Supplementary materials

Application of a Pillared-Layer Zn-Triazolate Metal-Organic Framework in the Dispersive Miniaturized Solid-Phase Extraction of Personal Care Products from Wastewater Samples

Providencia González-Hernández [1], Ana B. Lago [2], Jorge Pasán [2], Catalina Ruiz-Pérez [2], Juan H. Ayala [1], Ana M. Afonso [1] and Verónica Pino [1,3,*]

[1] Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), La Laguna, Tenerife 38206, Spain

[2] Laboratorio de Rayos X y Materiales Moleculares (MATMOL), Departamento de Física, Universidad de La Laguna (ULL), La Laguna, Tenerife 38206, Spain

[3] University Institute of Tropical Diseases and Public Health, Universidad de La Laguna (ULL), La Laguna, Tenerife 38206, Spain

Table of contents

Figure S1. XRD patterns of (**A**) activated CIM-81, (**B**) CIM-81 without activation, and (**C**) theoretical XRD pattern.

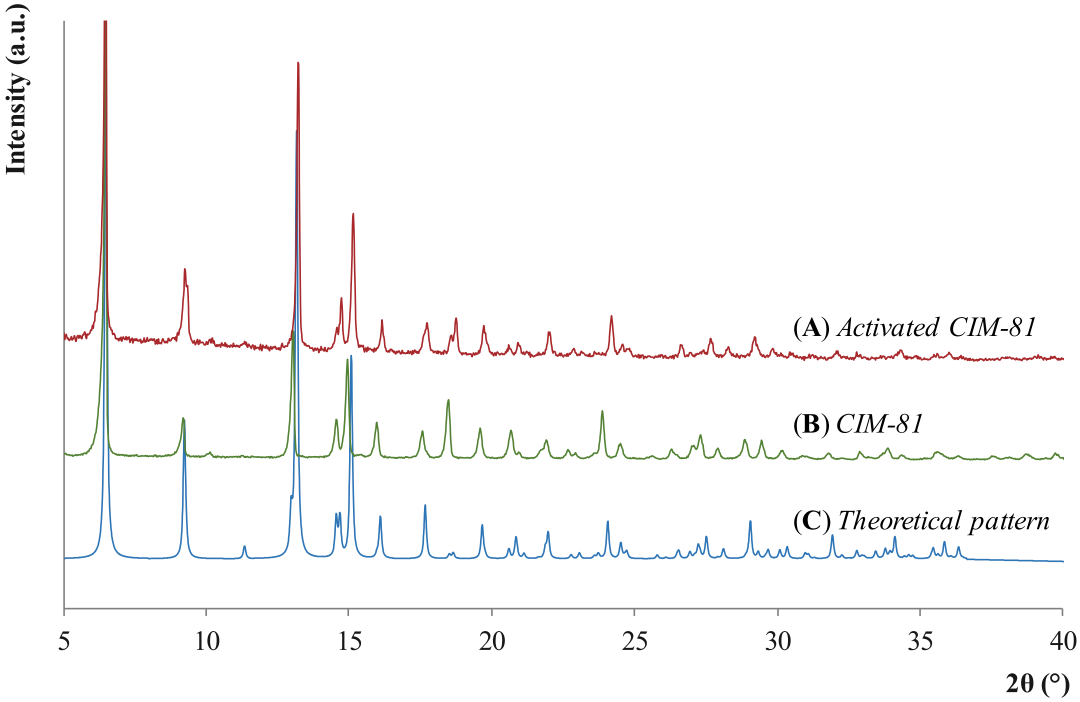


Figure S2. A view of the crystal structure of CIM-81, obtained of ref. (36), along the crystallographic a (left) and c axes (right).

