

1 **Electronic Supplementary Information**

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3 **Magnetic dispersive micro-solid phase extraction with CuO/ZnO@Fe<sub>3</sub>O<sub>4</sub>-**  
4 **CNTs nanocomposite sorbent for the rapid pre-concentration of**  
5 **chlorogenic acid in the medical extract of plants, food, and water samples**

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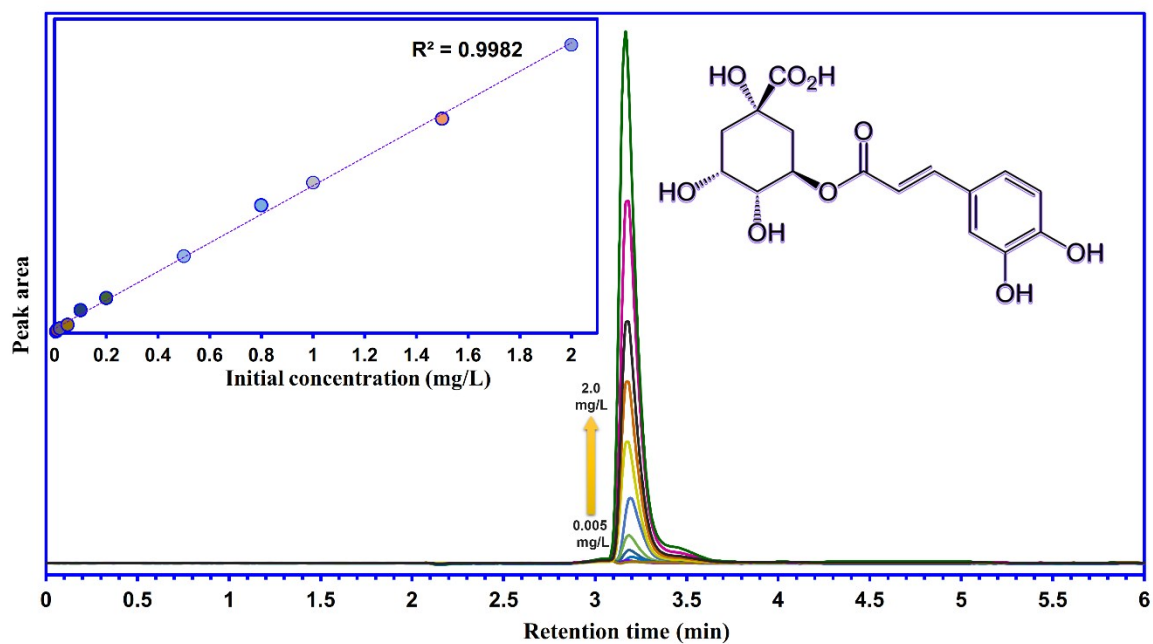
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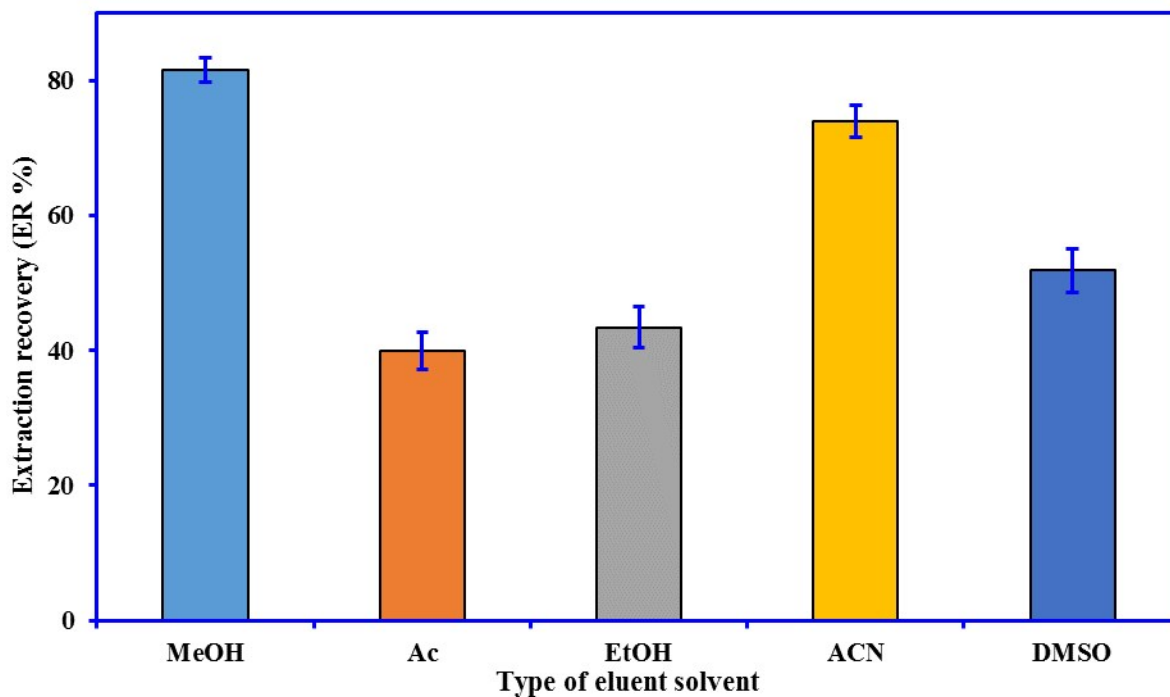
12 **Contents**

