated (i.e., extraction equilibrium was attained) at 50 min, and further extension of the extraction time did not improve the efficiency. Accordingly, an extraction time of 50 min was chosen as optimal for subsequent analyses. Extraction time was optimized in the range of 30–60 min based on preliminary studies. The observed rapid increase in extraction efficiency up to 50 min followed by a plateau indicates that equilibrium was reached, consistent with typical liquid-phase microextraction kinetics.

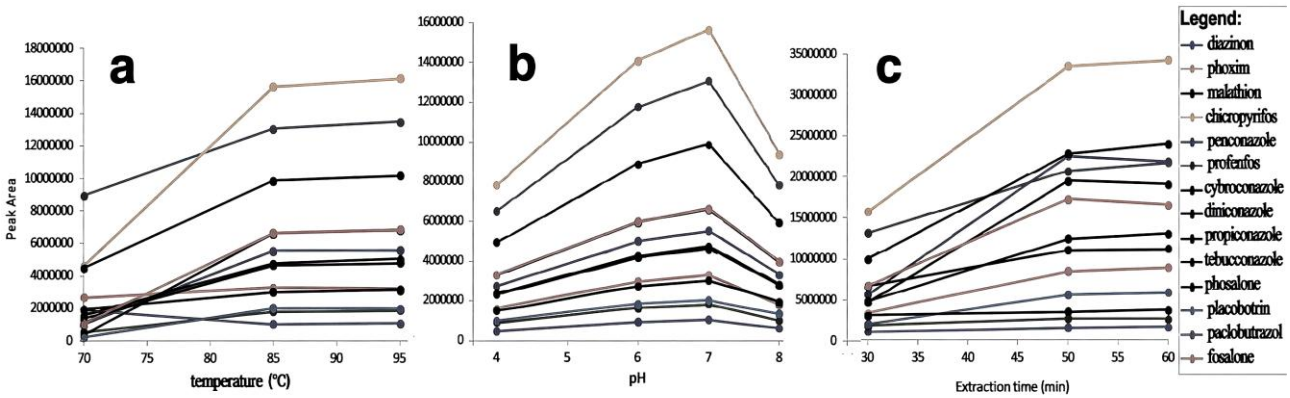


Fig. 3. The effect of (a) temperature, (b) pH and (c) contact time on the HS-SPME

3.7. Calibration Curves

Calibration curves were constructed for each analyte under the optimized conditions. The linearity ranges of the HS-SPME method for all target analytes are summarized in Table 1. The coefficients of determination (R^2) obtained from the calibration curves confirmed a good linear relationship between the analytical signal (peak area) and the analyte concentration.

Table 1
Analytical parameters obtained by HS-SPME with LDH/PEGs nanocomposite fiber for determination of studied pesticides

Pesticide	Linearity range (µg L^{-1})	R^2	LOD (µg L^{-1})	RSD (%)
Diazinon	1–1000	0.995	0.3	7.8
Fenitrothion	1–1000	0.998	0.1	5.7
Malathion	1–1000	0.996	0.1	7.6
Chlorpyrifos	0.1–1000	0.997	0.05	4.5
Penconazole	1–1000	0.998	0.1	8.1
Profenofos	1–1000	0.997	0.15	8.9
Cyproconazole	0.1–1000	0.994	0.07	8.5
Diniconazole	1–1000	0.991	0.1	5.5
Propiconazole	1–1000	0.985	0.1	6.4
Tebuconazole	1–1000	0.985	0.5	6.6
Fenpropathrin	1–1000	0.980	0.1	5.3
Phenothrin	1–1000	0.996	0.5	3.9
Phosalone	1–1000	0.987	0.1	8.6

3.8. Limit of Detection (LOD) and Limit of Quantification (LOQ)

In chromatographic methods, LOD and LOQ are commonly determined based on the signal-to-noise (S/N) ratio. The LOD corresponds to the lowest detectable analyte concentration yielding a signal equal to three times the noise level (S/N = 3). The LOQ is the minimum concentration that can be quantified with acceptable accuracy and precision, typically at an S/N ratio of 10 (S/N = 10). The LOD values of the method were calculated for each pesticide according to these definitions and are presented in Table 1.

3.9. Method Repeatability

The intra-day repeatability of the method was evaluated by performing three replicate extractions using the synthesized fiber under optimal conditions with independently prepared sample solutions. The repeatability is expressed as the relative standard deviation (RSD) for each analyte and is reported in Table 1.

