Electronic Supplementary Information

Dispersive micro-solid phase extraction based on Fe_3O_4@SiO_2@Ti-MOF as a magnetic nanocomposite sorbent for the trace analysis of caffeic acid in the medical extracts of plants and water samples prior to HPLC-UV analysis

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1. Figures

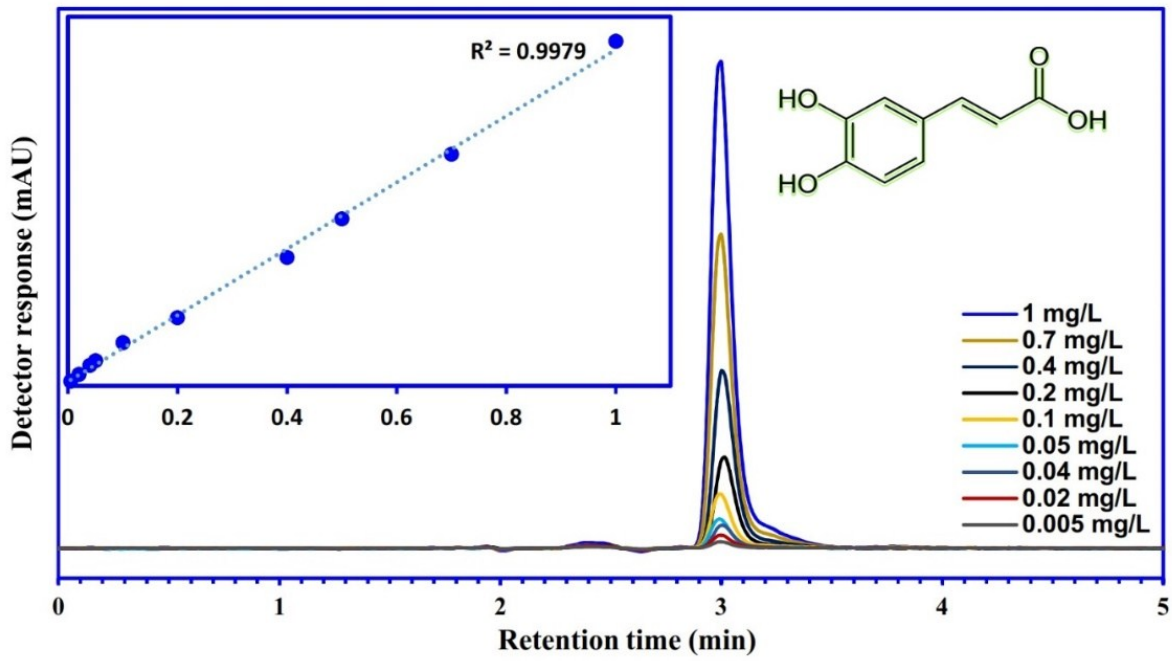

Fig. S1. Calibration curve of caffeic acid at different concentrations and its chemical structure (inset).

