ARTICLE

Development of bimetal-organic frameworks-polypyrrole composite as a novel fiber coating for direct immersion solid phase microextraction in-situ supercritical fluid extraction coupled to gas chromatography for simultaneous determination of furfurals in dates

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Supplementary material

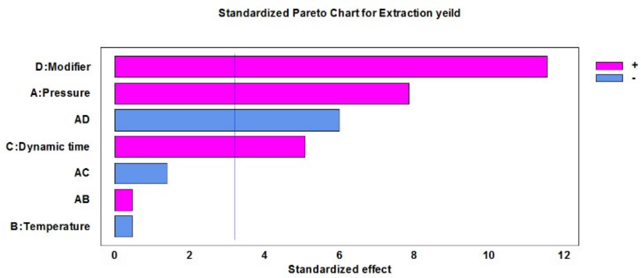

Figure S1. Pareto chart of the main effects obtained from the 2n-1 fractional factorial design for 2-F and 5-HMF

Apparatus

A Suprex (USA) MPS/225 system in SFE mode was utilized for all extractions. Extractions were accomplished using a 3 mL volume stainless steel extraction vessel. A Duraflow manual variable restrictor (Suprex; USA) was applied in the SFE system for collecting the extracted analytes. In order to prevent sample plugging, the restrictor point was warmed electrically.

An Agilent GC system equipped with a split/splitless injector and flame ionization detection system. (GC-FID) (7890A, Palo Alto, USA) was used for this experiment. GC separation was performed using a HP-1NNOWAX capillary column (15 m × 0.25 mm × 0.50μm). The initial temperature of column was 100 ◦C and held for 5 min, increased to 240 ◦C at a rate of 15 ◦C min−1. The injection mode was splitless for 5 min and temperature was set at 250 ◦C. The detector was set at 275 ◦C. Helium (99.999%) was used as the carrier gas at a flow rate of 1.2 mL min-1. The SEM images were obtained by a Mira3 TESCAN (Kohoutovice, Czech Republic). X-ray diffraction (XRD) patterns were obtained by a Philips PW 1729 diffractometer with Cu-K(α) radiation.

Central composite design condition

Table S1 shows the main factors and the levels examined for CCD. The experimental runs were fitted to the following second order polynomial model:

$$Y=\beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{11}X_1^2 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3+\beta_{22}X_2^2 +\beta_{23}X_2X_3 +\beta_{33}X_3^2$$

where X_1, X_2, and X_3 are the independent variables, β_0 is the intercept, β_1, β_2, β_3, β_{12}, β_{13}, β_{23}, β_{11}, β_{22} and β_{33} are the regression coefficients and Y is the response function (ER). Model terms were selected or rejected based on the p-value at a 95% confidence level.

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Table S1: Experimental variables, levels and star points of the central composite design (CCD).

Variable	Key	Level			Star points (α= 1.682)	
		Lower	Central	Upper	-α	+α
Pressure (atm)	A	300	325	350	282.95	367.04
Dynamic extraction time (min)	B	10	15	20	6.59	23.40
Modifier volume (μL)	C	100	150	200	65.91	234.09

The required number of experimental runs can be calculated as ($2^f + 2f + C$), where f is the number of independent variables and C is the number of repetitions of the experiments at the center point. This CCD (α = 1.682) was carried out in 19 randomized runs ($2^3 + (2\times3) + 5$) consisting of a (2^3) factorial design augmented with (2 × 3) star points and 5 central points. The significant factors, their levels and results are provided in Table S2

Table S2: The central composite design (CCD) program and results for SFE-DI- SPME-GC-FID of 2-F and 5-HMF

Run no.	Pressure (atm)	Dynamic time (min)	Modifier volume (μL)	ER%
1	350	10	100	30.3
2	325	15	150	89.5
3	325	15	234.09	63.9
4	325	23.409	150	80
5	282.955	15	150	6.1
6	367.045	15	150	25.2
7	325	15	65.9104	17.1
8	300	10	200	56
9	325	6.59104	150	62
10	325	15	150	89.5
11	325	15	150	89.5
12	300	20	200	57.2
13	350	20	100	51.3
14	350	20	200	87.8
15	325	15	150	89.5

16	325	15	150	89.5
17	350	10	200	40.6
18	300	10	100	14
19	300	20	100	9.8

The normal probability graph and the histogram of residuals indicated that the residuals were normally distributed and that this model successfully described the system under study.

ANOVA was applied to evaluate the data and the Pareto chart in Fig. S2. The ANOVA results demonstrated goodness of fit (R2 = 0.98) and goodness of prediction (adjusted R2 = 0.97). Comparison of models using adjusted R2 is a standard method for determining their fit with multiple linear regression. The adjusted R2 value of 0.97 implies that 97% of the variation associated with the furfural extraction yield can be attributed to the independent variables of pressure, modifier volume and dynamic extraction time.

