Extraction of pesticide residues from plant extracts using regenerative MCM41 mesoporous materials

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Abstract. The aim of the current study was to determinate the adsorption degree of pesticide residues on MCM41 mesoporous material from plant extracts usually used in phytotherapeutic treatments. The choice of the material was based on the high adsorption capacity, due to the specific surface area, over 800 m2/g and for the possibility of their regeneration/ reusability capacity. The silica matrix was synthesized starting from tetraethylorthosilicate (TEOS) - the silica source and hexadecyltrimethylammonium bromide (CTAB) - as a template agent, the whole process taking place in continuous flow at room temperature and normal pressure. The material obtained was characterized by microscopy techniques (transmission and scanning electron microscopy TEM and SEM) for determination of pores morphology, by standard method Brunauer-Emmet-Teller for pore size distribution and specific surface area (textural analysis - B.E.T), by Fourier-transform infrared spectroscopy (FTIR) for spectral fingerprint and by dynamic light scattering (DLS) for determination of hydrodynamic diameter of particles. The tests were carried out on extracts performed with organic solvents from some medicinal species (Menthae officinalis, Salvia officinalis, Matricaria chamomilla), using mesoporous material MCM41 for isolation / concentration of pesticide residues. Quantitation of pesticide residues was performed using a gas chromatograph coupled with a triple quadrupole mass spectrometer (GC-MS/MS), for both extracts and MCM41 material.

1. Introduction
The current trend in the treatment of acute and chronic diseases is a return to traditional medicine based on phytotherapy, used as a complementary treatment in conventional medicine [1, 2]. Most often, the patients uses the following preparations of medicinal plants: infusions, tinctures, macerates and decoctions [3, 4]. Due to the increasing demand for medicinal plants and preparations thereof, the shift to cultivation in conventional agricultural systems requiring protective treatments is inevitable [5, 6]. For economic and productivity reasons, an entire industry focused on getting chemicals, especially pesticides, to combat pests has been developed. Among the pesticides used in the world (synthetic and natural) the most toxic (carcinogenic, mutagenic, teratogenic, etc.) and which have a high persistence/remanence in soil, water and foodstuffs are synthetic pesticides from organochlorine and...
organophosphorus classes [7-10]. In addition, they also have a significant bioconcentration rate at the organ level, especially in adipose tissue.

Organochlorine compounds are known for their high toxicity, slow degradation and bioaccumulation. Even though many pesticides in this class have been banned in developed countries, they are identified in the most unexpected places and products, sometimes in high concentrations [8].

In order to control the use of pesticides, the monitoring plans of residues have been developed at European level (European Food Safety Authority - EFSA), with the continuous development of extraction and quantitation methods. In the production of extracts, there is a considerable risk that the pesticides will be transferred from plants to the final extract [11]. Consequently, the most appropriate route would be to apply decontamination / purification procedures to extracts. Recent research shows that adsorbent materials seem to be an efficient solution in this regard [12, 20, 21]. In this category there is an increased interest for the mesoporous materials, especially MCM41, because of their high specific surface area ($S_{SA} > 800 \text{m}^2/\text{g}$) and high pore volume ($> 0.5 \text{cm}^3/\text{g}$). One of the most used methods of mesoporous materials synthesis is the sol-gel method. Variations such as silica source, template agent, synthesis temperature, reaction medium and pH can lead to materials with different morphologies and properties [13-15]. Due to the free -OH groups, the polarity of the material surface can be modified by functionalization processes to create and/or increase affinity for the target compounds [16-18, 22].

The purpose of this paper is to develop a decontamination method (eliminate pesticides residues) and its use at tinctures obtained from 3 species of medicinal herbs: Menthae officinalis, Salvia officinalis, Matricaria chamomilla. The strategy is to use a mesoporous material based on silica type MCM41 functionalized with trimethylchlorosylane (TMCS). Grafting the -Si(CH$_3$)$_3$ groups to the free -OH groups leads to the modification of the MCM41 polarity, allowing selective extraction of nonpolar compounds.

Quantification of pesticides was performed using a gas chromatographic system coupled with a triple quadrupole mass spectrometer (GC-MS/MS).