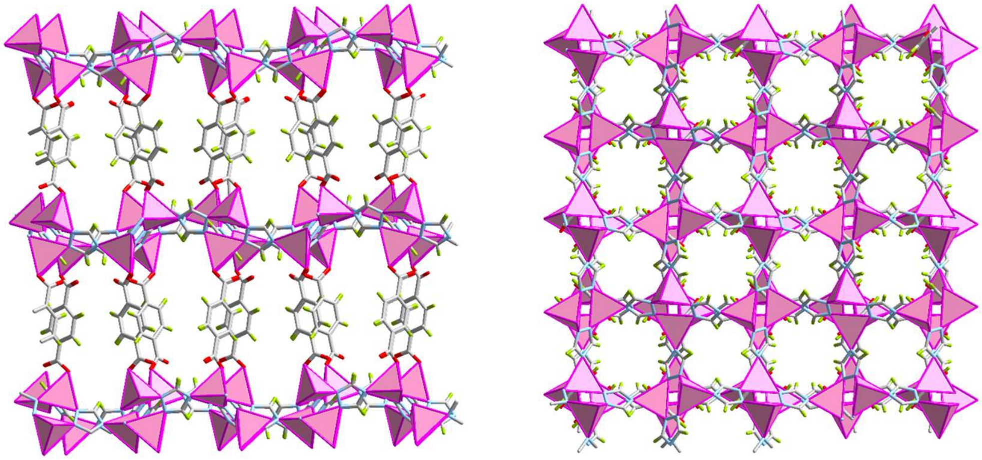


Figure S3. FT-IR spectra of CIM-81 before the solvent-exchange procedure (red line), and after the activation procedure (green line).

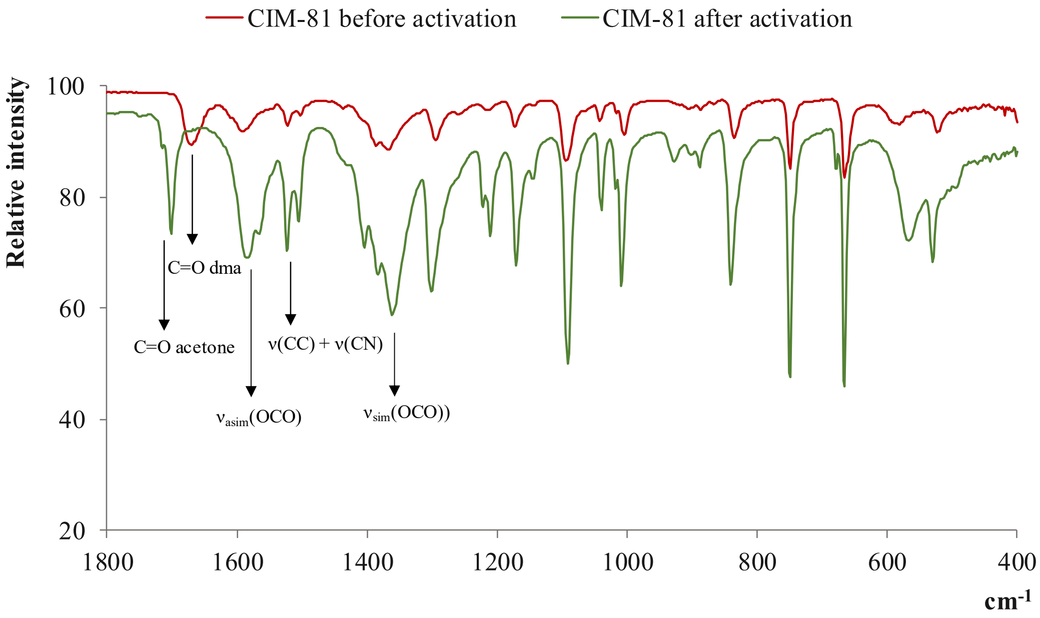


Figure S4. Thermogravimetric curve of CIM-81.