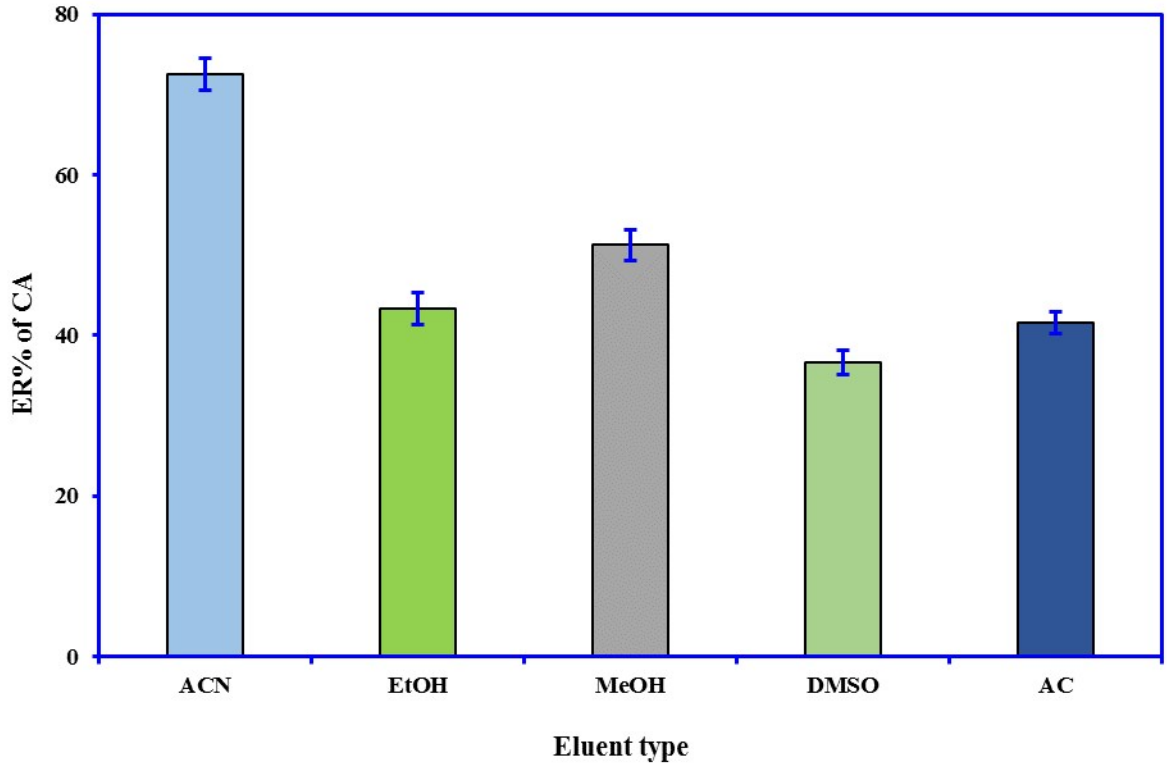

Fig. S2. Effect of different types of desorption (eluent) solvent on the extraction of CA with Fe_3O_4@SiO_2@Ti-MOF nanocomposites (conditions: initial pH value of 6.0 for sample solution, magnetic nano-sorbent mass of 12 mg, sonication, vortex, and desorption time of 2.0, 2.0, and 5 min, respectively, and 150 µL of eluting phase at room temperature).