3.10. Comparison with Previous Studies

The RSD and LOD obtained with the present method were compared with those reported in earlier studies that extracted and measured similar pesticides. A summary of this comparison is given in Table 2. The LOD and RSD values achieved in this study are either lower than or comparable to those of the previously reported methods, demonstrating the favorable performance of the proposed technique. To better position the current work, a critical comparison with recently reported methods for the extraction of similar pesticides is presented in Table 2. While several nanomaterial-based coatings (e.g., Nafion-SBA-15, Fe_3O_4@SiO_2@C8, and PDMS-based fibers) have been successfully used, most of them are either limited to fewer analytes, applied to simpler matrices (water or fruit juice), or require more complex and costly preparation procedures. Moreover, the application of LDH-based composites in HS-SPME remains very scarce. The proposed LDH/PEG nanocomposite offers distinct advantages including facile and low-cost synthesis, good thermal stability, high reusability (>50 cycles), and suitable performance for multiclass pesticides in real vegetable samples. These features, combined with comparable or better LODs and precision, highlight the added value of the present contribution to the field of microextraction.

Table 2
Comparison of the analytical performance of the proposed method with other reported methods for the determination of pesticides.

Analyte(s)	Real sample	LOD (μg L^{-1})	RSD (%)	Method	Extraction Phase	Ref.
Penconazole, Diniconazole, Tebuconazole	Water	0.05, 0.02, 0.08	4.3–6.9	HS-SPME-GC-FID	Nafion-SBA-15 nanomaterial	[28]
Diazinon, Fenitrothion	Water	0.01–0.03, 0.025–0.04	4–10	HS-SPME-GC-MS	PDMS 100 μm & PA 85 μm	[29]
Diazinon, Chlorpyrifos	Fruit	0.48, 0.45	0.3–7.4	HS-SPME-GC-ECD	PDMS–2OHMe18C6	[30]
Diazinon, Chlorpyrifos, Penconazole	Water & Wastewater	0.53, 1.32, 1.56	2.2–3.9	SBSE-DLLME-GC-FID	Octadecylsilane / tetrachloroethane	[31]
Diazinon, Chlorpyrifos, Penconazole, Diniconazole, Tebuconazole	Fruit & Vegetable	0.03–0.09	3–6	SBSE-DLLME-GC-FID	Fe_3O_4@SiO_2@C8 nanoparticles	[32]
Diazinon, Malathion, Chlorpyrifos, Profenofos	Strawberries & Cucumbers	0.02–0.2	1.3–5.71	HS-SDME-GC-ECD	PDMS 100 μm	[33]
Fenitrothion, Chlorpyrifos	Milk	4.5–4.8	-	HS-SPME-GC-MS	PDMS-DVB, 65 μm	[34]
Studied pesticides (13 compounds)	Cucumber & Tomato	0.05–0.50	3.9–8.9	HS-SPME-GC-FID	LDH/PEG nanocomposite	This work

Footnote: HS-SPME: Headspace solid-phase microextraction; GC-FID: Gas chromatography-flame ionization detection; GC-MS: Gas chromatography-mass spectrometry; GC-ECD: Gas chromatography-electron capture detection; SBSE: Stir bar sorptive extraction; DLLME: Dispersive liquid-liquid microextraction; PDMS: Polydimethylsiloxane; DVB: Divinylbenzene; PA: Polyacrylate.

3.11.Real Sample Analysis and Matrix Effect

To evaluate the applicability of the method, the HS-SPME procedure with the LDH/PEG fiber was applied to the analysis of tomato and cucumber samples under optimal conditions. The resulting gas chromatograms did not show detectable levels of the target pesticides in the blank samples. To investigate matrix effects, the samples were spiked with a known amount of the pesticide mixture to obtain a final concentration of 10 µg L^{-1}. Figure 4 displays a representative chromatogram of a spiked tomato sample. Table 3 summarizes the analytical results for the spiked cucumber and tomato samples obtained using the proposed method under optimized conditions.

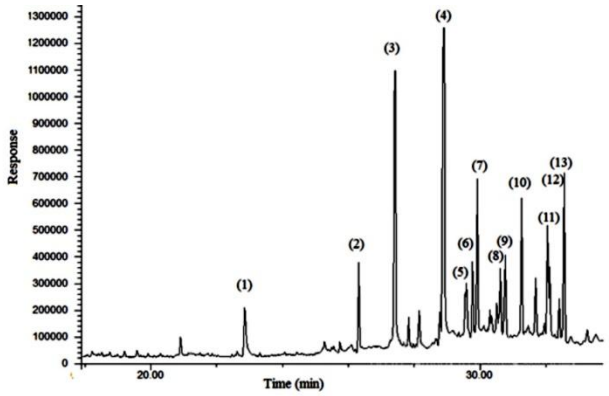


Fig. 4. The chromatogram of extracted pesticides spiked at 10 µg L^{-1} in tomato sample using HS-SPME with LDH/PEG fiber (1-diazinon, 2-fenitrothion, 3-malathion, 4-chlorpyrifos, 5-penconazole, 6-profenofos, 7-cyproconazole, 8-diniconazole, 9-propiconazole, 10-tebuconazole, 11-fenpropathrin, 12-phenothrin, 13-phosalone).

