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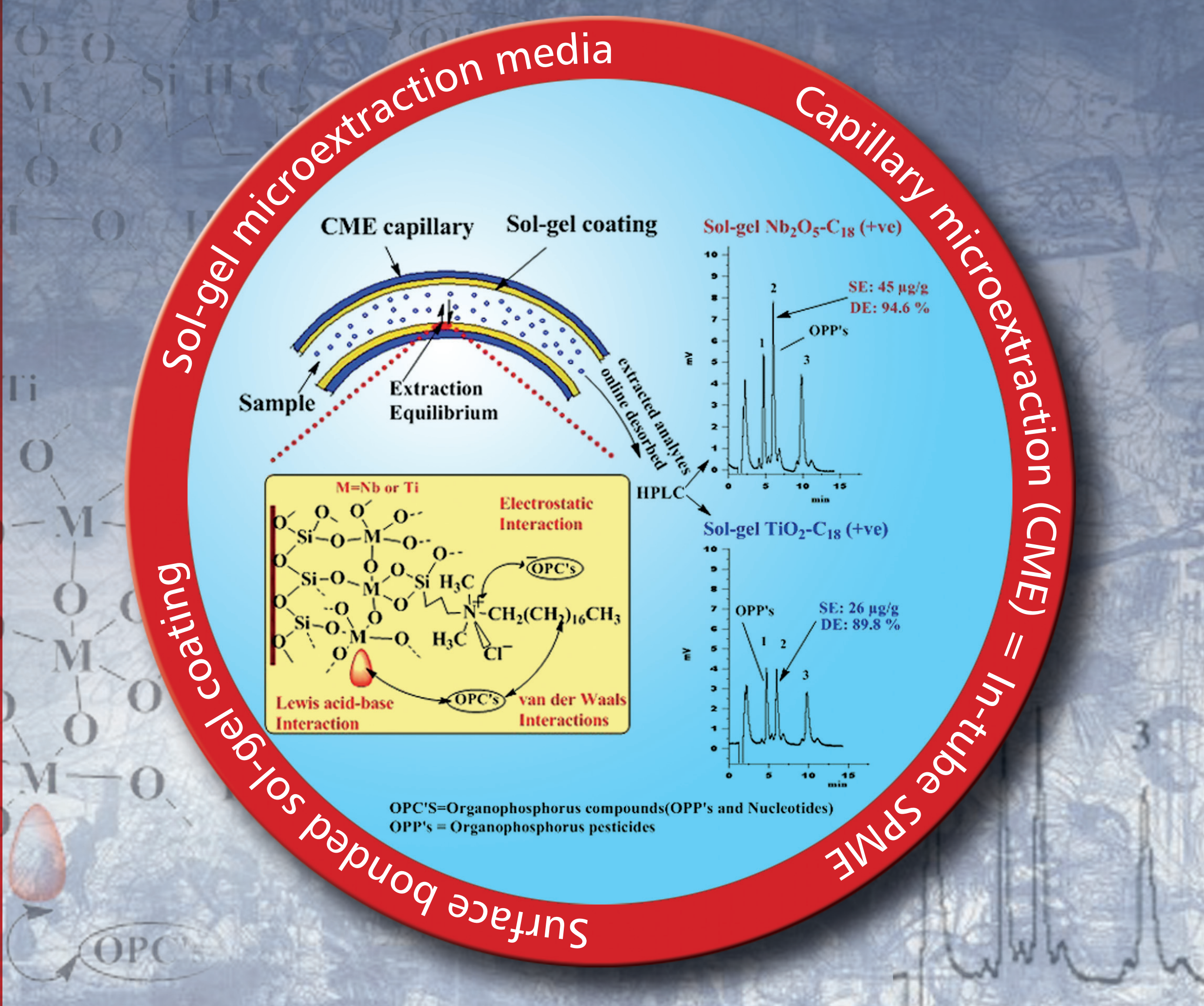
Sol-gel CME Online Coupled to HPLC

$$\text{specific extraction (SE)} = \frac{\text{mass of analyte extracted } (\mu g)}{\text{mass of Sol-gel sorbent (g)}}$$



$$\text{desorption efficiency (DE)} = \frac{\text{amount desorbed}}{\text{amount extracted}} \times 100$$

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RESEARCH ARTICLE

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Characterization and application of a lanthanide-based metal–organic framework in the development and validation of a matrix solid-phase dispersion procedure for pesticide extraction on peppers *(Capsicum annuum L.)* with gas chromatography–mass spectrometry