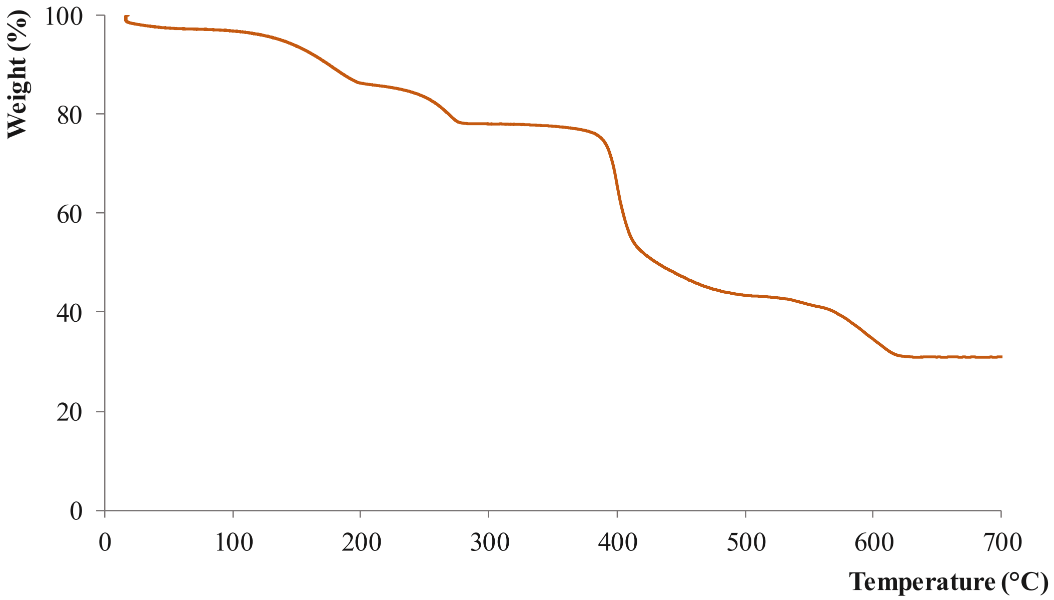


Figure S5. Nitrogen adsorption isotherm of CIM-81 at 77K.

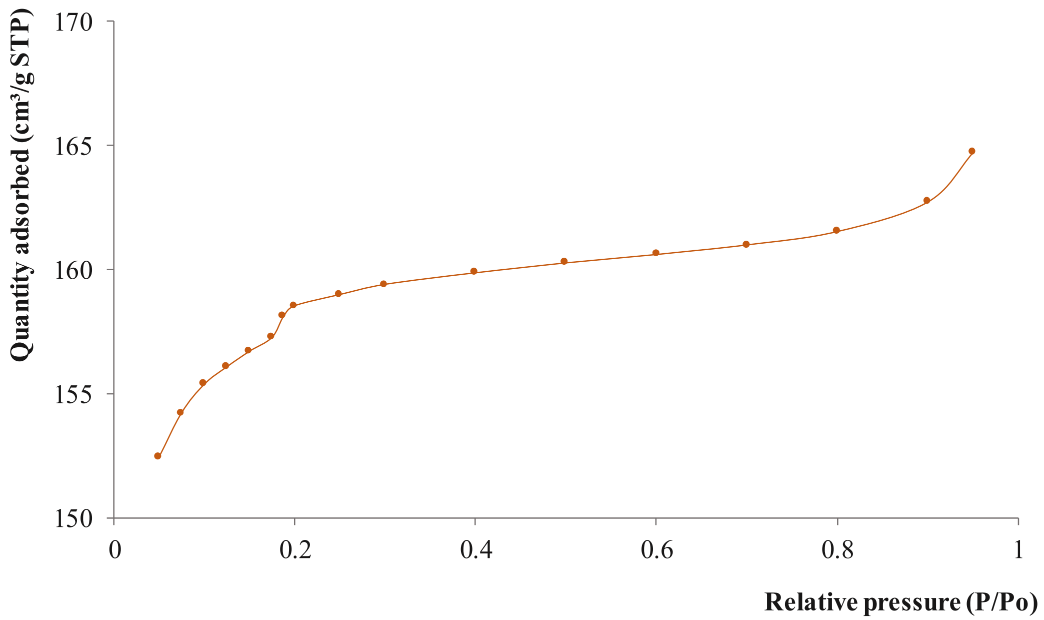


Figure S6. Evaluation of several organic solvents as possible desorption solvents for PCPs trapped by the MOF CIM-81 in D-µSPE-UHPLC-UV. Specific conditions of the experiments described in the text.