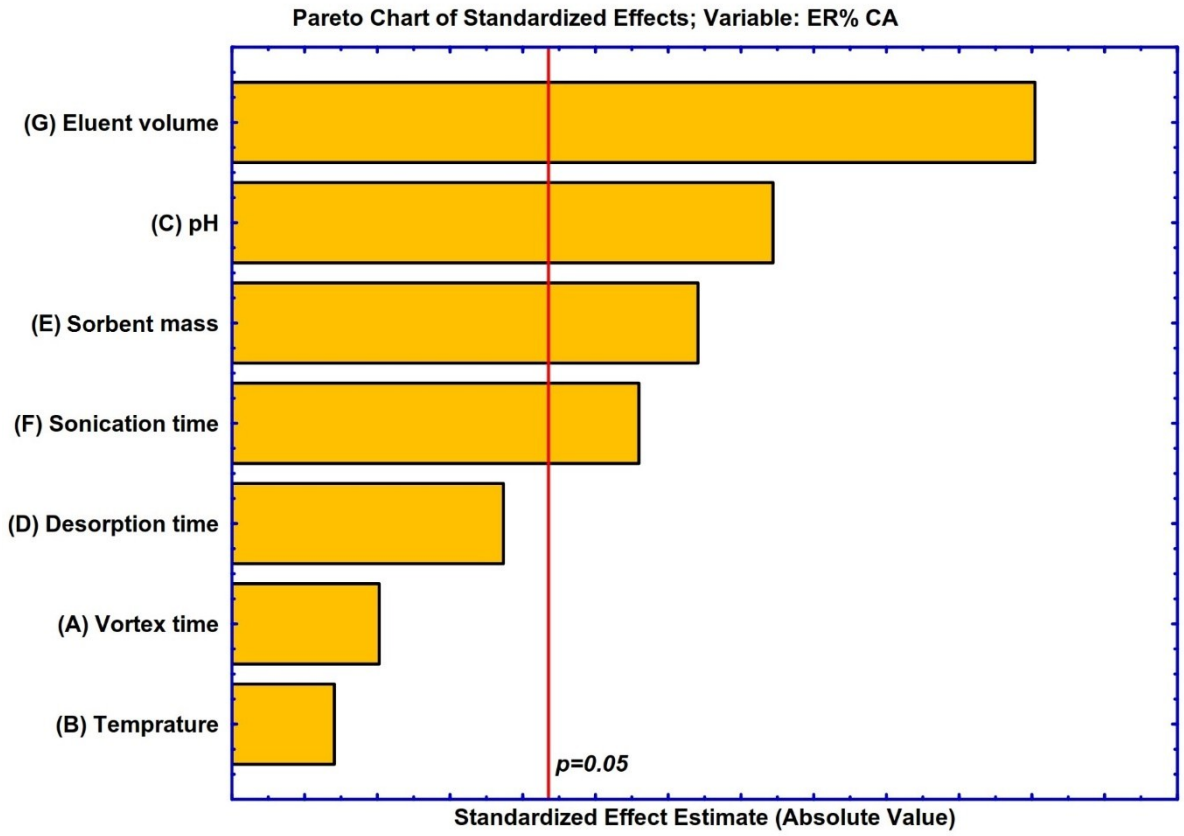

Fig. S3. Standardized (P = 0.05) Pareto chart showing the estimated effects of parameters obtained from the Plackett-Burman screening design for CA.