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The metal–organic framework $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$ was synthetized and characterized by X-ray diffractometry, differential thermogravimetric analysis, and infrared spectroscopy. The material was tested for the development and validation of a matrix solid-phase dispersion procedure for extraction of atrazine, bifenthrin, bromuconazole, clofentezine, fenbuconazole, flumetralin, procymidone, and pirimicarb, from peppers, with analysis using gas chromatography with mass spectrometry in the selected ion monitoring mode. The method developed was linear over the range tested (50.0–1000.0 μg/kg for procymidone and 200.0–1000.0 μg/kg for all other pesticides), with correlation coefficients ranging from 0.9930 to 0.9992. Experiments were carried out at 250.0, 500.0, and 1000.0 μg/kg fortification levels, and resulted in recoveries in the range of 52.7–135.0%, with coefficient of variation values between 5.2 and 5.4%, respectively, for $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$ sorbent. Detection and quantification limits ranged from 16.0 to 67.0 μg/kg and from 50.0 to 200.0 μg/kg, respectively, for the different pesticides studied. The results were compared with literature data. The developed and validated method was applied to real samples. The analysis detected the presence of residues of pesticides procymidone, fenbuconazole, flumetralin, clofentezine, atrazine, and bifenthrin.

KEYWORDS
matrix solid-phase dispersion, metal–organic frameworks, peppers, pesticides

1 | INTRODUCTION

Fresh vegetables are an important part of a healthy diet because of the presence of significant amounts of nutrients and minerals [1]. Vegetables, however, can also be a source of noxious toxic substances: pesticides [2].

Abbreviations: MOF, metal–organic framework; MSPD, matrix solid-phase dispersion

Conflict of interest: The authors declare that there is no conflict of interest.

Normally, the qualitative and quantitative analysis of pesticides includes a sample preparation procedure to isolate them from dietary, environmental, or biological matrixes, a key step in the development of an analytical method. In many cases this procedure requires a disruption of the overall structure of the contaminated matrix [3].

The breaking of solid matrixes with the use of an abrasive solid (sorbent) as support was introduced in 1989 by Barker [3,4] as an extraction technique known as matrix solid-phase dispersion (MSPD). This technique generates a chromatographic material that has special characteristics for the extraction of the dispersed matrix contaminants [4]. Materials commonly used as sorbents in the process, such as silica, alumina, and octadecyl silane, are efficient in the development of analytical methods for pesticide analysis, but in some cases do not have sufficient and high enough sorption capacity to be selective for specific analytes, nor do they have lower and/or incomplete desorption capacity of the analytes [5].

The last decade has seen a large growth in synthesis, characterization, and study of materials known as metal–organic frameworks (MOF) [6]. According to the International Union of Pure and Applied Chemistry, MOFs are an interdisciplinary field with origins in inorganic and coordination chemistry that has expanded rapidly. Recently, it has also attracted the interest of the chemical industry [7]. Usually, MOFs are formed from metal ions and organic linkers that self-assemble to create network coordination in up to three dimensions. These materials have well-defined microcrystalline structures formed by polynuclear clusters and often have permanent porosity [8].

The MOF applications range from catalysts [9,10] to biological applications [11] and chemical sensors [12,13]. Several studies have been published regarding the application of these materials to chromatography [14–21]. MOFs have also been applied in pre-treatment samples [22]. Recently, Jesus et al. [23] used zinc-based MOFs as sorbents for the extraction of multiclass pesticides from coconut palm. LC with UV diode array detection was used as the analysis technique. Jesus et al. [24] used MOF containing lanthanide ions for the extraction of pesticides in five samples of graviola, soursop exotic fruit (*Annona muricata*), applying the MSPD technique. In work carried out by our group, we observed that MOF based on lanthanum and dipicolinate linkers are efficient for pesticide extraction MSPD [25,26] at low cost. However, these results were obtained from the application of MOF in an analytical method developed and previously validated using silica gel and neutral alumina as the sorbents. To date, no analytical method has been developed and validated using only MOF with sorbent.