13 **1. Figures**



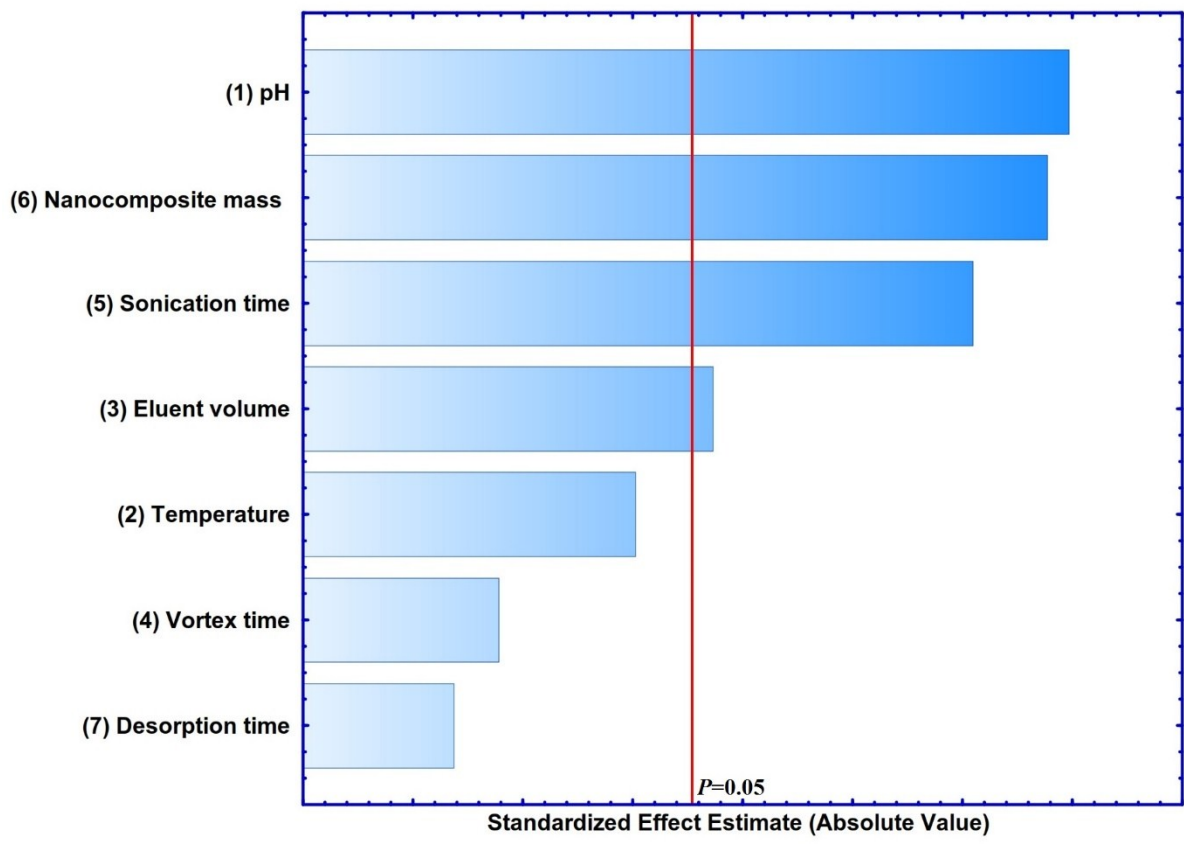
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15 **Fig. S1.** Calibration curves of chlorogenic acid at different concentrations and the chemical  
16 structure.



