## Automated growth of metal-organic framework coatings on

## flow-through functional supports

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## **Electronic Supplementary Information**

#### Experimental

#### Materials

Methanol ( $\geq$  99.8%), dichloromethane ( $\geq$  99.9%), hexane ( $\geq$  96%), Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (98%), 2-methylimidazole (99%), were purchased from Sigma-Aldrich and used as received. A 2000 µg/mL EPA phthalates esters mix analytical standard in hexane was purchased from Supelco, containing dimethyl phthalate (DMP); diethyl phthalate (DEP); di-n-butyl phthalate (DBP); Bis(2-ethylhexyl) phthalate (DEHP); butyl benzyl phthalate (BBP); di-*n*-octyl phthalate (DNOP). 3M Empore high performance extraction disks (47 mm diameter) with chelating or cation exchange moieties were used as functional supports.

#### Flow-based instrumentation

The instrumental set-up for the flow-based preparation of porous coatings was composed by a computer controlled bi-directional syringe pump and multiposition valve (**Fig. 1**). The syringe pump is a 5000-step automatic burette (model Bu4) from Crison (Alella, Barcelona, Spain, http://www.crison.es). The automatic burette was equipped with a 5-mL glass syringe from Hamilton (Bonaduz, Switzerland, http://www.hamiltoncompany.com). The syringe pump contained a three-way solenoid head valve (SV, N-Research, West Caldwell, NJ, <u>http://www.nresearch.com</u>), where the syringe was connected.

The three-way valve had a common port (COM), a normally open (NO) and a normally closed (NC) auxiliary ports. The COM port was connected to the head of the syringe. The NO port was used to load or dispense fluids to the carrier reservoir, which contained the washing solvent. The NC port connected the syringe to the central port of the multiposition valve (MPV), and enabled the injection or aspiration of fluids from or towards the flow network. An eight port multiposition valve (MPV, Sciware SL, Spain, <u>http://www.sciware-sl.com</u>) was used for the sequential selection of the metallic and organic precursor for the preparation of the hybrid supports, and the sample and eluent loading for the automated preconcentration of phthalate esters. All tubing used was made of polytetrafluoroethylene 0.8 mm i.d. including a 3 mL holding coil to load the different solutions from the multiposition valve without reaching the syringe content.

The extraction device<sup>1</sup> was a two-piece poly(methyl methacrylate) cylinder with a 1 mm i.d. channel and an internal cavity to hold a 10 mm diameter round portion of membrane

(obtained from the 47 mm membrane using a circular cutter). The methodologies for the support coating and extraction of pollutants controlling simultaneously the syringe pump and the multiposition valve were developed using the software package AutoAnalysis 5.0 (Sciware SL) based on dynamic link libraries.

#### Synthesis of ZIF-8 crystals

Pure ZIF-8 crystals were synthesized from a 2-methylimidazole (Hmim) solution prepared by dissolving 810.6 mg (9.874 mmol) in 50 mL of methanol and another one prepared by dissolving 734.4 mg (2.469 mmol) of Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in 50 mL of the same solvent. Both solutions were mixed, transferred to a closed vessel and heated in a microwave oven at 373 K for 4 h. ZIF-8 crystals were separated by centrifugation, washed three times with fresh methanol and dried at room temperature.

#### Characterization

Powder X-ray diffraction data were collected using CuK $\alpha$  ( $\lambda$  = 1.54056 Å) radiation on a Siemens D5000 diffractometer. Thermogravimetric analysis (TGA) was carried out in an air atmosphere using a TA Instruments SDT 2960 simultaneous DSC-TGA. The morphology and elemental distribution of the original and modified supports was analyzed by a scanning electron microscope (SEM) Hitachi S-3400N, equipped with a Bruker AXS Xflash 4010 for the acquisition of energy dispersive X-ray spectra. Fourier transform infrared spectroscopy of the samples were performed on a infrared

microscope HYPERION 2000 equipped with an MCT cryodetector, working at 3 cm<sup>-1</sup> resolution.