2. Materials and methods

2.1. Materials & Equipment

2.1.1. Materials. For MCM-41 synthesis and functionalization were used the following reagents:
- Tetraethyl orthosilicate (TEOS) - 98% purity, Sigma- Aldrich;
- Hexadecyltrimethylammonium bromide (CTAB) - > 99% purity, Sigma- Aldrich;
- Sodium hydroxide - > 98% purity, Sigma- Aldrich;
- Acetic acid - 100% purity, Sigma- Aldrich;
- Ammonium hydroxide - puriss. p.a. 25% NH3 basis, Honeywell Fluka;
- Ethyl alcohol - > 99% purity, Honeywell Fluka;
- Trimethylchlorosilane (TMCS) - > 99% purity, Fluka AG, Buch SG;
- Dichloromethane - > 99% purity, Carlo Erba.

For determination of pesticides residues content we used:
- Pesticide standard (high purity > 99%, aldrin, alfa-BHC, beta-BHC, delta-BHC, gamma-BHC, cis-chlordane, trans-chlordane, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, heptachlor epoxide, methoxychlor, purchased from LGC standards)
- Acetonitrile HPLC purity for extraction, anhydrous magnesium sulphate (purity > 99.9%) with desiccant role, crystalline sodium chloride (purity > 99.9%), PSA (primary-secondary amine) SPE Bulk Sorbent for dispersion clean-up, active carbon Supelco code 57210 U, QuEChERS (quick, easy, cheap, effective, rugged, and safe) sample clean-up kits for different volume and compositions, depending on concentration of pigments, 50 ml conical centrifuge tubes;
- Medicinal herbs (dry): Menthae officinalis, Salvia officinalis, Matricaria chamomilla.
2.1.2. Equipment. Thermo Scientific TRACE 1310 gas chromatograph coupled with a triple quadrupole mass spectrometer (TSQ 8000 EVO); analytical balance Mettler Toledo Excellence XS 205 DU/M, Hettich laboratory centrifuge, angular tip shaker Multi-Bio RS-24, water purification system Millipore Integral 3, semi-automatic pipettes Thermo; ball mill Retsch PM100, scanning electron microscopy dual SEM-FIB SEM equipment Lyra3XMU (TESCAN), JEOL 2100 transmission electron microscope (HR-TEM), Malvern Nano ZS Zetasizer instrument (DLS), Micromeritics apparatus ASAP 2420 (B.E.T.), Thermo Scientific Nicolet 6700 FT-IR / NIR.

2.2. Methods
2.2.1. MCM41 Synthesis. The synthesis of the mesoporous material took place at room temperature by the sol-gel method using CTAB as template, TEOS as silica source, in alkaline medium (sodium hydroxide) and ammonium hydroxide as catalyst. The final reaction and the precipitation phenomena occurs when the alkaline solution interacts with the acid solution (acetic acid). The material obtained is subsequently subjected to a series of washing procedures using a specific amount of ethyl alcohol, in order to reduce the surfactant template amount. The dried product was then calcinated for 24 h at 550°C to remove the traces of the surfactant template and organic compounds; the calcinated product was classified as MCM41.

2.2.2. The functionalization process of MCM41 with TMCS. In a 500 mL round bottom flask, were homogenized MCM41, dichloromethane and TMCS; the functionalization reaction took place under the action of microwaves, at reflux, in 4 rounds of 20 minutes each, with a 15 minute break between them (Figure 1).

**Figure 1.** The microwave irradiation reflux system.

The purpose of functionalization process is to graft \(-\text{Si(CH}_3\text{)}_3\) groups to the free \(-\text{OH}\) groups on the surface of the mesoporous material, leading to a decrease in polarity [19, 23, 24].

2.2.3. Characterisation MCM41 and MCM41-TMCS. SEM. Surface morphology was determined by using scanning electron microscopy dual SEM-FIB SEM equipment Lyra3XMU (TESCAN) with an acceleration voltage of 200 V 30 kV with SE resolution: 1.2 nm at 30 kV in High Vacuum mode.
HRTEM. High-resolution images for the shape and size of the pores were collected by JEOL 2100EM-27102IAU/EM-24511SIOD transmission electron microscope, with an acceleration voltage of 200 kV.