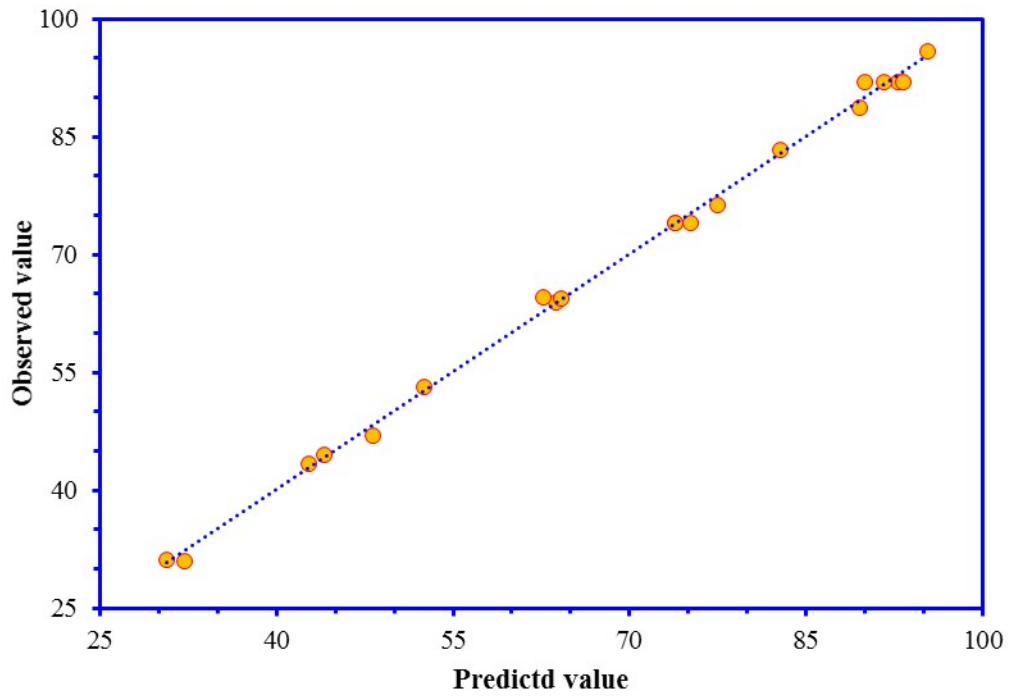
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18 **Fig. S2.** Effect of the elution solvent on the extraction of the chlorogenic acid from water  
19 samples (N=3). Extraction conditions: 15 mL of water, pH 6.0 spiked at 200 ng mL<sup>-1</sup> of  
20 analyte, 10 mg of CuO/ZnO@Fe<sub>3</sub>O<sub>4</sub>-CNTs-NC, and 200 μL of each eluent.



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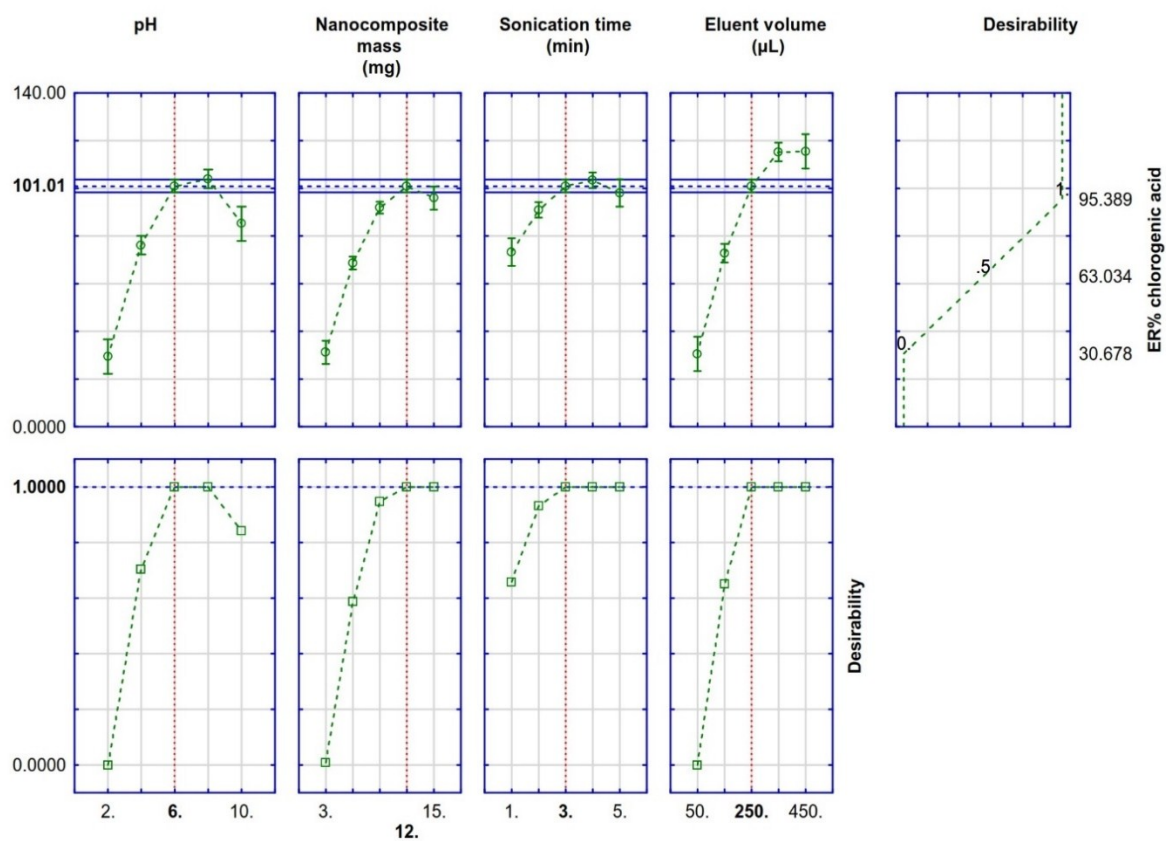
22 **Fig. S3.** Standardized main effect Pareto chart for the Plackett–Burman design. Vertical line  
 23 in the chart defines the 95% confidence level.