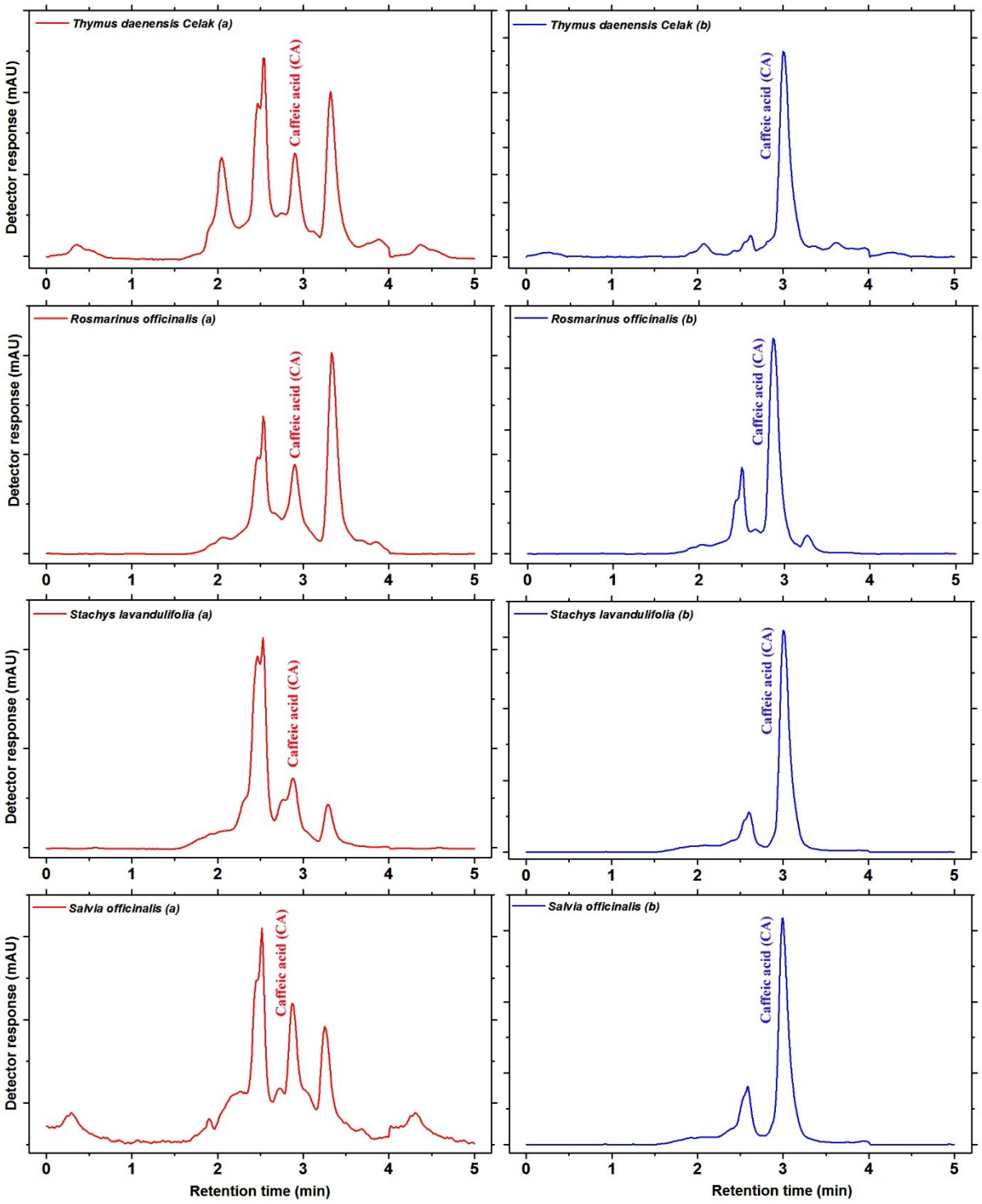

Fig. S4. Chromatograms of methanolic extract of plants before (a) and after (b) microextraction under optimal conditions.