DLS. Hydrodynamic particle diameter measurements were determined by using Malvern Nano ZS Zetasizer instrument. The determination was perform in duplicate, with 0.3% suspensions of MCM41 in ultrapurified water Milli-Q, after sonication, at room temperature, at an angle of 173°. The final report represents the mean value of 5 measurements (each measurement had 14 scans) per sample.

B.E.T. Nitrogen adsorption isotherms was obtained by using Micromeritics instrument ASAP 2420 (USA 2012), at −196°C. The sample was outgassed in a vacuum at 200°C for 1h, before running the experiment. The textural analysis (SSA, pore volume and size) were measured by N₂ adsorption-desorption isotherms. With the help of the Brunauer-Emmett-Teller (B.E.T.) method was calculated SSA.

FT-IR. The FT-IR spectra of samples were recorded with a Smart Multi-Bounce Combo HATR zinc selenide (ZnSe) crystal infrared spectrometer (Thermo Scientific Nicolet 6700 FT-IR/NIR) in the range 4000 to 600 cm⁻¹. Approximately 40-50 mg of sample were placed on the surface of the ZnSe crystal and measured directly, with a gently pressing. Were perfomed 64 aquisition per sample, at 8 cm⁻¹ spectral resolution.

FT-IR spectroscopy was used to see if the -Si(CH₃)₃ groups were grafted on the free –OH groups.

2.2.4. The process of obtaining the fortified tinctures of medicinal plants. A multistandard mixture solutions of individual pesticide standards, prepared in HPLC-grade acetonitrile (from Sigma-Aldrich) at certain concentrations (1µg/mL for each individual pesticide standards) was used. This solution has been used for the fortification of 8g of each medicinal species: Menthae officinalis, Salvia officinalis, Matricaria chamomilla.

After concentration of pesticide residues in the selected species, we determined the pesticide residues content to verify the homogeneity of the fortification process.

The tinctures were prepared according to GMP standards (Good Manufacturing Practice). Samples were analyzed together with quality control tinctures for each matrix (uncontaminated with the selected pesticides).

2.2.5. Extraction and quantitation method for pesticide residues from plant product. Extraction and cleanup have been made by using the QuEChERS method: to 1 g of homogenized plant product (weighed into 50 ml centrifuge tube), add 10 ml acetonitrile as extraction solvent. Shake vigorously for 1 minute. 0.5 g NaCl is added for partition of the pesticide residues from plant product to the solvent and 1 g of MgSO₄ to retain traces of water from the extract. Shake manually for 1 min, then use an angular shaker for an additional 10 min. Centrifuge at 8000 rpm for 5 min. From the resulting supernatant, 1 ml was cleaned-up using special kits containing activated charcoal, PSA and magnesium sulphate. Centrifuge at 10000 rpm for 5 min. The resulting supernatant was filtered using 0.22µm PTFE filters directly in autosampler vials and analyzed (samples were analyzed in duplicate). Quantitation of pesticides residues was performed through a validated screening method (single point calibration), according to Sanete guidelines- SANTE/11813/2017 [25].

The data were analyzed using the Chromeleon v. 7.2.7 software, Chromatography data system with the "Cobra" automatic integration algorithm.

2.2.6. Extraction and quantitation method for pesticide residues from tinctures. From the resulting extractive solutions, 2 ml extract of each were analyzed (transferred in a 50 ml tube), by adding 8 ml of acetonitrile; vigourous agitagation for 15-30 seconds to ensure proper mixing. NaCl (0.5 g) and MgSO₄ (2 g) were added in the resulting solution, shake immediately by short and energetic movements, in order to avoid the formation of magnesium sulphate agglomerates; continue shaking with the angular shaker for another 10 minutes, followed by centrifugation at 8000 rpm for 5 min. 1 mL of the resulting supernatant is transfered to purification kits. The mixture was vortexed for 5 minutes followed by 5 minutes centrifugation at 9000 rpm. The resulting supernatant was filtered using 0.22µm PTFE filters directly in autosampler vials and analyzed (samples were analyzed in duplicate).
For the decontamination process of tinctures, MCM41 functionalized with TMCS was used, by adding 0.2 g MCM41 at 2 mL of tincture. The decontamination process took place for 60 minutes under vigorous stirring, followed by centrifugation at 8000 rpm for 15 minutes; the resulting supernatant was analyzed following the steps described above.