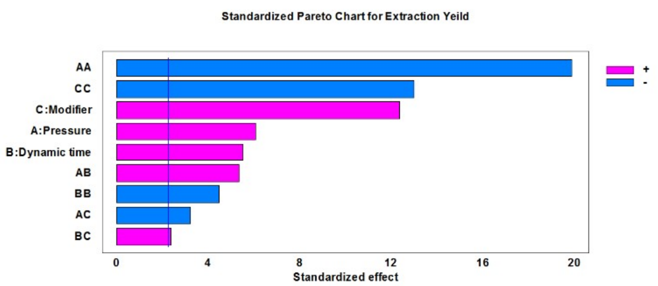


Fig. S2: Pareto chart of the main effects in the central composite design for 2-F and 5-HMF. AA, BB, and CC are the quadratic effects of the pressure, dynamic extraction time and modifier volume, respectively. AB, AC, and BC are the interaction effects between pressure and dynamic extraction time, pressure and modifier volume, and dynamic extraction time and modifier volume, respectively

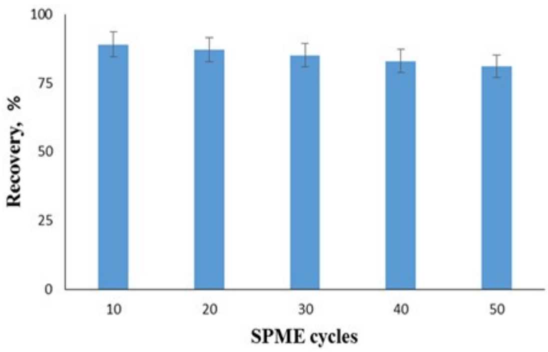
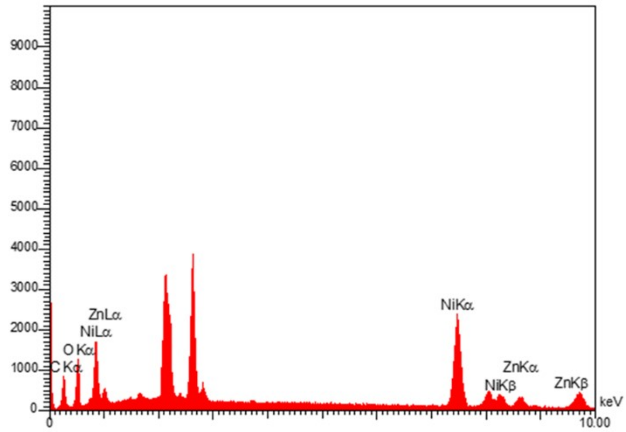
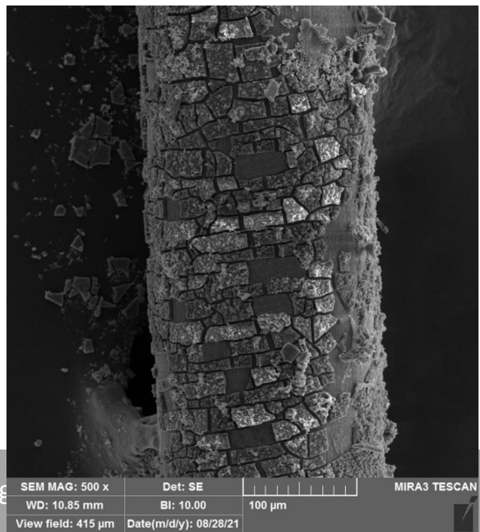


Fig. S3: Reusability of SPME fiber

Fig. S4: The SEM image of fiber after 50th use





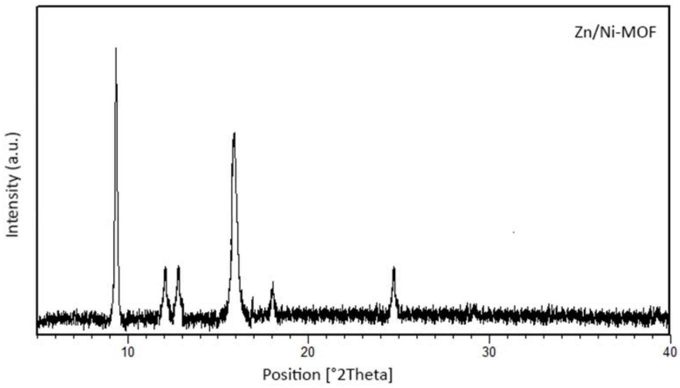


Fig. S6: XRD pattern of the MOF-coated fiber