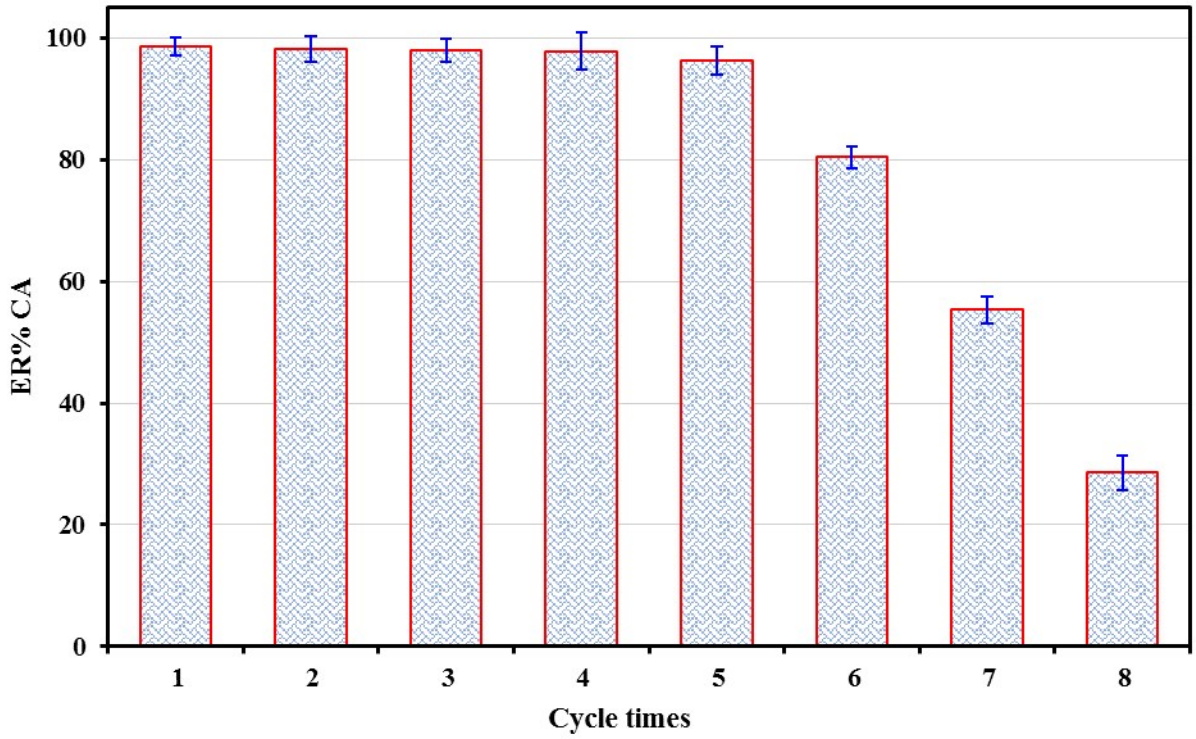

Fig. S5. Reusability tests of the Fe_3O_4@SiO_2@Ti-MOF-NCs for the recovery efficiency toward CA.

2. Tables

Table. S1. Analysis of variance (ANOVA) for response surface quadratic model of CA extraction determined from CCD.

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*P* value
Model	5496.04	14	392.57	307.33	< 0.0001
X_1	840.50	1	840.50	657.98	< 0.0001
X_2	620.22	1	620.22	485.54	< 0.0001
X_3	61.52	1	61.52	48.16	0.0009
X_4	51.21	1	51.21	40.09	0.0015
X_1X_2	35.53	1	35.53	27.82	0.0033
X_1X_3	44.70	1	44.70	34.99	0.0020
X_1X_4	26.09	1	26.09	20.42	0.0060
X_2X_3	321.19	1	321.19	251.44	< 0.0001
X_2X_4	56.14	1	56.14	43.95	0.0012
X_3X_4	79.15	1	79.15	61.97	0.0005
X_1^2	20.06	1	20.06	15.71	0.0107
X_2^2	29.53	1	29.53	23.12	0.0050
X_3^2	832.46	1	832.46	651.69	< 0.0001
X_4^2	1248.99	1	1248.99	977.77	< 0.0001
Residual	6.39	5	1.28		
Lack of Fit	1.67	2	0.84	0.53	0.6342
Pure Error	4.71	3	1.57		
Corr. Total	5502.43	19			

Table. S2. Figure of merits for MD-μ-SPE of CA.

Quantitative analysis	**Values**
Sample volume (mL)	15
Extraction solvent (mL)	0.24
Linear range (ng mL^{-1})	0.15-3200
Coefficients of determination (R^2)	>0.987
Limit of detections (LODs) (ng mL^{-1})	0.016-0.021
limit of quantification (LOQs) (ng mL^{-1})	0.052-0.068
Enrichment factors (EFs)	105.92-132.03
Preconcentration factor (PF)	62.5
Reproducibility (RSD, %)	3.65-8.66
Repeatability (RSD, %)	1.84-5.54

Table S3. Langmuir, Freundlich isotherm constants, and separation factors (R_L) for the sorption of CA onto Fe_3O_4@SiO_2@Ti-MOF-NCs sorbent.

Isotherm	**Freundlich isotherm**			**Langmuir isotherm**			
Equation	$\log q_e = \lg K_F + (1/n) \log C_e$			$C_e/q_e = (1/Q_{max} K_L) + C_e/Q_{max}$			
				$R_L = (1)/(1+K_L C_0)$			
Plot	$\log q_e$ vs. $\log C_e$			C_e/q_e vs. C_e			
Parameters	**1/n**	**K_F**	**R^2**	**Q_{max}**	**K_L**	**R^2**	**R_L**
Unit	**-**	**L mg^{-1}**	**-**	**mg g^{-1}**	**L mg^{-1}**	**-**	**-**
Fe_3O_4@SiO_2@Ti-MOF-NCs	0.769	5.053	0.968	183.71	0.321	0.996	0.055-0.342