Quantitation of sample results were performed by fortification of quality control tinctures with known concentrations of pesticides and analyzed following the same method of preparation.

The data were analyzed using the Chromeleon v. 7.2.7 software, Chromatography data system with the "Cobra" automatic integration algorithm.

2.2.7. Chromatographic system working parameters for determining pesticide content. The parameters of the acquisition method are as follows:
- Column: TG-5SilMS, 30 m, $\varnothing = 0.25$ mm, film = 0.25 μm, 5% phenylmethylpolysiloxane (Thermo Scientific P/N: 26096-1420);
- Flow rate: 1.2 ml / min;
- Transfer temperature: 280°C, ionisation source: 250°C, programe ramp oven temperature:
  - $T_{\text{initial}}= 40^\circ\text{C}$ 1.5 min
  - 25°C/ min→90 °C  1.5 min
  - 25°C/ min→180 °C  0 min
  - 5°C/ min→280 °C  0 min
  - 10°C/ min→300 °C  5 min
- Injector: PTV (programmed temperature vaporisation) Solvent Vent with temperature ramps according as follows:
  - $T_{\text{initial}}= 50^\circ\text{C}$  0.2 min  flow= 10 ml/ min
  - 14,5 °C/sec→89 °C  time=0.05 min  flow= 50 ml/ min
  - 2,5 °C/sec→300 °C time=2 min
  - 14,5 °C/sec→330 °C time=5 min flow= 50 ml/ min
  - Split flow= 50 ml/ min
  - Splitles time= 1 min
  - Purge flow= 5 ml/ min
  - Gas saver flow= 5 ml/ min
  - Gas saver time= 6 min

Acquisition Mod: Selective reaction monitoring SRM- fragmentation of ion produced in precursor ion (Table1).

### Table 1. Selective reaction monitoring-SRM.

| Pesticide  | Retention | Q1 mass | Q3 mass | Collision |
|------------|-----------|---------|---------|-----------|
| BHC, Alpha | 11.85     | 182.8   | 146.7   | 14        |
|            | 11.85     | 218.8   | 146.6   | 20        |
| BHC, Beta  | 12.36     | 180.9   | 145     | 14        |
|            | 12.36     | 218.7   | 146.6   | 18        |
| BHC, gamma | 12.57     | 180.9   | 145     | 14        |
|            | 12.57     | 218.7   | 143     | 8         |
| BHC, delta | 13.13     | 182.8   | 146.7   | 14        |
|            | 13.13     | 218.8   | 146.5   | 20        |
| Heptachlor | 14.25     | 99.8    | 65      | 12        |
|            | 14.25     | 271.8   | 236.9   | 12        |
Table 1. Selective reaction monitoring-SRM.