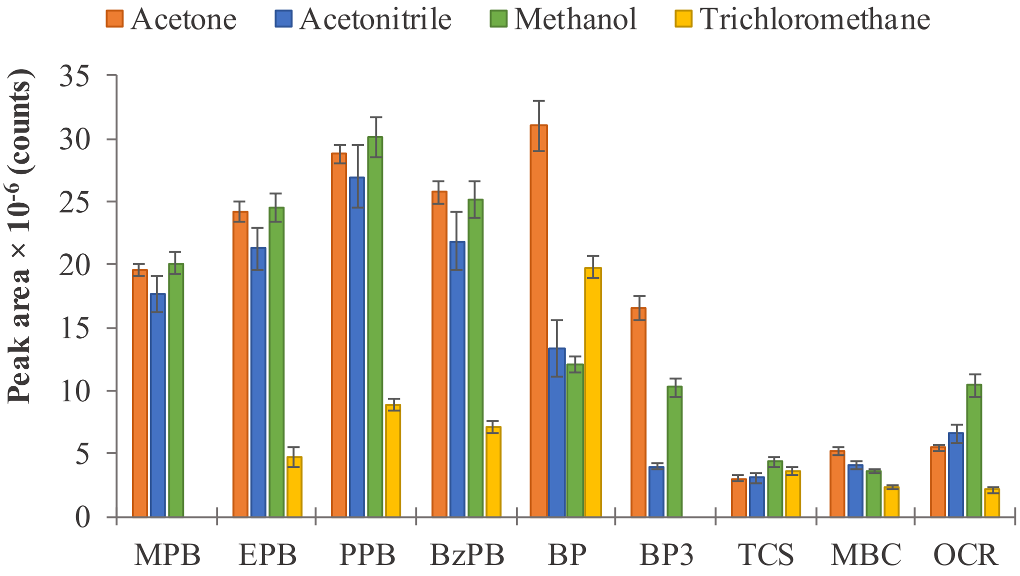
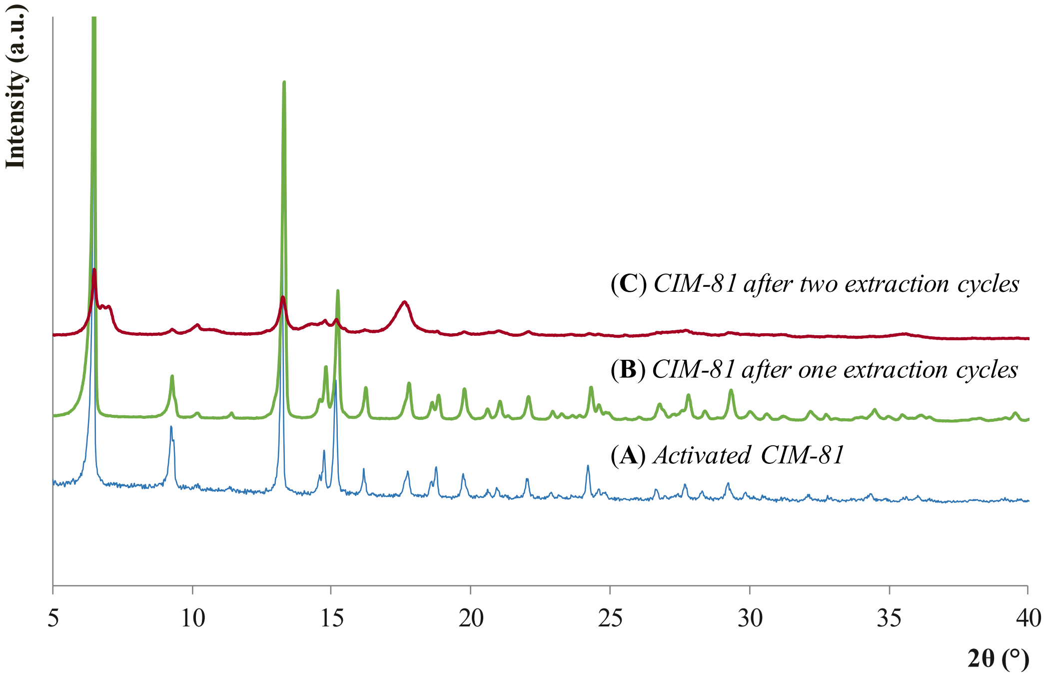


Figure S7. XRD patterns of (**A**) activated CIM-81, (**B**) CIM-81 after one extraction cycles, and (**C**) CIM-81 after two extraction cycles.