Table 3
Obtained results for the analysis of spiked real samples (10 µgL^{-1}) byHS-SPME with LDH/PEGs nanocomposite as extraction fiber.

	Concentration(µgL^{-1})	
Analyte	**Tomatoes**	**Cucumbers**
Diazinon	10±0.5	10±0.6
Fenitrothion	10±0.2	10±0.4
Malathion	10±0.7	10±0.6
Chlorpyrifos	10±0.6	10±0.7
Penconazole	10±0.7	10±0.8
Profenofos	10±0.2	10±0.8
Cyproconazole	10±0.3	10±0.5
Diniconazole	10±0.4	10±0.2
Propiconazole	10±0.5	10±0.6
Tebuconazole	10±0.4	10±0.5
Fenpropathrin	10±0.6	10±0.8
Phenothrin	10±0.2	10±0.6
Phosalone	10±0.3	10±0.9

3.12. Reusability and Stability of the LDH/PEG Fiber

The reusability and long-term stability of the SPME fiber are critical factors for its practical application. To evaluate the stability of the LDH/PEG nanocomposite coating, the same fiber was repeatedly used for extraction/desorption cycles under the optimized conditions. After each extraction, the fiber was thermally desorbed at 275 °C for 2 min in the GC injector and then reused for the next cycle. The peak areas of all thirteen pesticides were monitored.

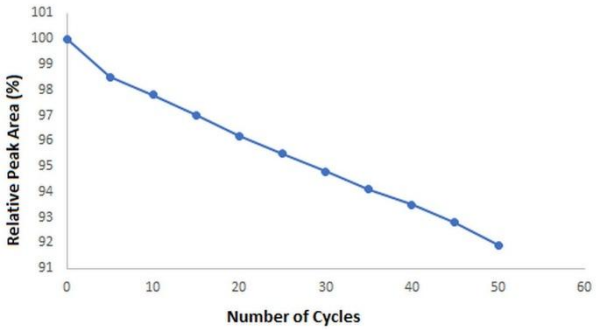


Fig. 5. Reusability of the LDH/PEG nanocomposite fiber over 50 extraction/desorption cycles. Conditions: spiked concentration 100 µg L^{-1}, extraction temperature 85 °C, extraction time 50 min, pH 7. Error bars represent standard deviations (n = 3).

As shown in Figure 5, the LDH/PEG fiber maintained more than 92% of its initial extraction efficiency even after 50 consecutive extraction/desorption cycles. No significant decline in performance or physical damage to the coating was observed. This excellent reusability can be attributed to the high thermal and mechanical stability of the LDH/PEG nanocomposite, as confirmed by TGA analysis. These results demonstrate that the prepared fiber is highly durable and cost-effective for routine laboratory use.

4. CONCLUSION

In this study, a novel layered double hydroxide/polyethylene glycol (LDH/PEG) nanocomposite was successfully synthesized via co-precipitation method and applied as a new fiber coating for headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-flame ionization detection (GC-FID). The structural, morphological, and thermal properties of the LDH/PEG coating were thoroughly characterized by XRD, FT-IR, SEM, and TGA, which confirmed the successful intercalation of PEG into the LDH interlayers and the formation of a stable, uniform nanocomposite film on the fiber surface.

The fabricated fiber showed excellent mechanical stability and could be reused for more than 50 extraction/desorption cycles without significant loss of extraction efficiency. Under the optimized conditions (extraction temperature: 85 °C, pH: 7, extraction time: 50 min), the proposed HS-SPME-GC-FID method enabled the simultaneous determination of thirteen pesticides (diazinon, fenitrothion, malathion, chlorpyrifos, penconazole,

profenofos, cyproconazole, diniconazole, propiconazole, tebuconazole, fenpropathrin, phenothrin, and phosalone) in cucumber and tomato samples. The method exhibited linear ranges of 0.1–1000 μg L^{-1} for chlorpyrifos and cyproconazole and 1–1000 μg L^{-1} for the other analytes, low limits of detection (0.05–0.50 μg L^{-1}), and satisfactory precision (RSDs ranging from 3.9% to 8.9%). Real sample analysis demonstrated good relative recoveries and negligible matrix effects, confirming the reliability and applicability of the method for the determination of pesticide residues in complex vegetable matrices. Compared with commercially available SPME fibers, the prepared LDH/PEG nanocomposite offers simple and low-cost preparation, high extraction efficiency, long operational lifetime, and good reusability. These results indicate that the LDH/PEG nanocomposite is a promising and effective sorbent for HS-SPME and has considerable potential for monitoring pesticide residues in food samples.

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