| Pesticide              | Retention | Q1 mass | Q 3 mass | Collision |
|------------------------|-----------|---------|----------|-----------|
| Aldrin                 | 15.21     | 262.7   | 191      | 30        |
|                        | 15.21     | 262.7   | 192.9    | 32        |
|                        | 15.21     | 330     | 298.9    | 10        |
|                        | 16.31     | 262.9   | 192.9    | 30        |
| Heptachlor epoxide     | 16.31     | 352.8   | 262.9    | 16        |
|                        | 16.31     | 354.7   | 264.9    | 12        |
|                        | 16.99     | 271.7   | 236.8    | 12        |
| Chlordane trans        | 16.99     | 372.7   | 263.7    | 20        |
|                        | 16.99     | 374.7   | 265.9    | 22        |
|                        | 17.37     | 372.8   | 265.8    | 20        |
| Chlordane cis          | 17.37     | 374.7   | 265.8    | 20        |
|                        | 17.37     | 376.6   | 268      | 20        |
|                        | 17.39     | 240.6   | 205.9    | 14        |
| Endosulfan peak 1      | 17.39     | 271.88  | 236.89   | 15        |
|                        | 17.39     | 273.88  | 238.89   | 15        |
|                        | 18.08     | 246     | 176.1    | 28        |
| DDE p, p               | 18.08     | 317.8   | 246      | 20        |
|                        | 18.08     | 317.8   | 248      | 18        |
|                        | 18.25     | 262.8   | 190.9    | 30        |
| Dieldrin               | 18.25     | 262.8   | 192.9    | 30        |
|                        | 18.25     | 276.92  | 240.92   | 10        |
|                        | 18.84     | 245     | 173      | 22        |
| Endrin                 | 18.84     | 262.8   | 192.9    | 30        |
|                        | 18.84     | 280.8   | 245.3    | 8         |
|                        | 19.22     | 194.7   | 125      | 22        |
| Endosulfan peak 2      | 19.22     | 207     | 172      | 15        |
|                        | 19.22     | 239     | 204      | 15        |
|                        | 19.41     | 235     | 165.1    | 20        |
| DDD p,p                | 19.41     | 235     | 199      | 14        |
|                        | 19.41     | 236.8   | 165      | 20        |
|                        | 20.44     | 238.7   | 203.9    | 12        |
| Endosulfan sulfate     | 20.44     | 271.7   | 234.9    | 12        |
|                        | 20.44     | 271.7   | 236.8    | 12        |
|                        | 20.63     | 235     | 165.1    | 22        |
| DDT p,p                | 20.63     | 235     | 199.5    | 10        |
|                        | 20.63     | 236.8   | 165      | 22        |
| Methoxychlor           | 22.409    | 227.1   | 141.1    | 32        |
|                        | 22.409    | 227.1   | 169.1    | 22        |
|                        | 22.409    | 227.1   | 212.1    | 12        |

3. Results and discussions
From the surface morphology analysis, for the synthesized MCM41 sample, a homogeneous structure is observed with uniform spherical formations in form and size, with intergranular spaces and a narrow distribution of particle size. At the 2000-10000 nm scale, a porous ultrastructure, given by the mesoporic structure (better emphasized in the TEM analysis), can be seen (Figure 2).

In the images obtained by HR-TEM we observe a homogeneous morphology with uniform spherical formations with a particle average diameter of 800-1000 nm, a hexagonal ultrastructure with a good mesoporous ordering with a diameter of 2-6 nm, properties that include the material obtained in the MCM41 category (Figure 3).

The DLS results indicate that the particle average size of MCM41 is 2373 nm; the analyse was made in duplicate. The polydispersity index of MCM41 has the value PdI= 0.436 (the average of both analyzes) which shows that MCM41 material has a good particle size distribution (Figure 4).
The hydrodynamic diameter obtained by DLS analysis correlates with particle sizes measured by the HR-TEM technique, with the mention that solvation shell - a phenomenon occurring at particle dispersion in the solvent, gives an apparently larger size than the real particle size.

Figure 2. SEM analysis of synthesized mesoporous material MCM41 (magnification 5000x - 20000x).

Figure 3. TEM analysis of synthesized mesoporous material MCM41.

Figure 4. The hydrodynamic particle dimension result.
B.E.T. results for synthesized MCM41: according to the textural analysis, the obtained material has a specific surface area of more than 800 m$^2$/g (1112 m$^2$/g), the diameter of the mesopores ranging between 2-6 nm (2.7 nm), confirmed by the HR-TEM analysis, pore volume: 0.76 cm$^3$/g and the isothermal adsorption / desorption of nitrogen is of Category IV, allowing it to be classified as MCM41 (Figure 5).

![Figure 5. The isotherm of synthesized MCM41.](image)

Figure 6 highlights by FTIR measurement, the steps taken in the synthesis and purification of mesoporous material MCM41 with observation of the gradual removal of the template agent, spectrally seen by decreasing of the intensity of the CTAB specific bands: ~2920 cm$^{-1}$, ~2850 cm$^{-1}$, ~1550 cm$^{-1}$, ~1480 cm$^{-1}$, ~1410 cm$^{-1}$, ~980 cm$^{-1}$, obtaining the spectral fingerprint of MCM41 characterized by the spectral bands: ~1230 cm$^{-1}$, ~1060 cm$^{-1}$, ~806 cm$^{-1}$ (this three spectral bands are assigned to internal and external asymmetric Si-O stretching modes), ~1620 cm$^{-1}$ (-Si-OH deformational vibrations of adsorbed molecules).