In this work, we developed and validated an analytical method based on MSPD extraction employing MOF as sorbent and GC–MS analysis for the simultaneous determination of atrazine, bifenthrin, bromuconazole, clofentezine, fenbuconazole, flumetralin, pirimicarb, and procymidone, belonging to different chemical groups, in fresh peppers. The compounds were selected due to their applications on fresh vegetable crops. Flumetralin was chosen due to its application in tobacco plantations neighboring the cultivation of vegetables, as located in the municipality of Itabaiana, state of Sergipe, Brazil (10°41′06″S, 37°25′31″W). After validation, the method was applied to determine pesticide residues in fresh peppers, purchased in various markets in the city of Aracaju, state of Sergipe, Brazil.

2 | MATERIALS AND METHODS

2.1 | Chemical and reagents

Lanthanum(III) and samarium(III) oxides (99 and 9%), and pyridine-2,6-dicarboxilic acid (99%) were purchased from Aldrich (St. Louis, MO, USA) and used without further purification. Standards of pesticides (>97%) were from AccuStandard (New Haven, CT, USA). Hexane and acetonitrile solvents were from Qhemis (São Paulo, Brazil). Anhydrous sodium sulfate and acetone were from Synth (São Paulo, Brazil). Chromatography Silica Gel 60 (70–230 mesh) was from Macherey-Nagel (Germany).

2.2 | Synthesis of the MOF

The crystals were obtained from the reaction between lanthanum oxide (La_2O_3 = 1.8 mmol), samarium oxide dopant (Sm_2O_3 = 0.2 mmol), pyridine-2,6-dicarboxylic acid (H_2DPA = 8.0 mmol), and water (40.0 mL) in a stainless-steel autoclave of 100 mL capacity and coated internally with Teflon. The reactor was kept under high pressure at 180°C for 72 h and then cooled to room temperature. The solid obtained was filtered, washed with acetone, and air dried.

2.3 | Solid-phase characterization

The X-ray measurements were carried out in a Bruker D8 Advance Diffractometer Cu Kα radiation and nickel filter at room temperature (T = 293 K). Differential thermogravimetric thermal analysis curves were acquired through a SHIMADZU DTG-60H instrument in the range from room temperature to 1100°C using an alumina crucible, under dynamic nitrogen atmosphere (50 mL/min) and with a heating rate of 10°C/min. FTIR spectroscopy was performed on a Spectrometer ABB model MB3000 with a spectral resolution of 4 cm^{-1} in the wavenumber range of 4000 to 500 cm^{-1} at room temperature.

2.4 | Pesticides standard solution

Stock solutions of the pesticides atrazine (241 μg/mL), bifenthrin and bromuconazole (500 μg/mL), clofentezine (277 μg/mL), fenbuconazole (400 μg/mL), flumetralin (392 μg/mL), and procymidone and pirimicarb (100 μg/mL) were prepared using dichloromethane as solvent. These solutions were stored under refrigeration to prevent decomposition of the active ingredients. Working solution was prepared at a concentration of 5 μg/mL diluted from the stock solutions in the same solvent. The calibration curve of standard dilutions was obtained by varying the concentration from 0.05 to 1.00 μg/L for all pesticides.

2.5 | GC–MS system and operating conditions

The extracts obtained were analyzed by GC–MS (Shimadzu QP2010 Plus, Kyoto, Japan) equipped with a split/splitless injector operating in the splitless mode at 280°C. Pesticides were separated in a capillary column (Restek Rtx®-5 MS Crossbond® 5% diphenyl/95% polydimethylsiloxane; 30 m × 0.25 mm id × 0.25 m, Bellefonte, PA, USA), using helium 99.99% as the carrier gas at a 1.0 mL/min flow rate. The oven temperature was as follows: 50°C (1 min); followed by 180°C at 20°C/min; and 280°C at 10°C/min, where it was held for 6 min. The mass detector conditions were: transfer line temperature 240°C; ion source temperature 230°C; and ionization mode electron impact at 70 eV. The analyses were done in selected ion monitoring mode. One target and two qualifier ions were monitored for all the selected pesticides. For each of the following pesticides, the first ion was the target ion and the other two the qualifier ions (*m/z*): 137, 102, and 75 (clofentezine); 200, 215, and 58 (atrazine); 166, 72, and 238 (pirimicarb); 96, 67, and 283 (procymidone); 143, 107, and 96 (flumetralin); 173, 295, and 145 (bromuconaloze); 181, 166, and 295 (bifentrin); and 198, 129, and 103 (fenbuconaloze). The quantification and confirmation of the selected pesticides was done in single runs, by monitoring the target and qualifier ions together.