Scheme

Reagents to synthetize MOFs

Copper(II) nitrate hemipentahydrate (98%), zirconium chloride (98%), aluminum(III) nitrate nonahydrate (98%), benzene-1,3,5-tricarboxylic acid (95%) (H_3btc), and benzene-1,4-dicarboxilic acid (H_2bdc) (98%), were purchased from Sigma-Aldrich. Absolute ethanol and methanol were supplied by Panreac (Barcelona, Spain). Dimethylformamide was acquired to Merck KGaA (Darmstadt, Germany) and hydrochloric acid (37%) to Honeywell (Seelze, Germany).

Synthesis of MOFs

All MOFs were synthetized by a solvothermal method.

HKUST-1, formulated as $[Cu_3(btc)_2(H_2O)_3]$, was synthetized following our previous study [22]. An aqueous solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1.255 g, 5.4 mmol) was added dropwise to 15 mL of an ethanol solution of H_3btc (0.630 g, 3 mmol), followed by stirring for 20 min. The mixture was transferred to the solvothermal reactor (45 mL), and then heated to 110 ºC during 24 hours. The obtained blue crystals were filtered by gravity, washed with ethanol, and dried at room temperature. HKUST-1 was heated at 150 ºC for 24 hours in order to remove guest molecules from the pores of the crystalline structure. The yield was 90%.

MIL-53(Al), formulated as [AlOH(bdc)], was synthetized following our previous study [22]. $Al(NO_3) \cdot 9H_2O$ (1300 mg, 3.5 mmol) and benzene-1,4-dicarboxylic acid (288 mg, 1.7 mmol) were dissolved in 15 mL of ultrapure water. The mixture was transferred to the solvothermal reactor (23 mL), and heated to 220 ºC during 72 hours. The obtained crystals were filtered by gravity, washed with ultrapure water, and dried at 50 ºC for 24 hours. MIL-53(Al) was heated at 400 ºC for 16 hours in order to remove guest molecules from the pores of the crystalline structure. The yield was 45%.

UiO-66, formulated as [$Zr_6O_4(OH)_4(bdc)_6$], was synthetized following our previous study [19]. $ZrCl_4$ (233 mg, 1 mmol) and benzene-1,4-dicarboxylic acid (246 mg, 1.5 mmol) was dissolved in 15 mL of dimethylformamide and 1 mL of concentrated HCl. The mixture was transferred to the solvothermal reactor (45 mL), and heated to 150 ºC during 24 hours. The obtained colorless crystals were filtered by gravity, and washed with dimethylformamide and methanol. UiO-66 was then heated at 150 ºC for 24 hours in order to remove guest molecules from the pores of the crystalline structure. The yield was 95%.

Characterization of MOFs

All MOFs were characterized by XRD, IR and N_2 adsorption measurements, showing that the synthesized compounds are in agreement with the previously reported data.

Table S1. Several quality analytical parameters of the UHPLC-UV method.

PCP	**t_R ± SD (n = 60)**	**Working range (µg·mL^{-1})**	**(Slope ± S_b[a]) × 10^{-4}**	**R^2 [b]**	**$S_{y/x}$[c] × 10^{-3}**	**LOD[d] (µg·L^{-1})**	**LOQ[e] (µg·L^{-1})**	***RSD[f] (%) intra-day / inter-day* (0.15 µg·mL^{-1})**	***RSD[f] (%) intra-day / inter-day* (0.45 µg·mL^{-1})**
MPB	1.68 ± 0.03	0.01 – 1.00	390 ± 5	0.9990	5.2	3.0	10	1.6 / 4.8	3.9 / 3.3
EPB	2.10 ± 0.03	0.01 – 1.00	343 ± 5	0.9987	5.1	4.0	13	1.7 / 7.8	4.9 /3.5
PPB	2.84 ± 0.04	0.01 – 1.00	306 ± 5	0.9984	5.0	2.0	6.7	1.7 / 2.3	4.3 / 4.2
BzPB	3.98 ± 0.05	0.01 – 1.00	270 ± 4	0.9989	3.7	1.0	3.3	1.6 / 3.3	4.2 / 4.1
BP	5.27 ± 0.04	0.10 – 1.00	389 ± 6	0.9985	5.0	1.0	3.3	0.22 / 3.2	3.9 / 3.4
BP3	6.26 ± 0.04	0.10 – 1.00	258 ± 5	0.9973	4.4	5.0	17	5.9 / 7.1	1.7 / 3.6
TCS	7.65 ± 0.06	0.10 – 1.00	63 ± 2	0.9930	1.7	5.0	17	3.5 / 8.2	5.6 / 6.7
MBC	9.30 ± 0.05	0.10 – 1.00	347 ± 7	0.9942	5.7	2.0	6.7	2.8 / 5.9	3.6 / 4.9
OCR	11.07 ± 0.05	0.10 – 1.00	119 ± 3	0.9937	2.6	3.0	10	7.0 / 10	2.7 / 6.1