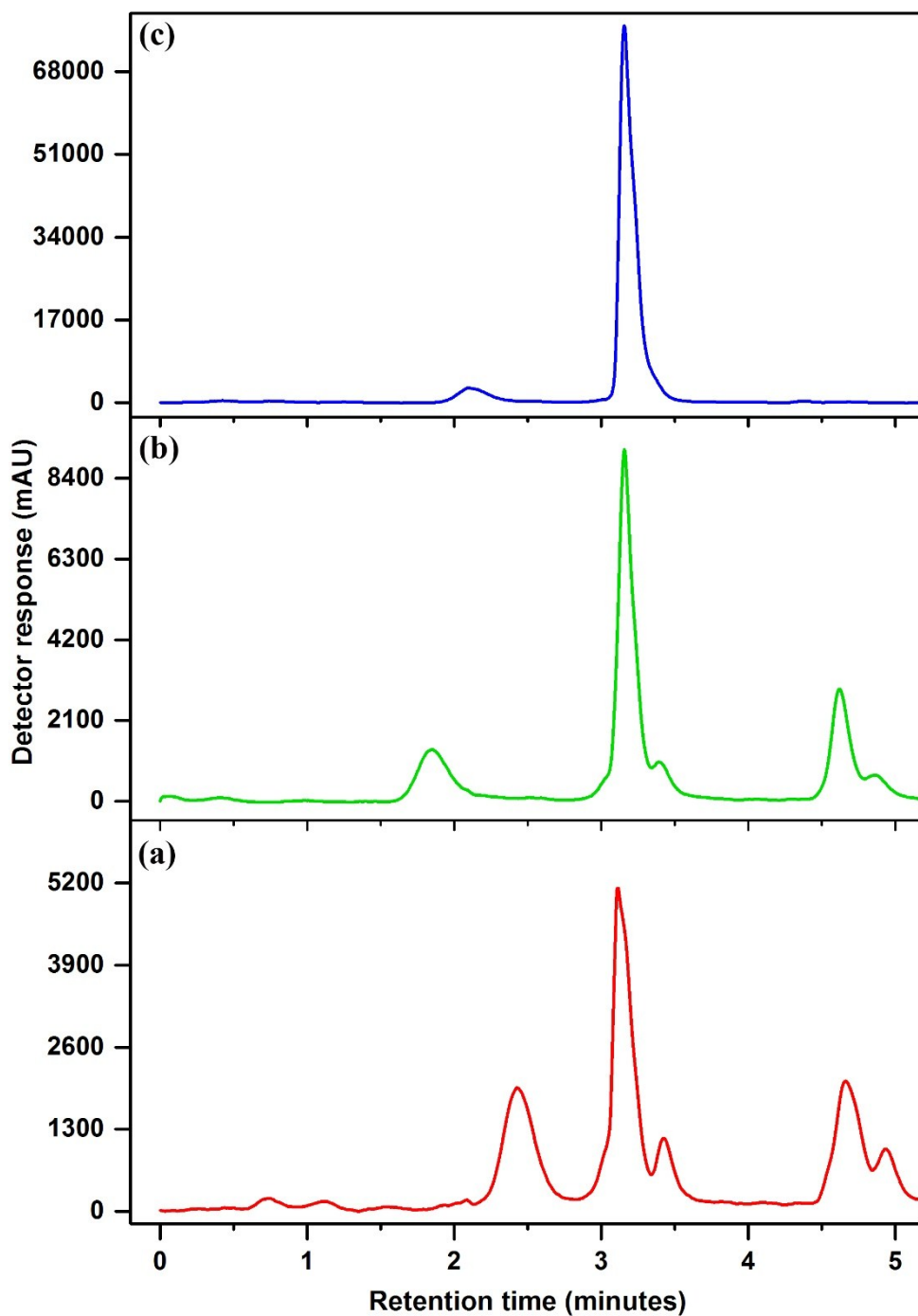
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25 **Fig. S4.** Correlation of experimental with predicted values of ER% of chlorogenic acid.