2.6 | Sample preparation and fortification

The pepper samples used for method development were obtained from an organic farm (pesticide-free) located in the city of Aracaju in the State of Sergipe, Brazil. A representative portion of the sample was diced with a stainless-steel knife. Fortified samples were prepared by adding 50 μL of multicomponent standard solutions to 500 mg of the sample, resulting in levels of 0.5 mg/kg. The fortified pepper was left to stand for 30 min at room temperature, to allow evaporation of the solvent, before extraction. Replicates were analyzed at the fortification level. The extraction procedure is described below.

2.7 | Extraction procedure

An aliquot of pepper (500 mg) was placed into a glass mortar and 350 mg of MOF was added. The mixture was homogenized and transferred to a glass syringe (3.0 mL) containing 1.0 g of anhydrous sodium sulfate, previously calcined at 400°C for 2 h, and 500 mg of silica. A 10 mL portion of dichloromethane was added to the column and the sample was allowed to elute dropwise. The extract was filtered using nylon membrane of 0.45 μ and concentrated using a rotary vacuum evaporator (45°C). One microliter of this extract was injected into the GC–MS.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$

The synthesized material was obtained as colorless crystals after the hydrothermal reaction. X-ray diffraction power measurements (Figure 1) showed that the synthesized compound is isostructural with the pure lanthanum compound previously reported [27]. Thus, the obtained material was formulated as $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$. This led to the conclusion that the replacement of La^{3+} centers for other Sm^{3+} did not cause structural changes. The compounds crystallized in the monoclinic space group $P2_1/c$, and unit cell parameters were very similar to the previous published report on the compound [27].

In this compound we have each molecule of the ligand coordinated with three Ln^{+3} ions from the nitrogen atom of the pyridine ring and the oxygen of the two carboxylate groups, forming a 3D structure. There are two independent coordination centers. Ln (1) is non-chained, with the formula LnO_7N_2 being one of the oxygen atoms originating from a water molecule. Ln (2) is an octacoordinate, with the formula LnO_7N, being two oxygens from two water molecules [27]. Thus, the MOF is able to form different bonds at the various adsorption sites. MOF presents apolar (hydrophobic) centers in the pyridine rings that form π–π interactions with aromatic nuclei present in the molecules of pesticides and polar (hydrophilic) centers in the carboxylated oxygen and water molecules interacting with molecules of the pesticides with different polarities.

IR spectroscopy and thermal decomposition data align with the crystallographic structure. Signals observed in the IR spectrum contain characteristic peaks of the compound. The FTIR data (cm^{-1}) selected were: 3532 (m), 3079 (m), 1613 (w), 1438 (s), and 1389 (s). The thermogravimetric

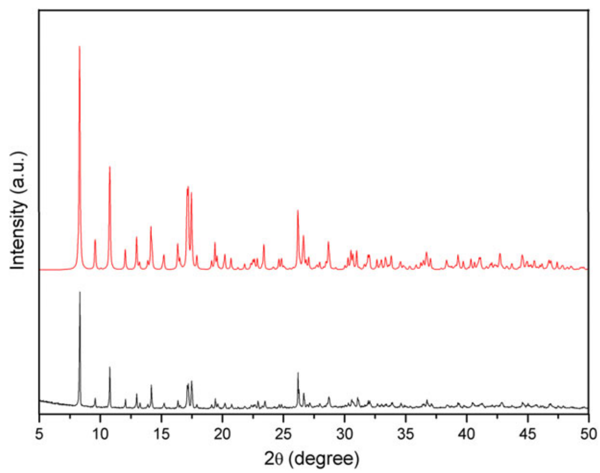

FIGURE 1 Powder XRD patterns of $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$: red: calculated; black: experimental

analysis showed three distinct mass loss events. One of these steps was characterized by a full loss of water molecules coordinated to the metal at 165°C. This step corresponded to an endothermic process. The experimental mass loss was 6.9% (Calculated: 6.5%). The decomposition of the ligands occurred with mass loss of 47.2%, starting from 438°C. This process occurs with the formation of unstable oxycarbonates $Ln_2O_2(CO_3)$ at higher temperatures. The decomposition of oxycarbonates led to the formation of lanthanide oxide, compatible with the final product obtained after decomposition. The IR spectrum (Supporting Information Figure S1) and thermogravimetric curve (Supporting Information Figure S2) can be seen in the Supporting Information.