#### Glassware and reagent control for phthalate analysis

To avoid undesirable phthalate contamination, all glassware was rinsed with acetone, dichloromethane and acetone again, followed by drying at 573 K for at least 4 h and then stored covered with aluminium foil. All reagents were checked in advance for potential phthalate contamination. A stock standard solution of the six phthalate esters with a concentration of 10 mg/L each, was prepared by appropriate dilution of the commercial mixture of the phtalate esters in hexane. Stock intermediate solutions were prepared by stepwise dilution in water. Working solutions were prepared daily, immediately prior their use. All standard solutions were kept in the dark at 253 K. Working solutions were stored at 277 K in the refrigerator.

#### Gas chromatography – mass spectrometry analysis (GC-MS)

The GC-MS analysis of phthalate esters was performed using a Hewlett–Packard (Agilent Technologies, Palo Alto, CA, USA) HP 7890 series gas chromatography system, with a split/splitless injector and a HP 5973C mass selective detector system. The mass spectrometer was operated in the electron impact (EI) mode (70 eV using helium (99.999%) as the carrier gas at a flow rate of 1 mL/min. Analytes were separated on a 30 m × 0.25 mm i.d. × 0.25 mm film thickness DB5 (methyl 5% phenylpolysiloxane) gas chromatography column (Agilent Technologies, Palo Alto, CA, USA).

The GC oven temperature method started at 323 K (holding this temperature for 1 min). The temperature was increased at 303 K/min up to 553 K, and then up to 583 K (holding for 4 min) at 288 K/min. The injected sample volume was 1  $\mu$ L. The sample was injected in pulsed splitless mode at a constant temperature of 563 K; pressure pulse: 35 psi and a pulsed time of 0.5 min, using an ultra-inert commercial liner packed with glass wool (Agilent). Later on, the inlet pressure is automatically increased up to a constant flow of 1 mL/min.

The El ion source, the quadrupole mass analyzer, and the interface temperature were maintained at 503, 423, and 553 K, respectively. The MS was tuned to *m*/*z* 69, 219, and 502 for the El corresponding to perfluorotributylamine. The MS was operated in the total ion current mode, scanning from *m*/*z* 50 to 550 for identification purposes. In order to obtain the highest possible sensitivity, the acquisition was performed in the selected ion monitoring mode. The quantitative ion for each analyte was set as follows: DMP: 163,194; DEP: 149, 177, 222; DBP: 144, 167, 205, 223; BBP: 91, 149, 206; DEHP: 149, 167, 279 and DNOP: 149, 167, 261, 279.

The enrichment factors were calculated from the ratio of the peak areas obtained from the GC-MS chromatograms with and without extraction.

#### Flow-based methodology the preparation of coatings

The general approach for the preparation of an standard ZIF-8 coating was detailed in **Table 1**. The flow through support containing the unmodified membrane was placed in the port 1 of the MPV. The glass syringe contained the same solvent used to prepare the metal and the organic precursor solutions, which were located in ports 2

and 3 of the MPV. Initially, the membrane was swollen in the pure solvent contained in the syringe. The metal solution was loaded into the holding coil, and was subsequentially pumped through the support followed by an excess of washing solvent, in order to remove the non-retained metals. The last step was repeated using the organic ligand precursor solution. The syringe was completely refilled with solvent, finishing one cycle. The final extent of the coating was defined on depending of the number of applied cycles.