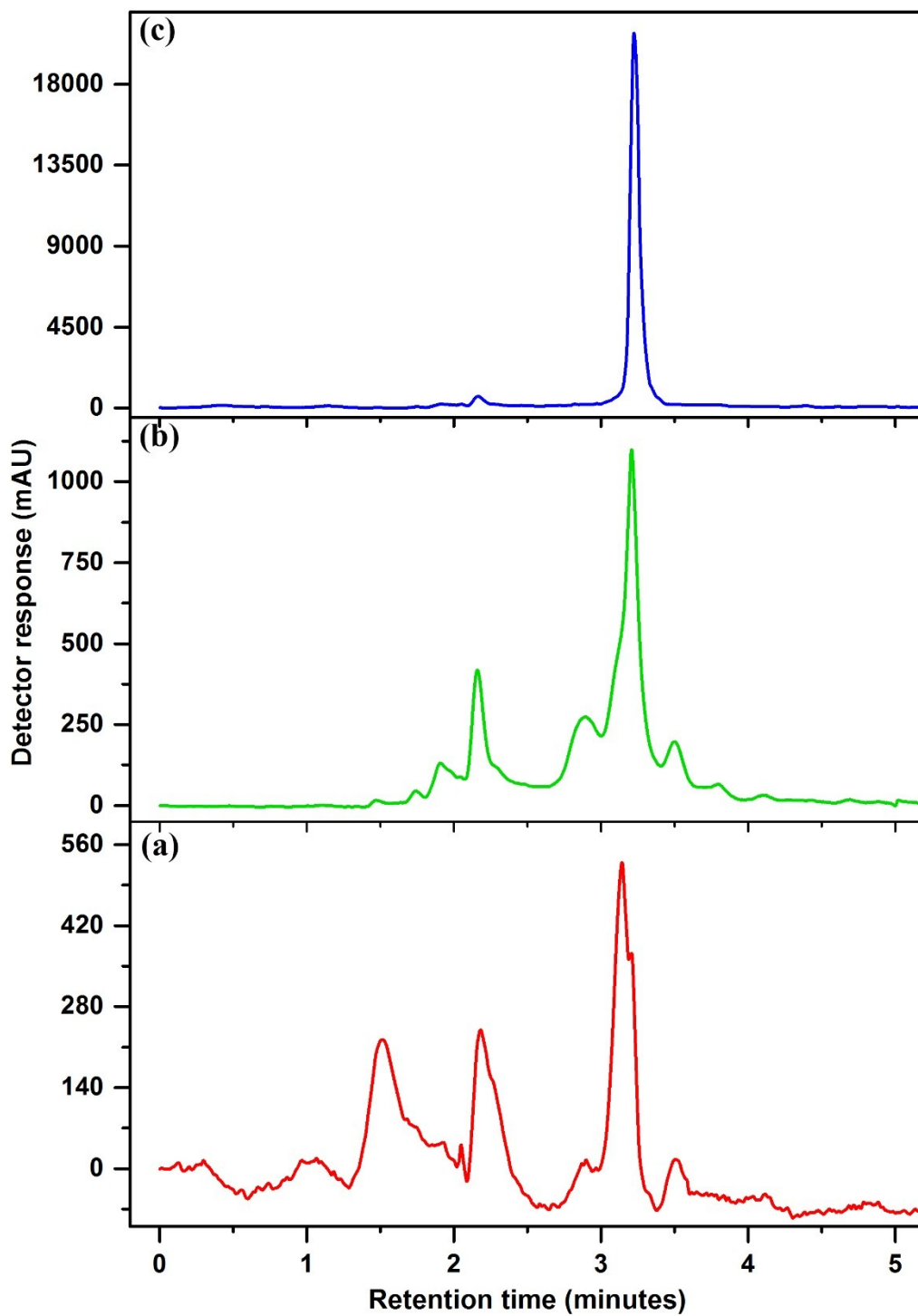
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**Fig. S5.** The conditions of profile optimum by the CCD design for the recovery of chlorogenic acid.