3.2 | Optimization of extraction method for MSPD

The optimization of the extraction method started from a fixed mass (350 mg) of $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$. The elution solvent parameters and their volume, matrix mass, matrix: sorbent ratio, and the type of solid phase to clean-up, influenced the efficiency of extraction and purity of the final extract [28]. Then, solvents of different polarities and different volumes were evaluated for as to efficiency and process costs. They were optimized by combinations from a factorial planning 2^n (n = number of parameters) four more combinations at the central point, resulting in 20 experiments. The minimum and maximum level of each parameter is shown in Supporting Information Table S1. The study on the extraction efficiency was based on the percentage of recovery of pesticides in the fortified sample at a concentration of 500 μg/kg. Tests with hexane and silica as clean-up showed a high matrix effect. This result can be attributed to the chemical interaction of lipophilic compounds of the matrix with the solvent and to the hydrophilic character of silica. Therefore, we chose to use dichloromethane, which has hydrophilic properties, to reduce the matrix effect.

The best results were obtained using 500 mg of the matrix, elution with 10 mL dichloromethane, and silica for clean-up. One advantage of these optimized conditions was the use of a small amount of sorbent, resulting in a lower cost analysis and reduction in the amount of material to be synthesized.

The method of the external standard was applied to the quantification of pesticides in concentrations ranging from 50.0 to 1000.0 μg/kg. The coefficients of determination were higher than 0.9930 and the linear response range was 50.0 to 1000.0 μg/kg for procymidone and 200.0 to 1000.0 μg/kg for the other pesticides.

The LOD and LOQ were established using the S/N ratio of each analyte. The ratio of 3:1 was the estimated detection limit and the ratio of 10:1 was the limit of quantification. The LOD ranged between 16.0 and 67.0 μg/kg and LOQ between 50.3 and 200.0 μg/kg. Table 1 shows the analytical parameters obtained by the method using the MOF as sorbent for the extraction of pesticides by MSPD pepper matrix and maximums residues limits, as established by the National Sanitary Surveillance Agency of Brazil.

To examine the accuracy and precision of the method, recovery rates and RSD were determined by conducting intraday and interday extractions (Table 2). For intraday precision, three consecutive extractions were carried out for maximum (1000.0 μg/kg) and minimum (250.0 μg/kg) fortification levels and five extractions for the intermediate fortification level (500.0 μg/kg). In the intraday study, the recoveries ranged from 48.4 to 102.8% at the lowest concentration (250.0 μg/kg), with RSD values of 14.8 and 15.7%, and from 52.7–135.0% at the highest concentration (1000.0 μg/kg), with RSD values of 5.2 and 5.4% for procymidone and atrazine, respectively. In the interday study, the recoveries ranged from 55.6 to 106.9% at the concentration level of 500.0 μg/kg, with RSD values of 25.7 and 19.7% for procymidone and atrazine, respectively.

The MOF used as an adsorbent in the MSPD process was, on average, more efficient in extracting polar pesticides (atrazine, $\log k_{ow}$ = 2.7 and pirimicarb, $\log k_{ow}$ = 1.7) [29]. This is due to the predominance of its hydrophilic character, as a result of the presence in the polar sites of the material coming from the oxygen atoms.

We compared the recovery percentages obtained for pirimicarb and procymidone at a fortification level of 500.0 μg/kg with published values by Barreto [25]. We noted that the analyte interaction with the matrix influenced the process of sorption, even when we used MOF as sorbent. On a lettuce matrix, the recovery percentages were 95.0 and 105.0% for pirimicarb and procymidone respectively, whereas with the pepper matrix, the percentages were 105.6 and 52.7% respectively. We noticed that the recovery obtained for pirimicarb agreed with previously published data. For procymidone, however, our conditions were less efficient. Taking into consideration the elution solvent employed in this work and the lipophilic character of procymidone, we observed that the use of acetonitrile improved elution of this pesticide, compared to the dichloromethane used in this work. Thus, this method was deemed not appropriate for procymidone.

When we compared our results with the data obtained by Liu et al. [30] for the pesticides atrazine, pirimicarb, procymidone, and bifenthrin in peppers, using octadecyl silane with the QuEChERS method, we verified that percentages obtained in our work were compatible with those published, demonstrating that the performance of MOF was similar to the performance of the commercial material.