![Figure 6. FT-IR spectra of synthesized MCM41, washed MCM41 and calcinated MCM41.](image)
From the silylated spectrum (Figure 7), the presence of new peaks indicates that there is interaction between TMCS and silanol group on wall surface of MCM41: -Si-C (~847 cm\(^{-1}\)), -Si-(CH\(_3\))\(_3\) (~760 cm\(^{-1}\)) and the –C-H (stretching vibration) (~2900 cm\(^{-1}\), ~2960 cm\(^{-1}\)). In the same time it can be observed the disappearance of the spectral band of -Si-OH (~1620 cm\(^{-1}\)).

![Figure 7. FT-IR spectrum of functionalization process of MCM41 with TMCS.](image)

Regarding the GC-MS / MS analysis of the selected medicinal plants, can be observed a homogenous fortification of the plants samples (1μg/mL on 8g plant, equivalent of a theoretical concentration of 0,125 μg/g plant), with a percentage recovery of pesticides, ranging from 76 to 124% (Table 2).

### Table 2. The GC-MS/MS results from the plants samples with percentage recovery of pesticides.

| Pesticide residues | Theoretical concentration (μg/kg) | Menthae officinalis |  | Salvia officinalis |  | Matricaria chamomile |  |
|--------------------|----------------------------------|---------------------|---|-------------------|---|---------------------|---|
|                    |                                  | Amount (μg/kg) | Recovery (%) | Amount (μg/kg) | Recovery (%) | Amount (μg/kg) | Recovery (%) |
| BHC-alfa           | 125                              | 133,9            | 107,12       | 133,5          | 106,8        | 95,7              | 76,56         |
| BHC-beta           |                                  | 140,6            | 112,48       | 111,9          | 89,52        | 149,7             | 119,76        |
| BHC- gamma         |                                  | 134,3            | 107,44       | 120,1          | 96,08        | 104,6             | 83,68         |
| BHC- delta         |                                  | 134,7            | 107,76       | 119,9          | 95,92        | 106,7             | 85,36         |
| Heptachlor         |                                  | 129,8            | 103,84       | 116,5          | 93,2         | 112,7             | 90,16         |
| Aldrin             |                                  | 133              | 106,4        | 106,6          | 85,28        | 109,2             | 87,36         |
| Heptachlor epoxide | 125                              | 144,9            | 115,92       | 115,7          | 92,56        | 123,7             | 98,96         |
| Chlordane trans    |                                  | 136,2            | 108,96       | 110,4          | 88,32        | 118,7             | 94,96         |
| Chlordane cis      |                                  | 148,6            | 118,88       | 122,2          | 97,76        | 130,9             | 104,72        |
| Endosulfan I       |                                  | 138,7            | 110,96       | 107,1          | 85,68        | 115,6             | 92,48         |
| Endosulfan II      |                                  | 155,3            | 124,24       | 118,5          | 94,8         | 131,2             | 104,96        |
Table 2. The GC-MS/MS results from the plants samples with percentage recovery of pesticides.

| Pesticide residues | Theoretical concentration (µg/kg) | Menthae officinalis | Salvia officinalis | Matricaria chamomile |
|--------------------|----------------------------------|---------------------|-------------------|---------------------|
|                    | Amount (µg/kg) | Recovery (%) | Amount (µg/kg) | Recovery (%) | Amount (µg/kg) | Recovery (%) |
| Endosulfan sulfate | 142.4          | 113.92      | 118.5           | 94.8        | 110.9          | 88.72        |
| p,p-DDE            | 144.1          | 115.28      | 122.5           | 98          | 120.1          | 96.08        |
| p,p-DDD            | 148.1          | 118.48      | 120.1           | 96.08       | 128.9          | 103.12       |
| p,p-DDT            | 145.4          | 116.32      | 110.8           | 88.64       | 112.1          | 89.68        |
| Dieldrin           | 137.6          | 110.08      | 117.1           | 93.68       | 127            | 101.6        |
| Endrin             | 133.1          | 106.48      | 112             | 89.6        | 121.1          | 96.88        |
| Methoxychlor       | 147.1          | 117.68      | 110.3           | 88.24       | 116            | 92.8         |