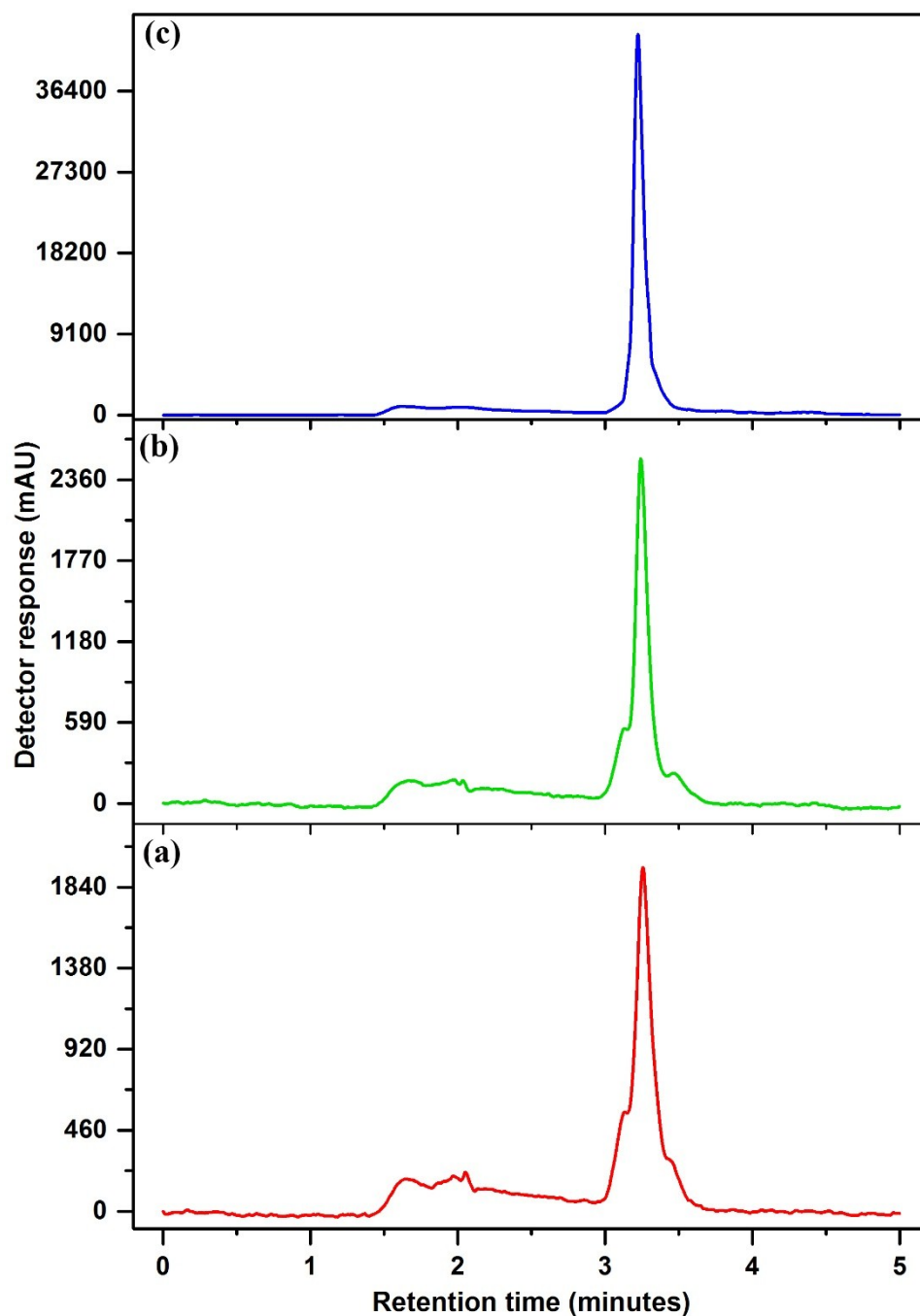


**Fig. S6.** Chromatogram of blank (a) spiked (b) and extracted from *Salvia officinalis* after MDMSPE (c) at  $200 \text{ ng mL}^{-1}$  for the extraction of chlorogenic acid with  $\text{CuO/ZnO@Fe}_3\text{O}_4$ -CNTs-NC under the optimum conditions.