3.3 | Analysis of real samples

We applied the proposed method in the analysis of real samples from six different markets of the city of Aracaju, state

TABLE 1 Analytical characteristics of the proposed method from pepper matrix using the MOF as sorbent and maximums residues limits

Pesticide (t_r, min)	Equation	R^2	Linearity (μg/kg)	LOD (μg/kg)	LOQ (μg/kg)	MRL[a] (μg/kg)
Clofentezine (6.37)	125.3x − 22717	0.9950	200.0–1000.0	67.0	200.0	-
Atrazine (11.79)	654.0x − 11167	0.9948	200.0–1000.0	67.0	200.0	-
Pirimicarb (12.58)	316.9x − 54103	0.9970	200.0–1000.0	67.0	200.0	1000
Procymidone (15.10)	73.5x + 63938	0.9930	50.0–1000.0	16.0	50.0	-
Flumetralin (15.57)	711.7x − 10025	0.9940	200.0–1000.0	67.0	200.0	-
Bromuconazole (20.01)	364x − 62292	0.9992	200.0–1000.0	67.0	200.0	500
Bifenthrin (20.13)	1601x − 25489	0.9986	200.0–1000.0	67.0	200.0	-
Fenbuconazole (24.84)	3612x − 59656	0.9978	200.0–1000.0	67.0	200.0	-

[a]MRL, maximum residue limit.

of Sergipe (Brazil). These samples were produced using conventional agriculture techniques. In a first step, a fast screening was given to each sample using the optimized conditions, to identify those containing pesticides. In a second step, the samples identified as containing pesticide residues were reanalyzed in three replicates, to confirm and quantify the pesticides detected in the previous screening. Procymidone and fenbuconazole were detected in all samples, at concentrations

TABLE 2 Average % recoveries (%RSD) of fortified pesticides in pepper using MSPD method with GC-MS analysis

		Intraday[a]		Interday[b]	
Pesticide	Fortification levels (μg/kg)	Mean Recovery (%)	RSD (%)	Mean Recovery (%)	RSD (%)
Clofentezine	250.0	56.4	13.5	-	-
	500.0*	68.9	10.2	59.7	15.1
	1000.0	73.0	8.6	-	-
Atrazine	250.0	102.8	15.7	-	-
	500.0*	123.3	20.8	106.9	19.7
	1000.0	135.0	5.4	-	-
Pirimicarb	250.0	96.9	16.7	-	-
	500.0*	105.6	43.6	93.6	19.8
	1000.0	133.7	8.0	-	-
Procymidone	250.0	48.4	14,8	-	-
	500.0*	57.4	12,5	55.6	25.7
	1000.0	52.7	5.2	-	-
Flumetralin	250.0	72.0	17.7	-	-
	500.0*	75.2	12.9	70.6	15.2
	1000.0	89.8	6.9	-	-
Bromuconazole	250.0	86.4	22.4	-	-
	500.0*	115.0	16.7	88.7	17.4
	1000.0	121.9	6.7	-	-
Bifenthrin	250.0	64.3	9.6	-	-
	500.0*	88.7	6.3	82.9	13.5
	1000.0	93.2	6.3	-	-
Fenbuconazole	250.0	61.8	21.4	-	-
	500.0*	71.0	14.3	78.4	17.8
	1000.0	90.1	14.3	-	-

[a]$n = 3$.
[b]$n = 9$ in triplicates for three days.
*$n = 5$.

below the LOQ. Flumetralin and atrazine residues were found in two samples and clofentezine and bifenthrin in one sample at concentrations below the quantitation limit. For procymidone, the results were not deemed to be reliable because the recoveries were lower than 60%.

4 | CONCLUDING REMARKS

The MOF $[(La_{0.9}Sm_{0.1})_2(DPA)_3(H_2O)_3]_\infty$ was synthetized and characterized. The material was used as sorbent for the development and validation of an analytical method for the multiclass determination of pesticides in pepper by MSPD. The analytical method was developed and validated. The recovery percentages showed that the MOF can be successfully used to analyze atrazine, clofentezine, pirimicarb, flumetralin, bromuconazole, bifenthrin, and fenbuconazole. The real samples analysis detected the presence of residues of the pesticides procymidone, fenbuconazole, flumetralin, clofentezine, atrazine, and bifenthrin. The new solid phase may be useful in screening protocols used by official regulatory laboratories to identify these pesticides in pepper.

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SUPPORTING INFORMATION

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