#### Method for the preconcentration of organic pollutants

A second method was developed (Table S2) with the flow system in order to study the performance of the developed coatings as sorbents for the extraction of environmental pollutants from water. Initially, the solvent reservoir was changed by one containing Milli-Q water and the content of the syringe and the lines of the system was automatically replaced with water. The sample was placed in port 6 of the multiposition valve. Sample was loaded and subsequentially injected through the membrane, achieving the extraction of the targets on the support. An excess of water was used to wash the extraction support before elution. Next step was the aspiration of air into the holding coil (using port 7) and its injection through the membrane, in order to remove residual water from the flow-through support. Air was again loaded into the system followed which mixture of organic by the eluent, was а solvents (methanol/dichloromethane, 25/75, v/v). The introduction of air in this step was required in order to avoid contact between the water carrier and the immiscible organic eluent. The eluent was injected through the support and collected in a vial due to an auxilliary valve, avoiding the introduction of water into the vial. The volume of the eluate was adjusted by evaporation under a gentle stream of nitrogen, before GC-MS analysis.

Table	S1.	General	operational	procedure	for	the	automated	preparation	of	porous
coating	s on	functiona	al supports.							

Step	Operation	Volume	Flow rate	Position	Position
		mL	mL/min	SV	MPV
1	Swell the support with the washing solvent.	2.0	1.0	NC	1
2	Load metal precursor solution	0.5	5.0	NC	2
3	Inject through the support the metal precursor solution followed by the washing solvent.	1.2	0.5	NC	1
4	Load organic ligand solution	0.5	5.0	NC	3
5	Inject through the support the organic ligand solution followed by the washing solvent.	1.2	0.5	NC	1
6	Refill the syringe with solvent	-	15	NO	1
7	Repeat steps 2-6 <i>n</i> times*				

\*n is equal to the number of cycles.

# **Table S2.** General operational procedure for the automated extraction of phthalate esters prior GC-MS.

Step	Operation	Volume	Flow rate	Position	Position
		mL	mL/min	SV	MPV
1	Swell the support with the washing solvent.	2.0	1.0	NC	1
2	Load sample containing phthalate esters	2.0	5.0	NC	4
3	Inject sample through the extraction support	3.0	1.0	NC	1
4	Load air	2.0	5.0	NC	5
5	Inject air to remove water from the support	1.5	1.0	NC	1
6	Load organic solvent (eluent)	0.5	2.0	NC	6
7	Inject eluent and excess of air through the extraction support*	0.7	1.0	NC	1
8	Wash the support with water	2.0	1.0	NC	1
9	Refill the syringe with solvent	-	15	NO	1

\*An additional solenoid valve is activated in this step to collect the eluate in a vial for GC-MS analysis.



**Fig. S1** FT-IR spectra of pure ZIF-8 crystals and of the support before and after 190 cycles of coating with Zn(II) and HMIM solutions. Precursors: 100 mmol/L Zn(II) and 50 mmol/L HMIM. Solvent, methanol.



**Fig. S2** XRD patterns of the support before and after 25, 50 and 150 cycles of coating with diluted Zn(II) and Hmim solutions. Precursors: 2 mmol/L Zn(II) and 2 mmol/L HMIM. Solvent, methanol.



**Fig. S3** XRD patterns of a sulfonic acid functionalized support before and after 75 cycles of of coating with Zn(II) and HMIM solutions. Precursors: 100 mmol/L Zn(II) and 50 mmol/L HMIM. Solvent, methanol.



**Fig. S4** TGA of an iminodiacetic acid support before, and after 25, 75 and 190 cycles of of coating with Zn(II) and HMIM solutions. Precursor solutions: 100 mmol/L Zn(II) and 50 mmol/L HMIM. Solvent, methanol.



We measured Zn(II) loading of the support by performing thermogravimetric analysis of the polymeric support (with and without a ZIF-8 coating) in air. The weight of the ZnO residue at 873 K gradually increased with the number of growth cycles of ZIF-8, being 1.2, 3.7 and 6.7 the values of the ZnO mass percentage of the residue after 25, 75 and 150 cycles, respectively.



**Fig. S5** High magnification SEM image of the surface of a support covered by a film of ZIF-8.



Fig. S6 Chemical structures of the phthalate esters used for their extraction at trace levels.

### References

1 http://www.sciware-sl.com/products/preconcentration-systems-optrodes/item/75-prec-disk