Incorporating PET-MIL-101(Fe) within cellulose acetate membrane for thin film microextraction of neonicotinoid insecticides in water

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Supplementary information and data

ST 1 Instrumentation

A portable pH/EC/TDS metre (HI 9811-5, HANNA Instruments, Woonsocket, RI, USA) was employed to modify the pH of the solutions. A scanning electron microscope (SEM) (TESCAN VEGA 3 XMU, LMH instrument, Brno, Czech Republic) coupled with energy dispersive spectroscopy (EDS) was used to examine the morphology and elemental content of the nanomaterials and membranes. Initially, the samples were carbon-coated using the Agar Turbo Carbon coater. This was done to increase the conductivity of the material. The transmission electron microscope (TEM Jeol JEM-2100F) was used in conjunction with a charge-coupled device (CCD) to explore the morphological properties of the materials. The TEM images of the samples were obtained at 200 kV. The NIs were quantified using an Agilent HPLC 1200 Infinity series fitted with a diode array detector (DAD) (Agilent Technologies, Waldron, Germany). The Agilent Zorbax Eclipse Plus C18 column was used for analyte separation. The temperature of the column was fixed to 25 °C. For the separation of analytes in isocratic mode at 1 mL/min, an acetonitrile/water mobile phase (30:70) was used, and the DAD was set to record the chromatograms at 260 nm.2.3 Synthesis of the materials

ST 2 Synthesis of the materials

ST 2.1 Preparation of terephthalic acid (BDC) from waste plastic bottles

In a beaker, 10 g of PET flakes were mixed with 10 mL of ethylene glycol (EG) and 100 mL of H_2O. The mixture was then placed in a 250 mL Teflon-lined autoclave, which was heated to 210 °C and held there for 8 hours. After the reaction, the product was centrifuged, washed twice with ethanol, and dried for 24 hours at 100 °C [1].

ST 2.2 Preparation of MIL-101 (Fe)

PET-MIL-101(Fe) was synthesised according to Duan et al. [2]. The mixture of 0.675 g of $FeCl_3 \cdot 6H_2O$ and 0.206 g of H_2BDC was added to 25 mL of DMF and agitated for 30 minutes. The uniform mixture was placed into a 100 mL Teflon autoclave reactor and heated to 110 °C for a day. Centrifugation was used to gather the product. Hot ethanol (60 °C, 3 h) and hot water (60 °C, 1 h) were used to wash the product to eliminate the DMF and excess H_2BDC. After that, the material was dried at 150 °C for 12 hours in a vacuum oven.

ST 2.3 Fabrication of CA-PET-MIL-101(Fe) membrane

The CA-PET-MIL-101(Fe) membranes were prepared using the phase inversion method [3]. The casting solution consisted of DMF, PVP, and CA. Different amounts of the composite are shown in Table S1. For fabrication of the nanocomposite membranes, CA-PET-MIL-101(Fe) nanocomposite was added to DMF and sonicated for 1 hour to obtain a homogenous solution. Then, CA and PVP were added to the PET-MIL-101(Fe) /DMF mixture and stirred for 24 hours. The solution was then kept at room temperature for 24 hours without stirring until there were no bubbles. The prepared solution was cast onto a glass plate using a casting knife, and then the glass was immersed in a coagulation bath (deionised water) for about a minute. Lastly, the prepared membranes were soaked in deionised water for 24 hours, after which the membranes were dried at room temperature.

ST 3 Method development

ST 3.1 Thin film- solid phase microextraction (TF-SPME) procedure

Small pieces of the CA-PET-MIL-101(Fe) membranes (0.03 g) were immersed in a 5 mL sample solution containing selected neonicotinoid insecticides (at 50 μg/L), and the solution was sonicated for 5-40 min. The analytes were adsorbed onto the surface of the membranes, and the liquid phase was discarded. Subsequently, the analytes were eluted from the membranes using 200-1200 µL of ethanol, and then it was sonicated for 5-20 min to desorb the analytes. The resulting solution was then filtered using 0.22 µm microfilters and analysed using HPLC-DAD.

Table S1: CA-PET-MIL-101(Fe) membrane compositions

Membrane ID	**CA wt.%**	**DMF wt.%**	**PVP wt.%**	**PET-MIL-101(Fe) wt.%**
M0	15	82	3	0
M1	15	81.8	3	0.2
M2	15	81.6	3	0.4
M3	15	81.5	3	0.6

Table S2 Central composite design matrix and respective average analytical response (%R), n = 3

Std run	pH	ST (min)	EV(uL)	ELT (min)	TM (%R)	CTN (%R)	ICD (%R)	TCD %R)
1	3	10	300	5	54.9	51.1	57.3	58.8
2	3	10	300	20	67.8	65.5	67.7	66.2
3	3	10	1200	5	73.7	79.2	74.9	73.9
4	3	10	1200	20	82.9	82.1	79.4	83.2
5	3	40	300	5	56.1	56.1	55.4	52.9
6	3	40	300	20	56.6	53.5	57.1	58.7
7	3	40	1200	5	73.8	67.9	74.6	77.7
8	3	40	1200	20	92.0	86.9	86.9	87.3
9	9	10	300	5	74.7	72.3	73.5	75.2
10	9	10	300	20	75.0	76.4	75.3	75.9
11	9	10	1200	5	87.2	93.5	90.3	93.8
12	9	10	1200	20	92.2	94.4	94.7	95.1
13	9	40	300	5	72.0	69.4	71.9	73.1
14	9	40	300	20	79.9	77.9	79.0	76.5
15	9	40	1200	5	95.1	96.6	93.7	95.1
16	9	40	1200	20	97.8	95.8	98.5	97.6
17	1.36	25	750	12.5	62.7	65.5	62.3	65.2
18	10.6	25.0	750	12.5	67.5	65.0	70.8	69.9
19	6	1.80	750	12.5	28.8	31.6	29.3	24.4
20	6	48.2	750	12.5	96.4	98.9	97.4	96.6
21	6	25	54.0	12.5	15.6	14.4	12.6	15.1
22	6	25	1446	12.5	98.8	95.1	96.9	99.2
23	6	25	750	0.90	12.0	9.3	11.0	14.8
24	6	25	750	24.1	97.7	98.9	97.4	97.5
25	6	25	750	12.5	98.8	97.6	98.6	98.1
26	6	25	750	12.5	99.3	98.6	97.8	97.7
27	6	25	750	12.5	99.3	97.7	98.4	97.7

Table S3: Estimated pKa values of the analytes

Compound	Key Functional Group	Approximate pKa	Ionization State (pH 7)
Clothianidin	Nitroguanidine	~4.5–5.0	Mostly unionized
Imidacloprid	Nitroguanidine	~11.1 (NH)	Protonated (minor)
Thiacloprid	Cyanoimine	~12.2	Neutral
Thiamethoxam	Nitroguanidine	~−0.6 to 2.0	Neutral

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2. Duan, M.-J. *et al.* A novel catalyst of MIL-101 (Fe) doped with Co and Cu as persulfate activator: synthesis, characterization, and catalytic performance. *Chem. Pap.* **72**, 235–250 (2018).
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