[a] Standard deviation associated to the slope

[b] Determination coefficient (8 levels of calibration)

[c] Error of the estimate (standard deviation of the residuals)

[d] Limit of detection calculated (and experimentally verified) as the concentration that provided a signal 3 times the noise

[e] Limit of quantification calculated (and experimentally verified) as the concentration that provided a signal 10 times the noise

[f] Relative standard deviation for 3 experiments in the same day (intra-day) and for 9 experiments in three non-consecutive days (inter-day)

Table S2. Experiments of the Doehlert design obtained for the coded matrix of two factors with a hexagonal spatial distribution.

Experiment	**Factor 1 (**$t_{desorption}$)		**Factor 2 (**$mL_{methanol}$)	
	C1	**X1 (min)**	**C2**	**X2 (in mL)**
1	0	4	0	1.1
2	0.5	5.5	-0.866	0.2
3	-0.5	2.5	0.866	2.0
4	-0.5	2.5	-0.866	0.2
5	0.5	5.5	0.866	2.0
6	-1	1	0	1.1
7	1	7	0	1.1

C_1 and C_2 are the coded values for the 5 and 3 levels, respectively
X_1 and X_2 are the real values of each factor in the experiment

Table S3. Results obtained from the analysis of the Doehlert design, where Factor 1 is the desorption time (in minutes) and Factor 2 is the volume of the desorption solvent (methanol, in mL).

PCP	**Optimum value of Factor 1**	**Optimum value of Factor 2**	**Constant**	**Coefficients**				
				A	**B**	**AA**	**AB**	**BB**
MPB	3.7	1.257	15298	32786	238	-3989	-2.81	-0.09
EPB	3.6	1.294	37150	18089	196	-1546	-5.35	-0.07
PPB	7.0	0.770	105717	1631	203	2641	-18.33	-0.05
BzPB	7.0	0.882	18644	39917	316	-1166	-24.50	-0.08
BP	7.0	2.000	53538	1282	-2	-836	6.18	-0.01
BP3	4.0	1.322	-8710	27698	208	-3013	-2.67	-0.07
TCS	4.2	1.174	-125176	114136	341	-13583	-0.25	-0.14
MBC	4.4	1.438	-24881	13616	299	-9099	46.76	-0.18
OCR	1.0	2.000	793672	-330717	-509	51200	-57.72	0.39

Table S4. Precision and recovery studies for the reuse of the MOF CIM-81 as sorbent in the D-µSPE-UHPLC-UV method proposed.

PCP	**Conc. level: 15 µg·L^{-1}**			**Conc. level: 45 µg·L^{-1}**		
	RSD*[a] *(%)	***RR*[b] *(%)***	***E_F*[c]**	***RSD*[a] *(%)***	***RR*[b] *(%)***	***E_F*[c]**
MPB	8.4	110	8.5	8.2	102	6.3
EPB	12	115	6.5	13	74.9	4.6
PPB	14	115	8.7	11	75.5	5.9
BzPB	14	113	6.8	6.4	86.7	5.5
BP	15	106	3.5	4.3	92.6	2.9
BP3	4.8	91.5	5.1	4.9	75.6	4.1
TCS	6.1	129	14	9.3	86.0	6.9
MBC	11	94.7	2.7	7.6	81.9	2.6
OCR	14	82.9	26	9.2	91.4	27

[a] Intra-day relative standard deviation (n = 3)
[b] Relative recovery
[c] Enrichment factor