If the amount of pesticide analyzed in medicinal herbs diffuses in extracts 100%, it should theoretically be found a concentration of 0.0125 µg/mL tincture. (0.025µg/2mL in our case), but practically we obtained a transfer rate ranging from 57% to 98% (Table3).

Table 3. Amount of pesticides diffused from medicinal herbs to hydroalcoholic extracts.

| Pesticide residues | Theoretical concentration (µg/kg) | Menthae officinalis | Salvia officinalis | Matricaria chamomile |
|--------------------|----------------------------------|---------------------|-------------------|---------------------|
|                    | Amount (µg/kg) | Transfer rate (%) | Amount (µg/kg) | Transfer rate (%) | Amount (µg/kg) | Transfer rate (%) |
| BHC-alfa           | 20.9            | 83.6              | 19.8             | 79.2               | 19.9          | 79.6           |
| BHC-beta           | 18.1            | 72.4              | 14.3             | 57.2               | 19.3          | 77.2           |
| BHC- gamma         | 23.7            | 94.8              | 20.3             | 81.2               | 23.3          | 93.2           |
| BHC- delta         | 19.8            | 79.2              | 18.9             | 75.6               | 20.6          | 82.4           |
| Heptachlor         | 19.3            | 77.2              | 16.7             | 66.8               | 18.2          | 72.8           |
| Aldrin             | 16.4            | 65.6              | 18.6             | 74.4               | 18.6          | 74.4           |
| Heptachlor epoxide | 20.1            | 80.4              | 20.9             | 83.6               | 20.1          | 80.4           |
| Chlordane trans    | 18.7            | 74.8              | 18               | 72                 | 19.1          | 76.4           |
| Chlordane cis      | 25              | 90                | 18.3             | 73.2               | 18.1          | 72.4           |
| Endosulfan I       | 17.9            | 71.6              | 15.3             | 61.2               | 18.2          | 72.8           |
| Endosulfan II      | 17.3            | 69.2              | 17.4             | 69.6               | 20            | 80            |
| Endosulfan sulfate | 20.2            | 80.8              | 19.6             | 78.4               | 19.4          | 77.6           |
| p,p-DDE            | 15.8            | 63.2              | 15.6             | 62.4               | 15.7          | 62.8           |
| p,p-DDD            | 17.7            | 70.8              | 15.3             | 61.2               | 17.3          | 69.2           |
| p,p-DDT            | 16.5            | 66                | 14.3             | 57.2               | 15.9          | 63.6           |
| Dieldrin           | 19.6            | 78.4              | 23.1             | 92.4               | 24.5          | 98             |
| Endrin             | 20.6            | 82.4              | 23.3             | 93.2               | 17.8          | 71.2           |
| Methoxychlor       | 20.9            | 83.6              | 18.9             | 75.6               | 21.6          | 86.4           |

During decontamination of the tinctures with MCM41-TMCS, only a part of the amount of the pesticide is removed. The lowest transfer rates were recorded for BHC-beta with a transfer rate of less than 40% (39.8%, 36.4% and 36.8%) for each type of tincture, while the best transfer rates were
observed for the p, p-DDE pesticide with a transfer rate of more than 60% (61.4%, 62.2% and 64.3%) (Table 4).