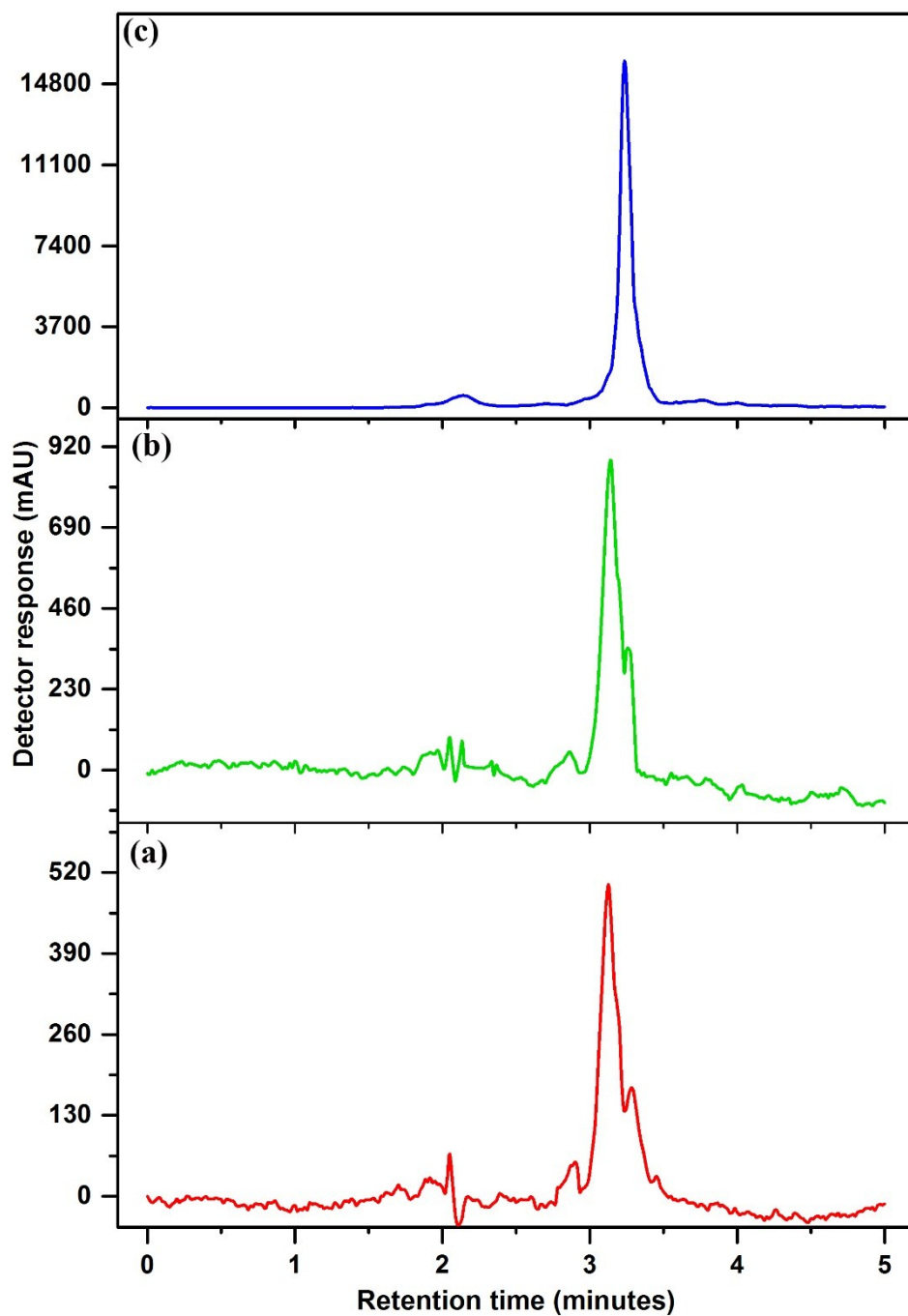


**Fig. S7.** Chromatogram of blank (a) spiked (b) and extracted from Broccoli (*Brassica oleracea*) after MDMSPE (c) at  $200 \text{ ng mL}^{-1}$  for the extraction of chlorogenic acid with  $\text{CuO/ZnO@Fe}_3\text{O}_4\text{-CNTs-NC}$  under the optimum conditions.



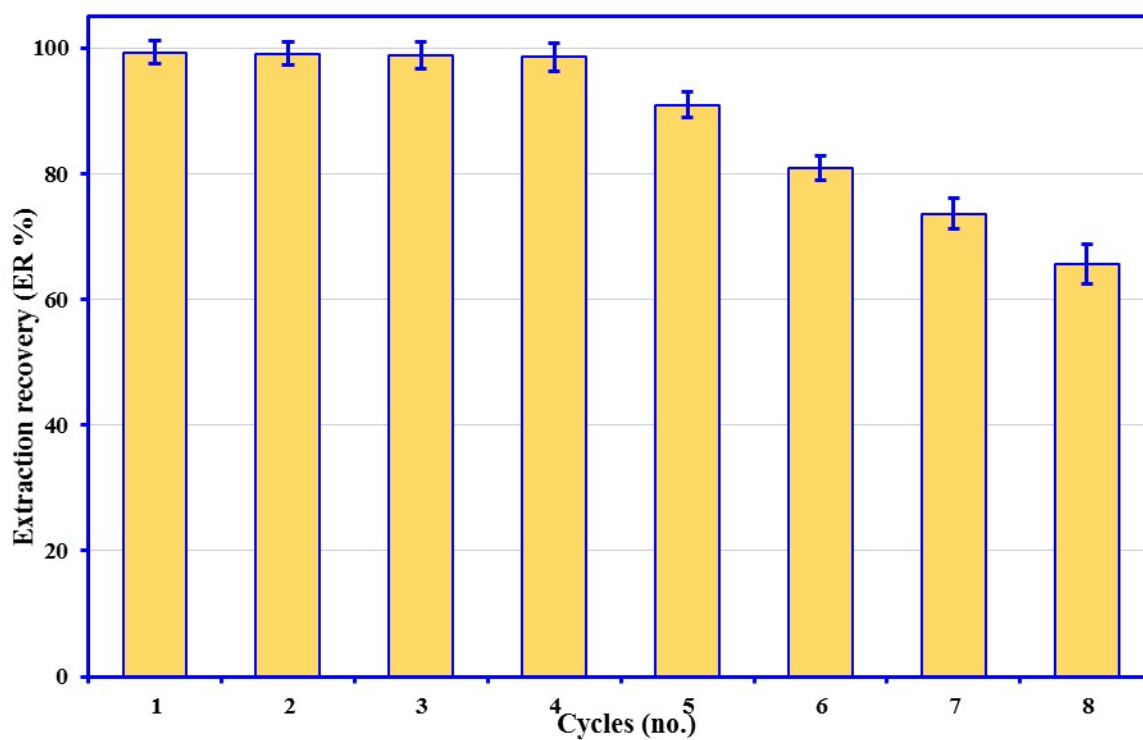


**Fig. S8.** Chromatogram of blank (a) spiked (b) and extracted from eggplants after MDMSPE (c) at  $200 \text{ ng mL}^{-1}$  for the extraction of chlorogenic acid with  $\text{CuO/ZnO@Fe}_3\text{O}_4\text{-CNTs-NC}$  under the optimum conditions.



27

28 **Fig. S9.** Chromatogram of blank (a) spiked (b) and extracted from tomato after MDMSPE (c)  
29 at  $200 \text{ ng mL}^{-1}$  for the extraction of chlorogenic acid with  $\text{CuO/ZnO@Fe}_3\text{O}_4\text{-CNTs-NC}$  under  
30 the optimum conditions.



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34 **Fig. S10.** Reusability of CuO/ZnO@Fe<sub>3</sub>O<sub>4</sub>-CNTs-NC for MDMSPE of chlorogenic acid  
35 under optimum conditions. The mean of three replicates was used as each extraction  
36 efficiency with error bar.