| Pesticide residues | Menthae officinalis | Salvia officinalis | Matricaria chamomille |
|--------------------|---------------------|-------------------|-----------------------|
|                    | Amount of pesticides in tincture (µg/kg) | Amount of pesticides after decontamination (µg/kg) | Transfer rate in MCM41-TMCS (%) | Amount of pesticides in tincture (µg/kg) | Amount of pesticides after decontamination (µg/kg) | Transfer rate in MCM41-TMCS (%) | Amount of pesticides in tincture (µg/kg) | Amount of pesticides after decontamination (µg/kg) | Transfer rate in MCM41-TMCS (%) |
| BHC-alfa           | 20.9                | 10.7              | 48.8                  | 19.8                | 10               | 49.5                  | 19.9                | 9.7               | 51.3                  |
| BHC-beta          | 18.1                | 10.9              | 39.8                  | 14.3                | 9.1              | 36.4                  | 19.3                | 12.2              | 36.8                  |
| BHC-gamma         | 23.7                | 10.9              | 54.0                  | 20.3                | 9.4              | 53.7                  | 23.3                | 11.7              | 49.8                  |
| BHC-delta         | 19.8                | 12.4              | 37.4                  | 18.9                | 10.7             | 43.4                  | 20.6                | 10.5              | 49.0                  |
| Heptachlor or     | 19.3                | 7.8               | 59.6                  | 16.7                | 8.7              | 47.9                  | 18.2                | 7.2               | 60.4                  |
| Aldrin            | 16.4                | 7.2               | 56.1                  | 18.6                | 8.7              | 53.2                  | 18.6                | 7.8               | 58.1                  |
| Heptachlor or     | 20.1                | 9.2               | 54.2                  | 20.9                | 9.9              | 52.6                  | 20.1                | 8.8               | 56.2                  |
| Chlor dane trans  | 18.7                | 9.3               | 50.3                  | 18                  | 7.9              | 56.1                  | 19.1                | 9.1               | 52.4                  |
| Chlor dane cis    | 22.5                | 7.5               | 66.7                  | 18.3                | 9.5              | 48.1                  | 18.1                | 8.7               | 51.9                  |
| Endosulfan I      | 17.9                | 8.8               | 50.8                  | 15.3                | 6.9              | 54.9                  | 18.2                | 7.4               | 59.3                  |
| Endosulfan II     | 17.3                | 9.4               | 45.7                  | 17.4                | 11.7             | 32.8                  | 20                  | 11.2              | 44.0                  |
| Endosulfan sulfur | 20.2                | 12.4              | 38.6                  | 19.6                | 13.5             | 31.1                  | 19.4                | 11.3              | 41.8                  |
| p,p-DDE           | 15.8                | 6.1               | 61.4                  | 15.6                | 5.9              | 62.2                  | 15.7                | 5.6               | 64.3                  |
| p,p-DDT           | 17.7                | 8.5               | 52.0                  | 15.3                | 7               | 54.2                  | 17.3                | 8.2               | 52.6                  |
| p,p-DDT           | 16.5                | 6.8               | 58.8                  | 14.3                | 5.5             | 61.5                  | 15.9                | 6                | 62.3                  |
| Dieldrin          | 19.6                | 10.9              | 44.4                  | 23.1                | 9.5             | 58.9                  | 24.5                | 10.2              | 58.4                  |
| Endrin            | 20.6                | 9.6               | 53.4                  | 23.3                | 11.5            | 50.6                  | 17.8                | 7.4               | 58.4                  |
| Methoxy chlor     | 20.9                | 9.4               | 55.0                  | 18.9                | 10.2            | 46.0                  | 21.6                | 9.3               | 56.9                  |

4. Conclusions

It was synthesized a mesoporous material based on silica, which could be classified as MCM41 type materials taking into consideration morphological and textural characterization.

The MCM41 material was subjected to functionalization process with TMCS, resulting in an increase in hydrophobicity, property that allows the extraction of non-polar compounds.

After the decontamination step, the functionalized mesoporous material can be recovered quantitatively and subjected to a calcination process, being possible the reuse of the regenerated material to other decontamination processes.

After exposure of hydroalcoholic extracts to MCM41-TMCS, there was a decrease in the amount of pesticides (35-70%), evidence that the decontamination process took place.

The results suggest the possibility to continue the study in order to evaluate the influence of matrix composition on pesticide extraction efficiency on the MCM41-TMCS support, considering that most active principles have the same polarity with contaminants. As a consequence, it is also considering the modification of the functionalizing agent to increase the selectivity of the pesticides residue retention.
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