37 **2. Tables**

38 **Table. S1.** Experimental parameters and their levels used in screening by the PBD for the  
 39 extraction recovery of chlorogenic acid as the response in MDMSPE.

Independent variables	Unit	Level		
		Low (-1)	Center (0)	High (+1)
(X <sub>1</sub> ) pH	-	3.5	6.0	8.5
(X <sub>2</sub> ) Temperature	°C	25	35	45
(X <sub>3</sub> ) Eluent volume	μL	100	200	300
(X <sub>4</sub> ) Vortex time	min	0.0	1.0	2.0
(X <sub>5</sub> ) Sonication time	min	1.0	3.0	5.0
(X <sub>6</sub> ) Nanocomposite mass	mg	5.0	10.0	15.0
(X <sub>7</sub> ) Desorption time	min	2.0	3.5	5.0

Run	Factors							ER%
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	Chlorogenic acid
1	0	0	0	0	0	0	0	80.66
2	-1	1	1	-1	-1	1	-1	58.86
3	0	0	0	0	0	0	0	79.87
4	1	-1	-1	-1	-1	1	1	69.98
5	-1	-1	1	1	-1	-1	1	73.45
6	-1	1	-1	-1	1	-1	1	55.54
7	-1	-1	-1	1	1	1	-1	45.87
8	1	1	1	1	1	1	1	59.78
9	1	1	-1	1	-1	-1	-1	75.11
10	1	-1	1	-1	1	-1	-1	75.98

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41 **Table. S2.** Analysis of variance of the fitted linear equation for recovery of chlorogenic acid.

Source	Degree of freedom	Sum of squares	Mean square	F-value	P-value
Model	14	8483.26	605.95	160.21	< 0.0001
A	1	47.73	47.73	12.62	0.0164
B	1	2093.76	2093.76	553.57	< 0.0001
C	1	580.48	580.48	153.47	< 0.0001
D	1	753.50	753.50	199.22	< 0.0001
AB	1	526.94	526.94	139.32	< 0.0001
AC	1	645.55	645.55	170.68	< 0.0001
AD	1	520.82	520.82	137.70	< 0.0001
BC	1	0.28	0.28	0.07	0.7955
BD	1	531.80	531.80	140.60	< 0.0001
CD	1	22.25	22.25	5.88	0.0597
A <sup>2</sup>	1	2779.85	2779.85	734.97	< 0.0001
B <sup>2</sup>	1	1170.39	1170.39	309.44	< 0.0001
C <sup>2</sup>	1	340.86	340.86	90.12	0.0002
D <sup>2</sup>	1	1137.16	1137.16	300.66	< 0.0001
Residual	5	18.91	3.78		
Lack of Fit	2	12.23	6.11	2.74	0.2102
Pure Error	3	6.69	2.23		
Corr. Total	19	8502.17			

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43 **Table. S3.** Analytical parameters of CuO/ZnO@Fe<sub>3</sub>O<sub>4</sub>-CNTs-NC as the MDMSPE sorbent  
 44 for HPLC-UV determination of chlorogenic acid.

Quantitative analysis	Values
Sample volume (mL)	15.0
Extraction solvent (mL)	0.250
Linear range (ng mL <sup>-1</sup> )	0.25-4300
Coefficients of determination (R <sup>2</sup> )	>0.9893
Limit of detections (LODs) (ng mL <sup>-1</sup> )	0.034-0.061
limit of quantification (LOQs) (ng mL <sup>-1</sup> )	0.114-0.202
Enrichment factor (EF)	102.43-123.76
Preconcentration factor (PF)	60.0
Repeatability (RSD, %)	1.42-6.06
Reproducibility (RSD, %)	2.18-8.39

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47 **Table S4.** Parameters of Langmuir and Freundlich isotherm models for the sorption of CGA onto both sorbents.

<b>Isotherm</b>	<b>Freundlich isotherm</b>			<b>Langmuir isotherm</b>			
Equation	$\log q_e = \log K_F + (1/n) \log C_e$			$C_e/q_e = (1/Q_{\max} K_L) + C_e/Q_{\max}$			
				$R_L = (1)/(1 + K_L C_0)$			
Plot	$\log q_e$ vs. $\log C_e$			$C_e/q_e$ vs. $C_e$			
<b>Parameters</b>	<b>1/n</b>	<b>K<sub>F</sub></b>	<b>R<sup>2</sup></b>	<b>Q<sub>max</sub></b>	<b>K<sub>L</sub></b>	<b>R<sup>2</sup></b>	<b>R<sub>L</sub></b>
<b>Unit</b>	-	<b>L mg<sup>-1</sup></b>	-	<b>mg g<sup>-1</sup></b>	<b>L mg<sup>-1</sup></b>	-	-
CuO/ZnO@Fe <sub>3</sub> O <sub>4</sub> -CNTs-NC	0.643	3.712	0.961	65.38	0.586	0.989	0.041-0.363
CuO/ZnO@Fe <sub>3</sub> O <sub>4</sub> -NC	0.278	2.655	0.928	22.55	0.661	0.975	0.036-0.335

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